Pyrite in acid sulfate soils: transformation and inhibition of its oxidation by application of natural materials

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Abstract

Worldwide estimate of acid sulfate soils is 12–14 million ha. In Malaysia, they occur mainly along the coastal plains of Peninsular Malaysia and Sarawak. The soils are characterized by very low pH and high amounts of exchangeable Al, resulting from oxidation of pyrite when the soils are drained. This paper explains the transformation of pyrite when the soils undergo weathering due to drainage. Soil samples containing pyrite from Cg-horizons of selected acid sulfate soils in Peninsular Malaysia were incubated in the laboratory. Some of the samples were treated with phosphate and peat so as to prevent the oxidation of pyrite. The changes in pyrite morphology were studied by SEM-EDAX. At the end of incubation, water-soluble metals were determined. The result showed that pyrite in the unoxidized state had Fe to S ratio of 1:2, indicating the absence of accessory elements (As, Cd, etc.,) in the pyrite structure. This means that when this pyrite disintegrates, there is no danger of heavy metal pollution. As the weathering continues, pyrite dissolves quickly forming jarosite. Phosphate treatment reduced pyrite oxidation. The amounts of Al and Fe in the water-soluble form were large which could be toxic to plants and aquatic life.

Keywords: acid sulfate soil, heavy metal, oxidation, pyrite, transformation

Introduction

Pyrite (FeS_2) occurs naturally in many marine sediments of the coastal plains of Peninsular Malaysia. This pyrite is formed under reduced conditions in the presence of ferric ions, sulfate, organic matter and special microorganism. When the pyrite is exposed to the atmosphere either naturally or otherwise, a large amount of acid is produced leading to development of acid sulfate soil (Dent, 1996). This soil is very common worldwide; it is widespread in the Southeast Asia. Pyrite crystal may be contaminated with As, Cd, Ni, Cu or Zn (Deer *et al.,* 1966). When this pyrite disintegrates, the contaminants are released, polluting the surrounding areas (Shamshuddin *et al.,* 1995; Shamshuddin and Muhrizal, 2000). Preventing or delaying pyrite oxidation is a way forward to manage an acid sulfate soil. This study aimed at reporting the transformation of pyrite under oxidizing environment and to determine the efficacy of applying natural materials to delay/prevent pyrite oxidation.

Materials and Methods

Two common acid sulfate soils in Peninsular Malaysia (Jawa and Linau series) which were planted to cocoa were selected for this study. The two soils, classified as

Typic Sulfaquepts, were sampled according to horizons. Important horizons mainly used for the study were the Ap- and Cg- horizons. Preliminary investigation showed that pyrite was present in the Cg-horizon of both soils. Texture, pyrite contents and organic carbon in the soils were determined. Other analyses include total analysis, XRD analysis to determine the general mineralogy of the soils and SEM-EDAX to study the morphology of the unoxidized and disintegrated pyrite. The Cg-horizon samples were subjected to incubation and treatments with natural materials.

Results and Discussion

General chemical properties of the soils

Mineralogically, the two soils were dominated by mica, smectite and kaolinite in the clay fraction. The pH of the topsoil of the Linau series was low, but the value for the Jawa soil was moderately high (Table 1). However, in the Cg-horizon the respective pH was 3.91 and 6.20. When the Cg-horizon samples were oxidized, the pH for the Linau soil was 3.91, while for the Jawa soil it was 4.94. The drop in pH was due to release of protons when the soils were incubated, which was related to pyrite oxidation.

Table 1 The pH, exchangeable Al, clay and pyrite contents in the Jawa and Linau soils.

Soil	Horizon	pH		Exch. Al	O.C	Clay	Pyrite
		Fresh	Oxidized	($cmol_c\ kg^{-1}$)	(%)	(%)	(%)
Jawa	Ap	-	5.20	0.32	2.45	35.35	0
	Cg	6.20	4.94	0.12	0.79	19.64	1.19
Linau	Ap	-	3.08	4.29	4.37	22.54	0
	Cg	3.91	2.31	11.56	6.23	24.01	2.08

The product of pyrite oxidation

The soil pH was dropped by I unit after 12 weeks of incubation. The production of high acidity was related to pyrite oxidation (van Breemen, 1976; van Breemen, 1993). It is generally believe that 2 moles of proton can be produced after oxidation of 1 mole of pyrite. This acidity is then responsible for dissolution of clay minerals in the acid sulfate soils, leading to release of large amounts of Al and Fe into the soils and the surrounding areas.

If the pyrite crystal is contaminated with heavy metals, the situation become much worse as these metals get into the water ways and food chains. Luckily, the soils under study did not contain pyrite contaminated with heavy metals as shown by SEM-EDAX. If there was a trace amount of heavy mineral present in the crystal, SEM-EDAX was not sensitive enough to detect them.

Total Fe in the soils was high. As expected, its amount in the water-soluble form was presumably present at toxic level. And so was water-soluble Al, which was toxic to crop such as cocoa; these soils were sampled in an area planted to cocoa.

The results of the study showed clearly that oxidation of pyrite-bearing sediments would result in the release of high amounts of Fe and Al into the soils and the environment. This would lead to a serious land degradation in the vicinity of acid sulfate soils. It is thus important to look for methods to avoid this from happening or if not possible to try to minimize its impact.

Pyrite disintegration

Pyrite was present in the soils, especially in the Cg-horizon (Table 1). The unoxidized pyrite as indicated by SEM-EDAX had Fe to S ratio of 1:2 (Figure 1), meaning that this pyrite crystal was free of heavy metals. As a result of the oxidation, the pyrite disintegrated forming a new mineral named jarosite/natrojarosite (Figure 2). The neoformation of this mineral during pyrite oxidation had already been reported by Shamshuddin *et al.* (1995). In the soils under study, pyrite present was free of Cd and As. Thus, opening land having these soils for agriculture development would not result in heavy metals pollution.

