

Chemical Pollution in Acid Sulfate Soils

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Abstract

Soils containing pyrite (FeS_2) formed by natural processes under anaerobic conditions are widespread in Southeast Asian countries. It is possible that the pyrite contains As and Cd. These soils, classified as acid sulfate soils, are utilized for crop cultivation. Studies conducted in Malaysia indicate that toxic materials can be released into the soils and groundwater in the surrounding areas when the pyrite in the soils undergoes oxidation. This paper reports release of toxic materials into the soils and the surrounding environment when acid sulfate soils are drained to make way for development. Soil samples were selected from among the acid sulfate soils in the country. Some of the samples were maintained in unoxidized state, while others were exposed to the atmosphere. They were analyzed by various methods, including standard chemical methods, XRD and SEM-EDAX. Pyrite was found in the unoxidized state, while jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) and natrojarosite ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$) were present in oxidized samples. The Fe to S ratio of the pyrite structure was 1:2, indicating that accessory elements were absent within the pyrite structure. Oxidation of the pyrite would not lead to contamination of As and Cd in the soils. In the oxidized samples, some Mn were also detected. The metal along with Fe and Al were present in large amounts in the water extract of the oxidized samples. This means that Al and Fe toxicity are a common problem in the areas covered by acid sulfate soils.

Pencemaran Kimia Dalam Tanah Asid Sulfat

Abstrak

Tanah yang mengandungi pirit (FeS_2), yang dibentuk oleh proses-proses semulajadi di bawah keadaan anaerobik adalah tersebar luas di negara-negara Asia Tenggara. Kemungkinan pirit ini mengandungi As dan Cd. Tanah ini yang dikelaskan sebagai tanah asid sulfat adalah sesuai digunakan untuk penanaman. Kajian yang dijalankan di Malaysia mendapati bahan toksik boleh dilepaskan ke dalam tanah dan air tanah kawasan sekitarnya apabila pirit dalam tanah mengalami pengoksidaan. Kertas ini melaporkan pembebasan bahan toksik ke dalam tanah dan persekitaran apabila tanah asid sulfat disalurkan keluar untuk tujuan pembangunan. Sampel tanah dipilih daripada tanah asid sulfat dalam negara. Sebahagian tanah dibiarkan dalam keadaan tak-teroksida, sementara yang lain didedahkan kepada atmosfera. Beberapa kaedah digunakan untuk analisis, termasuklah Kaedah Kimia Standard, XRD dan SEM-EDAX. Pirit dijumpai dalam sampel tak-teroksida manakala jarosit ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) dan natrojarosit ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$) hadir dalam sampel teroksida. Nisbah Fe kepada S dalam struktur pirit adalah 1:2, menunjukkan unsur sampingan tidak hadir dalam struktur pirit. Pengoksidaan pirit tidak akan membawa kepada pencemaran As dan Cd dalam tanah. Dalam sampel teroksida, sedikit Mn juga dijumpai. Logam ini hadir bersama dengan Fe dan Al dalam jumlah yang besar di dalam ekstrak air sampel teroksida. Ini menunjukkan ketoksikan Al dan Fe adalah masalah biasa dalam kawasan tanah asid sulfat.

INTRODUCTION

Acid sulfate soils are naturally occurring soils containing iron sulfides (pyrite) or containing acidic products of the oxidation of the sulfides. Pyrite is formed in the soils in the presence of SO_4^{2-} , Fe^{3+} , organic matter and special microorganism. When the soils are drained for commercial or agricultural development, the pyrite is exposed and subsequently oxidized, producing sulfuric acid and often releasing substantial quantities of toxic metals. As long as the pyrite remains under water, the soils are harmless as oxidation does not occur. As sulfuric acid moves through the soils, it destroys the clay minerals, releasing iron, aluminium and other metals into the soils. Some of the pyrite may contain As, Ni, Co, Mn, Cu, Pb and

Zn in its structure (Deer *et al.*, 1966; Viera e Silva *et al.*, 1994). If this is so, these metals would pollute the surrounding areas when the pyrite dissolves (Shamshuddin *et al.*, 1995).

The acid and toxic metals produced when the pyrite is oxidized will seep into waterways with catastrophic environmental and economic impacts. It reduces the commercial and recreational values of tidal streams and estuaries. Land use that may be affected by acid sulfate soils include agriculture, urban development, road and bridge construction, aquaculture, marinas, golf courses, residential development and drainage works.

