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THE DEVELOPMENT AND BEHAVIOUR OF (POTENTIAL) ACID SULFATE SOILS
- a literature review -

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Nota's (Notes) of the Institute are a means of internal communication and not a publication. As such their contents vary strongly, from a simple presentation of data to a discussion of preliminary research results with tentative conclusions. Some notes are confidential and not available to third parties if indicated as such

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INTRODUCTION

The world-wide extent of acid sulfate soils is about 13 million hectares: about one percent of the world's cultivated land. When the extent of the acid sulfate soils is compared with the extent of some of the world's other problem soils (table 1), it is clear that peat soils or saline and sodic soils, for example, are far more extensive and, incidentally, more persistent. Acid sulfate conditions constitute a problem that persists for a limited number of years, and that bedevils a small part of the earth's crust; a small part even of the total area of problem soils that the world is faced with. Several of the other kinds of problem soils, however, mainly lie in areas far away from great concentration of people. The acid sulfate soils tend to occur under favourable climates for food production (table 2), often near densely populated coastal areas or river plains, and their development would thus be of immediate interest (after BRINKMAN, 1982).

Table 1. World distribution of some problem soils (million ha) (after BEEK et al., 1980).

Region	Type of soils			
	Acid sulfate soils	Peat soils	Planosols	Saline and sodic soils
Asia and Far East	6.7	23.5	2.7	19.5
Africa	3.7	12.2	15.9	69.5
Latin America	2.1	7.4	67.2	59.4
North America	0.1	117.8	12.3	16.0
Near and Middle East	0.0	0.0	0.0	53.1
Australia	0.0	4.1	49.3	84.7
Europe	0.0	75.0	4.0	20.7
World total	12.6	240.0	151.4	322.9

Table 2. World distribution of acid sulfate soils (million ha) (after BEEK et al., 1980)

Region	Lenght of growing periods (days)				
	< 90	90-180	180-300	> 300	Total
Asia and Far East	0.0	0.2	5.1	1.4	6.7
Africa	0.4	0.7	1.5	1.1	3.7
Latin America	0.0	0.1	0.8	1.2	2.1
North America	0.0	0.0	0.0	0.0	0.1
Other regions	-	-	-	-	0.0
World total	0.4	1.0	7.4	3.7	12.6

1. GEOGRAPHICAL OCCURRENCE AND EXTENT OF ACID SULFATE SOILS

The Dutch were the earliest to recognise soils containing large amounts of sulfides or sulfates as being detrimental to agriculture, and called them 'cat-clays', a name associated with cat's excreta. Subsequently CHENERY (1954), proposed the name "acid sulfate soils" and this has been more favourably adopted.

An acid sulfate soil is defined as a soil containing sulfates of iron and aluminium, with a pH in water of below 3.5 and having characteristic pale yellow mottles. According to the USDA (1970) Soil Conservation Service a 'sulphuric' horizon is one in which the pH is below 3.5, and yellow jarosite mottles of hue 2.5Y or more yellow, and chroma 6 or more (MUNSELL, 1954) are present.

A potential acid sulfate soil is a soil that is undrained and unoxidized, with reserves of sulfides mainly occurring as pyrite. The USDA (1970) Soil Conservation Service defines 'sulfidic' material as being a water-logged soil containing more than 0.75% total sulfur (on dry weight), mostly in the form of sulfides, and calcium carbonate equivalent to less than 3 times the sulfur content; these soils have a potential of becoming very acid when drained or allowed to oxidize.