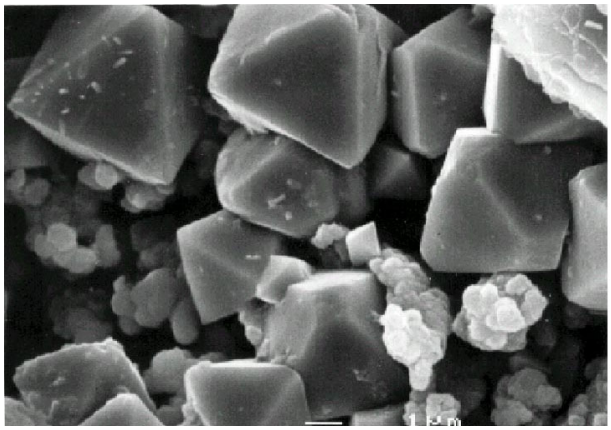

Figure 1 Unoxidized pyrite structure.

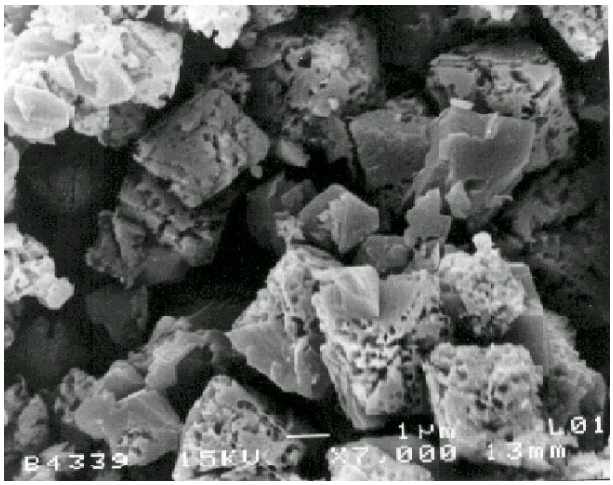

Figure 2 Structure of disintegrated pyrite.

Effects of natural materials on pyrite oxidation

The result indicated that phosphate application somewhat delayed or to some extent prevented pyrite oxidation. The morphology of the pyrite subjected to phosphate application appeared to be similar to the fresh pyrite shown in Figure 1 (Figure 3). It seemed that phosphate in the presence of Fe resulted in the formation of insoluble $FeSO_4$ which finally coated the pyrite crystal; this prevented pyrite from being exposed to oxygen that cause its oxidation. However, the SEM-EDAX analysis was unable to confirm the present of the coating material. In future study, we may be able to

determine the actual composition of the coating material by using thin film XRD. However, we were able to show the ability of phosphate to prevent pyrite oxidation by looking at Figure 4. Here it is seen that the pH of the sample applied with phosphate did not drop. It means that there was no proton produced that would lower the pH. In the control treatment, the pH was reduced from 6 to 3.

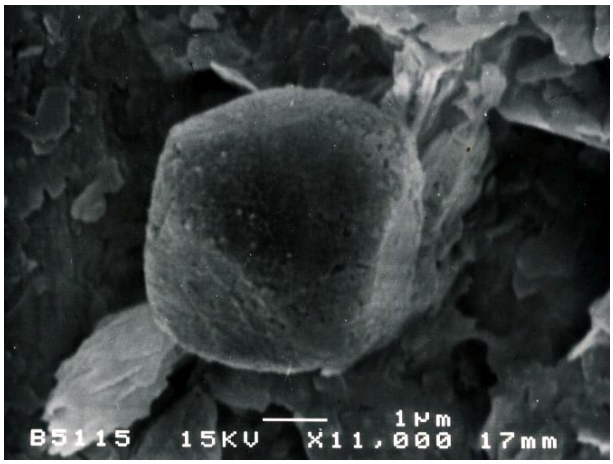

Figure 3 Unoxidized pyrite under phosphate treatment.

Figure 4 pH changes during pyrite oxidation as affected by addition of phosphate, silicate, lime and peat.

Conclusion

It seems that pyrite in the acid sulfate soils of Peninsular Malaysia is free of contaminants in its crystal. Hence, developing the soils for agriculture would not result in the surrounding areas being polluted by heavy metals such as Cd and As. The

oxidation of pyrite, to a certain extent, can be delayed/prevented by phosphate application.

Acknowledgements

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References

Dent, D.L. 1986. Acid sulphate soils: a baseline for research and development. ILRI Publication 39, ILRI Wageningen, The Netherlands.

Deer, W.A., R.A. Howie and J. Zuuzman. 1966. Introduction to rock-forming minerals. Longmans, London.

Shamshuddin, J., I. Jamilah and J.A. Ogunwale. 1995. Formation of hydroxi-sulfate from pyrite in coastal acid sulfate soil environment in Malaysia. Commun. Soil Science and Plant Analysis. 26(17,18):2769-2782.

Shamshuddin, J. and S. Muhrizal. 2000. Chemical pollution in acid sulfate soils, pp. 231- 233. *In* G.H. Teh, J.J. Peirera and T.F. Ng (eds.). Proc. Ann. Geol. Conf. 2000, Geol. Soc. Malays., Kuala Lumpur.

Van Breemen, N. 1976. Genesis and solution chemistry of acid sulphate soils in Thailand. Ph.D. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Van Breemen, N. 1993. Environmental aspect of acid sulphate soils, pp. 391-402. *In* D.L Dent and M.E.F. Mensvoort (eds.). ILRI Publication 53, ILRI, Wageningen, The Netherlands.