This paper is aimed at reporting the occurrence of acid sulfate soils in Malaysia as well as to determine the release of toxic materials when the soils are drained to make way for development.

MATERIALS AND METHODS

The occurrence and distribution of acid sulfate soils in Malaysia were studied from published literature. To study pyrite, samples from Cg horizons of common acid sulfate soils in Malaysia were taken. The samples were analyzed before and after pyrite in the soils underwent oxidation. Among the methods used were chemical methods, X-ray diffraction (XRD) and scanning electron microscopy (SEM-EDAX).

OCCURRENCE AND DISTRIBUTION

Based on literature, acid sulfate soils are found in coastal lowland areas such as estuaries and floodplains, tidal mangrove flats, lakes and wetlands, at elevation commonly less than 10 meters above sea level. In Peninsular Malaysia, the area covered by the acid sulfate soils is about 0.5 million ha. Around 7.5 million ha of acid sulfate soils occur in the tropics (Kawalec, 1975). The most recent estimate suggests a total of about 24 million ha of acid sulfate soils occur worldwide (Dent and Pons, 1995).

IDENTIFICATION OF ACID SULFATE SOILS

The soils can be classified as actual and potential acid sulfate soils. Actual acid sulfate soils are presently generating acid by oxidation of pyrite in the soils. The pyrite in potential acid sulfate soils has not been oxidized, but the potential for future oxidation of pyrite and generation of acid exists.

Actual acid sulfate soils can be identified in the field based on the following characteristics (Dent, 1986).

- low pH in soils, ground water and surface water;
- the presence of straw yellow jarosite mottles in the surface soils;
- clear blue-green water (indicating the presence of high amounts of soluble Al);
- rust coloured iron stains on any drain surfaces and ochre deposits; and
- stunted or dead vegetation, acid scalds and poor vegetation regrowth.

Potential acid sulfate soils are typically waterlogged, have near neutral pH, have dark grey or greenish gray in coloured, and rotten eggs smell when the soils excavated.

PYRITE STRUCTURE AND ITS IMPURITIES

To study the pyrite structure, two common acid sulfate soils in the country, namely the Jawa and Linau soils, were used. Pits were dug and pyritic samples were taken and sent to the laboratory for analyses.

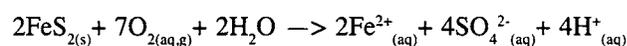
There was indication that pyrite occurred in the unoxidized samples, while jarosite and natrojarosite were present in the oxidized samples. The Fe to S ratio of the

unoxidized pyrite structure (Figure 1) as found by SEM-EDAX was 1:2. When the pyrite was oxidized, its morphology disintegrated. Several morphological types of disintegration of pyrite are shown in Figure 2. The initial stage of pyrite weathering was etching in the surface structure of the individual pyrite and at a later stage it disintegrated. The corroded individual crystals were generally FeS₂ as indicated from EDAX analysis. Chemical changes were observed in the EDAX by the excess of Fe over S, and the presence of Al, Mn and K, indicating that there was oxidation taking place, leading to acidification and liberation of some elements from the clay mineral. Jarosite, the oxidation product of pyrite, was distinguished clearly by its hexagonal form (Figure 3). Most probably the mineral was formed through neof ormation rather than pseudomorphic alteration of pyrite. In this study, it was found that the pyrite was free of As and Cd. Hence, the opening of land covered by acid sulfate soils in Malaysia would not contribute to As and Cd pollution (Shamshuddin *et al.*, 1995)

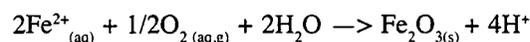
RELEASE OF IONS AND ANIONS

To study the release of metals into the soils, an oxidative/incubation experiment were carried out. The experiment was set up by putting about 300 g (wet basis) of the sediments in a plastic bag (15X20 cm). The materials in the bag were pressed to a form slab a 1 cm thickness as recommended by Soil Survey Staff (1992). Finally, the bags were folded but not sealed. The bags were then kept under 25°C in dark condition. This procedure was followed to approximate slow oxidation in the field without leaching losses of oxidation product (van Bremen, 1976). After 12 weeks, the soils were analyzed using water as an extracting agent at a soil to water ratio of 1:5. Metals in the extract were determined using AAS and ICP-AES.