The presence of acid sulfate soils and potential acid sulfate soils in the world has been estimated by various workers. Considerable areas were reported in:

Africa	Beye et al., 1975
Black Sea	Leventhal, 1983
Brasil	Roquero de Labura and Garcia-Casal, 1973
Brunei	Williams, 1980
China	Kung and Chou, 1964
Denmark	Postma, 1982
England	Fisher, 1986
Fiji	Richmond et al., 1975
Finland	Kivinen, 1950

Gambia	Thomas et al., 1979
Guinea-Bissau	Oosterbaan, 1982
Guyana	Evan, 1966
Hong-Kong	Grant, 1973
India	Raychauhuri and Ananthraman, 1960
Indonesia	Breemen, van, 1977; Collier, 1979; Didi Ardi et al., 1986; Diemont and van Reuler, 1984; Driessen and Ismangun, 1972a; Driessen and Ismangun, 1972b; Driessen and Soepraptohardjo, 1974; Eelaart, van den, 1982; Eelaart, van den and Boissevain, 1986; Ismangun and Driessen, 1986; Noorsyamsi and Hidayat, 1974; Roelse et al., 1986; Soepraptohardjo and Driessen, 1976; Soepraptohardjo and Suhardjo, 1977; Steenwinkel, 1982; Sudjadi, 1984 ; Tan, 1968; Westerhout, 1982; Wiersinga and Sudibjo, 1982; Wijk, van, 1951;
Japan	Kawasaki and Mekaru, 1978
Liberia	Virmani, 1978
Malagasy	Continet and Durand, 1966
Netherlands	Oenema, 1986
New Zealand	Metson et al., 1977
Niger	Marsh, 1966
Pakistan	Quadir, 1951
Peninsular Malaysia	Bloomfield and Powlson, 1977
Philippines	Breemen, van, 1978
Rhodesia	Thompson, 1972
Sénégal	Vieillefon, 1977
Sierra Leone	Jordan, 1964
Sri Lanka	Breemen, van, 1978
Surinam	Pons, 1965
Sweden	Wiklander et al., 1950
Thailand	Breemen, van, 1976
United States	Edelman and van Staveren, 1958
Venezuela	Sioli, 1964
Vietnam	Moorman, 1961

Other literature can be found in the 'Bibliography on Acid Sulfate Soils 1863-1973' compiled from literature reference lists assembled by KAWALEC, SOMBATPANIT and VAN BREEMEN (in the Proc. of the Int. Symp. on Acid Sulfate Soils, p. 275-291). Besides this alphabetical literature list an geographical ordered literature list is presented (p.293-295).

Potential acid sulfate soils can, according to PONS and VAN BREEMEN (1982), be formed in:
- saline and brackish tidal flats and tidal swamps;
- poorly drained inland valleys;
- bottoms of saline and brackish lagoons, seas and lakes.

The in these regions formed sediments are defined as respectively:
- normal (non-euxinic) terrigeneous marine sediments;
- non-marine freshwater sediments;
- marine euxinic sediments.

2. PYRITE FORMATION

The major factors controlling how much pyrite can form in a sediment are the amounts of organic matter and reactive iron minerals deposited in a sediment, and the availability of dissolved sulfate.

Organic matter appears to be the major control on pyrite formation in normal (non-euxinic) terrigeneous marine sediments where dissolved sulfate and iron minerals are abundant. By contrast, pyrite formation in non-marine, freshwater sediments is severely limited by low concentrations of sulfate. Under marine euxinic conditions sufficient H_2S is produced that the dominant control on pyrite formation is the availability of reactive iron minerals (after BERNER, 1984).

The first step in the overall process of sedimentary pyrite formation is the bacterial reduction of sulfate (fig. 1). This process occurs only in the absence of oxygen, under anaerobic conditions. Such conditions are realized in the majority of subaqueous sediments because sufficient organic matter is deposited to act as an oxygen-consuming barrier.

Dissolved oxygen migrates into the sediment from the overlying water via molecular diffusion, wave and current stirring, or bioturbational irrigation (ALLER, 1980; BERNER, 1980; FISHER, 1986). However, the oxygen is consumed by aerobic bacteria living near the sediment-water interface, which use the oxygen to convert organic matter to CO_2. Rapid consumption of all O_2 near the sediment-water interface prevents it from penetrating far into the sediment. As a result, anaerobic conditions, necessary for bacterial sulfate reduction appear below a depth normally of a few centimeters. Thus, bacterially decomposable organic matter is needed not only as a reductant for sulfate (fig. 1), but also as an agent for bringing about anaerobic conditions.