After 12 weeks of incubation, the pH dropped by more than 1 unit. The high acidity produced is clearly the results of pyrite oxidation. The oxidation process takes place according to the following reaction (van Bremen, 1976; van Bremen, 1993):



Further oxidation of Fe(II) to Fe(III) oxide, again produces acidity:



Two moles of pyrite will produce 4 moles of sulfuric acid.

Total Fe in the Cg horizon of the Jawa and Linau soils were very high, with values of 23,723 µg/g and 25,225 µg/g, respectively. Correspondingly, about 418 µg/g and 1257 µg/g were present in water-soluble form in the soils (Table 1). High amounts of Al and Mn were also present in the water-soluble form in both soils. Oxidations of pyrite bearing sediments would, therefore, result in the release of high amounts of these metals into the environment. This is a cause of alarm among soil scientists and environmentalists

as it leads to serious land degradation. The growth of plants and aquatic life in the vicinity of the acid sulfate soils would be seriously affected by their presence.

In the Cg horizon of the Jawa soil, As and Pb were present in trace amounts. But, their amounts are substantial in the Linau soil. Nevertheless, the water-soluble form of the metal was low. The total As concentration in the Ap horizon of the Linau soil was 31 $\mu\text{g/g}$ (Table 2). Immediately

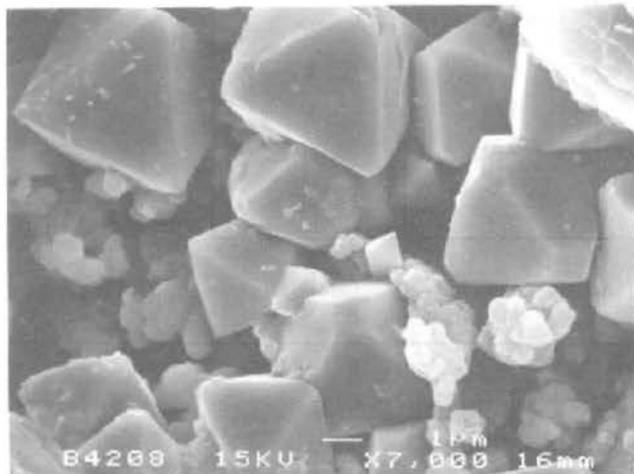


Figure 1: Unoxidized pyrite structure.

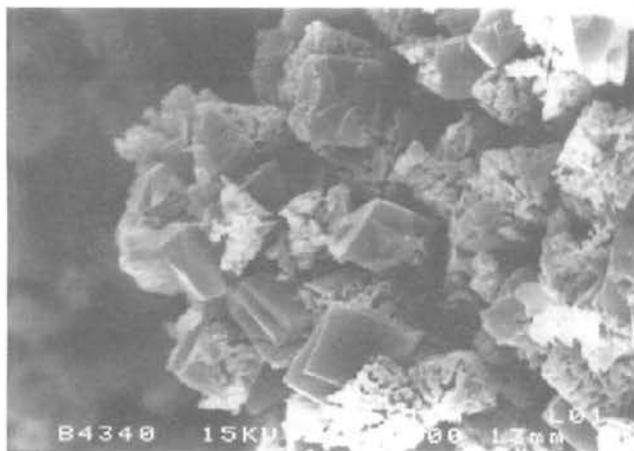


Figure 2: Structure of disintegrated pyrite.

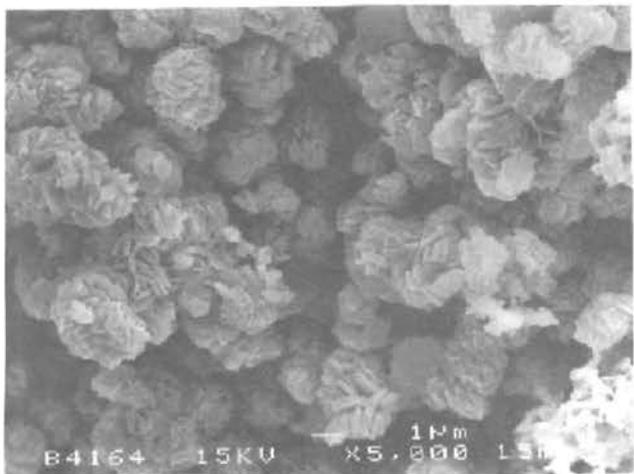


Figure 3: Jarosite in an oxidized sample.

below this horizon, the value was 29 $\mu\text{g/g}$. In the Jawa soil, the same decrease of total As concentration below the topsoil was observed. In general, the values for Cd were low, but there was a tendency for Cd concentrations to increase with depth. This study indicates that the As and Cd present in an earlier study (Shamshuddin and Hasniah, 1995) may have come from sources other than the dissolutions of pyrite. They may have come from agricultural practices, as these elements are components of pesticides or fertilizers.

The amount of nickel in the soil was moderately high (Table 2). The values increased with depth, indicating that it could not be due to addition of Ni by agricultural practices. This phenomenon needs further investigation as the elemental composition of pyrite may contain some Ni in its structure.

MANAGING THE SOILS

Our understanding of the properties of acid sulfate soils and their effects on crops and environment is good, but there is still much to be learned about a cost-effective way of managing the soils for sustainable land management. The presence of extreme acidity in the vicinity of acid sulfate soils creates problems for aquaculture, agriculture, road and bridges, foundations, drainage works, wetlands, marinas, residential development and golf courses. Inappropriate management practices may result in land degradation, long-term engineering problems, reduced soil productivity and less profitable incomes.

The main reasons for crop failure are Al^{3+} and Fe^{2+} toxicities. The potential acidity released by the oxidizing pyrite can be as high as 30 cmol/kg in sandy pyritic subsoils and 65 cmol/kg in clayey subsoils. Liming materials needed to neutralize this acidity amount to more than 100 tonnes/ha.

The best option to manage acid sulfate soils is to avoid disturbing or draining the pyritic layer as pyrite is harmless under reduced condition. Therefore, correct water management practice is the key to successful agricultural enterprise on acid sulfate soils. However, some acid sulfate soils cannot be managed properly by water management alone. Detoxifying Al and Fe by applying lime and organic matter are other options. Peat mixed with other organic materials such as green manure and rice straw can detoxify Al to certain extent. It is also recommended to grow crops tolerant to Al toxicity such as oil palm. The root length of the oil palm seedling is positively correlated with Al activity (Auxtero and Shamshuddin, 1991). Oil palm can survive provided that Al^{3+} activity does not exceed 100 μM . On the other hand, cocoa is sensitive to Al. Acid sulfate soils used for growing cocoa need to be limed adequately.

Removal of Al and Fe by leaching can also be done. Leaching means transferring acidity and toxic Al and Fe to the surrounding water ways and streams. However, it needs a huge amount of water to be effective.

Table 1. Total and water-soluble metal concentration in the pyritic layers (Cg horizon) of the Jawa and Linau soils.

Metal	Jawa Soils		Linau Soils	
	Total ($\mu\text{g/g}$)	Water-soluble ($\mu\text{g/g}$)	Total ($\mu\text{g/g}$)	Water-soluble ($\mu\text{g/g}$)
Fe	23723.1	418.4	25225.18	1256.7
Al	19290.0	136.5	39320.2	596.6
Mn	342.7	100.4	95.9	40.1
Zn	61.7	1.0	67.7	16.6
Ni	10	1.8	13.1	2.4
Cu	4.0	tr	8.12	tr
As	6.3	-	12.5	tr
Se	0.16	-	0.31	tr
Cd	0.04	-	0.6	0.12
Pb	15.6	-	27.5	0.02

Flooding is another measure to alleviate acidity and Al toxicity. This is only good if the area is allocated for wetlands. Upon flooding, the pH will rise because of the "self-liming" effect of reducible Fe (III) oxides.

CONCLUSIONS

Acid sulfate soils in Malaysia do not contain heavy metals. When the soils are opened up for development, high amounts of acidity are released. Toxic amounts of Al is released into the soils and the environment, affecting plants and aquatic life. The most effective method to control the production of acidity is controlling of water table. The acidity can be reduced by adding lime and/or organic matter.

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Table 2. Changes in total As, Cd and Ni concentrations in the Jawa and Linau soils with depth.

Horizon	Jawa			Linau		
	As ($\mu\text{g/g}$)	Cd ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)	As ($\mu\text{g/g}$)	Cd ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)
Ap	8.61	0.05	7.01	31.14	0.01	3.00
Bw1	8.08	0.01	7.39	29.21	0.01	3.42
Bw2	9.47	0.03	8.90	8.17	0.04	4.08
Bw3	17.07	0.03	10.01	21.79	0.13	7.05
Cg	6.27	0.04	10.14	12.45	0.15	13.07