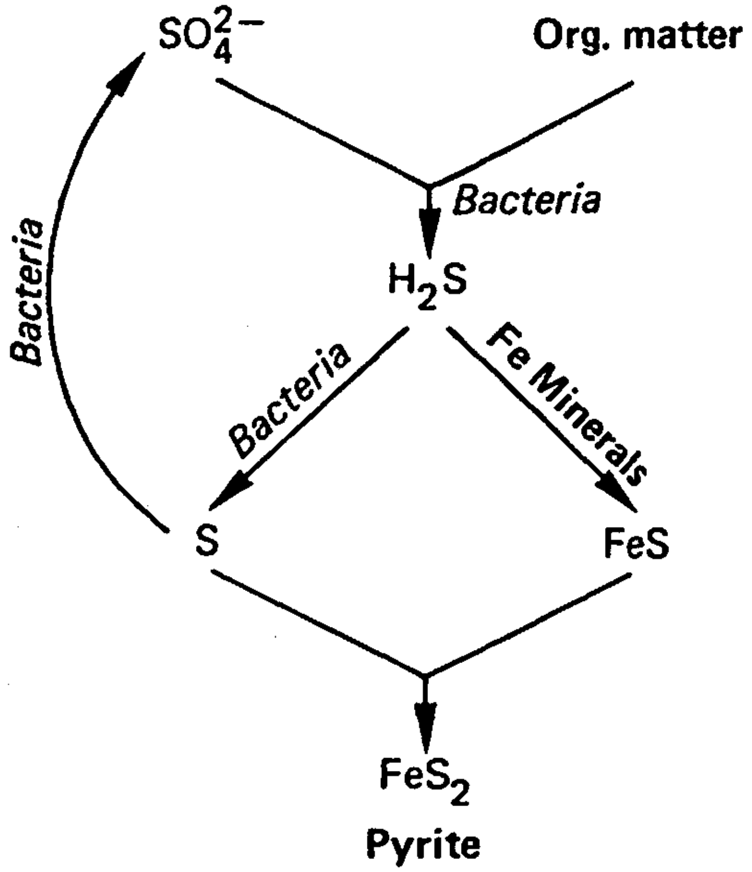

Figure 1. Diagramatic representation of the overall process of sedimentary pyrite formation (after BERNER, 1972).

Bacterial sulfate reduction is a complex process and proceeds via a variety of individual steps involving processes such as the breakdown of biopolymeric organic matter to simple organic molecules by fermentative micro-organisms, the utilization of the simple molecules by sulfate reducing bacteria themselves, and the further oxidation of organic reaction products (JÖRGENSEN, 1982). However, the overall process can be shown to be adequately represented by the simple reaction (WESTRICH, 1983).

$$2\ CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$$

where sedimentary organic matter is represented by the idealized formula CH_2O.

As the above reaction shows, two factors which should affect the rate of bacterial sulfate reduction are the avaialability of dissolved sulfate and of organic matter.

According to WESTRICH (1983) the rate-control by sulfate is not important at concentrations above about 5 mM. Since most pyrite forms at depths where sulfate concentrations are much higher (KAPLAN et al., 1963), the effect of sulfate on sulfate reduction and pyrite formation in most marine sediments, is relatively unimportant.

The major factor controlling the rate of bacterial sulfate reduction in normal marine sediments is the amount and especially the reactivity of organic matter deposited in the sediment. Experimental data of WESTRICH (1983) shows that the reactivity of organic matter decreases as the more reactive compounds are consumed first.
The less reactive compound that survive (or are formed during aging) bring about lower rates of sulfate reduction.

These results can be used to explain why bacterial sulfate reduction and pyrite formation are more extensive in certain areas of the present-day ocean than in others. Except for rare euxinic environments practically all bottom water contain dissolved oxygen. Consequently, pyrite formation must take place below the sediment-water interface. In many regions sedimentation rates are very low and organic compounds, representing the remains of marine organisms, are exposed to oxic destruction near the sediment-water interface (and in the overlying water column) for long periods, up to thousands of years. As a result, only small amounts of very resistant organic compounds support very little sulfate reduction and little pyrite forms. By contrast, in areas of high sedimentation, especially in nutrient rich waters which bring about a high rate of organic matter production and sedimentation, rapid burial enables relatively reactive compunds and more organic matter in general to become available for bacterial sulfate reduction at depth. Consequently, high levels of H_2S are attained and much pyrite forms. These considerations help to explain why there is a crude correlation between sedimentation rate on the one hand, and organic matter and pyrite contents on the other.

What has been said above concerning young marine sediments does not apply to young freshwater sediments. The reason is that dissolved sulfate concentrations in freshwater are much less, on the average several hundred fold less, than that found in seawater. As a result sulfate is rapidly and totally consumed via sulfate reduction at sediment depths of only a few centimeters, leaving behind little pyrite and much organic matter. Thus (in contrast to marine sediments) sulfate is the principal factor controlling pyrite formation in freshwater sediments. This results in a relative lack of correlation of pyrite sulfur with opganic carbon, and high carbon to sulfur (C/S) ratios in such sediments (see figure 2). The large difference in C/S ratios of organic-rich young marine and freshwater sediments suggests that this ratio might serve as a useful paleosalinity indicator. According to BERNER (1984) the C/S ratio is indeed a useful parameter for distinguishing original deposition under freshwater vs. marine conditions.

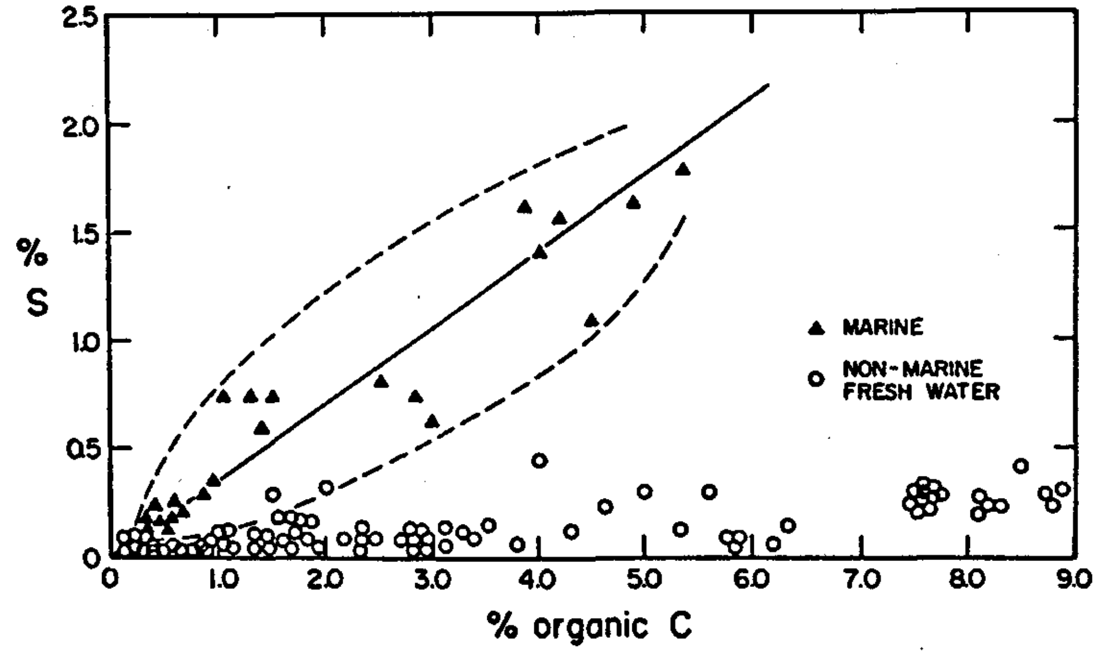

Figure 2. Plots of weight percent organic carbon versus weight percent reduced sulfur for modern fresh water lake sediments and normal marine sediments (after BERNER and RAISWELL, 1983).

In the above discussion it has been implied that greater production of H_2S, via bacterial sulfate reduction, simply means more pyrite formation, and this seems to be the case in many normal marine sediments. However, pyrite formation is also limited by the amount and reactivity of detrital iron minerals added to the sediment.

Apparently, in terrigeneous marine sediments deposited under normal aerobic conditions, the iron minerals are sufficiently abundant and reactive that they don't pose a serious problem. However, this is not the case for highly calcareous sediments. In localities far removed from sources of terrigeneous clays or silts and where the sediments instead consists almost entirely of calcium carbonate derived from the skeletal debris of marine organisms, there is insuffucient iron to bring about appreciable pyrite formation. Even in the presence of high organic matter concentrations and abundant H_2S, if the sediment is dominated by $CaCO_3$, the pyrite concentration is low.

The amount and reactivity of iron minerals also plays a major role in pyrite formation under euxinic conditions. The word euxinic (derived from the Black Sea whose ancient Latin name was Pontus Euxinus) refers to sediments deposited in bottom waters which are anaerobic and contain H_2S instead of O_2. The anaerobic bottom water result from strong density stratification from contact with the atmosphere. Under such conditions relatively fresh planktonically-derived organic material becomes available for bacterial sulfate reduction. As a result organic accumulations are high, bacterial sulfate reduction is extensive, and H_2S builds up in the bottom water as well as in the underlying sediments. Under euxinic conditions the reaction of H_2S with iron-minerals can occur both before and after burial, even during sedimentation itself. Thus, the amount of pyrite formed depends more on the amount and reactivity of detrital iron minerals, and less on the amount of locally deposited organic matter. However, regardless of the environment of deposition the amount of pyrite formed in a sediment, except in highly calcareous ones, is almost never limited by the amount of total iron deposited. Instead, pyrite content is controlled by the reactivity of detrital iron minerals. The most reactive fraction is made up of fine-grained hydrous ferric oxides, formed via continental weathering, which normally occur as rust coloured coatings on other mineral grains. Other less reactive sources of iron include that contained within clay minerals and that present in unweathered primary minerals such as biotite, pyroxenes, amphiboles, magnetite, and ilmenite.

3. ACID-NEUTRALIZING CAPACITY

A soil containing pyrite is only a potential acid sulfate soil if the potential acidity represented by the pyrite is greater than the acid-neutralazing capacity of the soil. The neutralizing capacity of the soil is provided by:

- carbonates
- exchangeable bases
- easily-weatherable silicates

Calcium carbonate stands out in both its rate of reaction and neutralizing capacity at pH values close to neutrality. Its neutralizing capacity is 20 moles acid kg^{-1}. If one mole of pyrite is equivalent to four moles H^+ the acidity from the oxidation of 1 per cent by mass of pyrite sulfur is balanced by 3 per cent of $CaCO_3$ (after DENT, 1986).

After dissolution of any carbonates present, further acid displaces exchangeable bases. In marine clays with a large proportion of smectite, as much as 0.5 per cent by mass of pyrite S may be neutralized. Clays that are predominantly kandite and soils of low clay content have very much lower neutralizing capacities.

At pH values below about 4, there is a significant dissolution of silicate clays (VAN BREEMEN, 1973; 1976). The rate of reaction is relatively slow and in most cases appears unlikely to prevent the development of acid sulfate conditions, although the severity of acidity is certainly reduced.

4. PYRITE OXIDATION

Potential acid sulfate soils become acid as a result of drainage. Pyrite is stable only under anaerobic conditions. Drainage allows oxygen to enter the soil and pyrite is then oxidized, generating sulphuric acid (see figure 3).

The reaction of pyrite with oxygen is a slow process that can be represented by the equation (DENT, 1986):

$$FeS_2 + {}^{15}/4\ O_2 + {}^{7}/2\ H_2O \rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 4H^+$$

Most of the ferric hydroxide crystallises as the reddish brown oxide goethite in mottles, coatings, and nodules wihtin the soil. Some Fe^{2+} may be lost from the soil in drainage waters, and will precipitate under more oxidizing conditions in drains and ditches - which can even be blocked by gelatinous deposits of hydrated Fe^{3+} oxides.

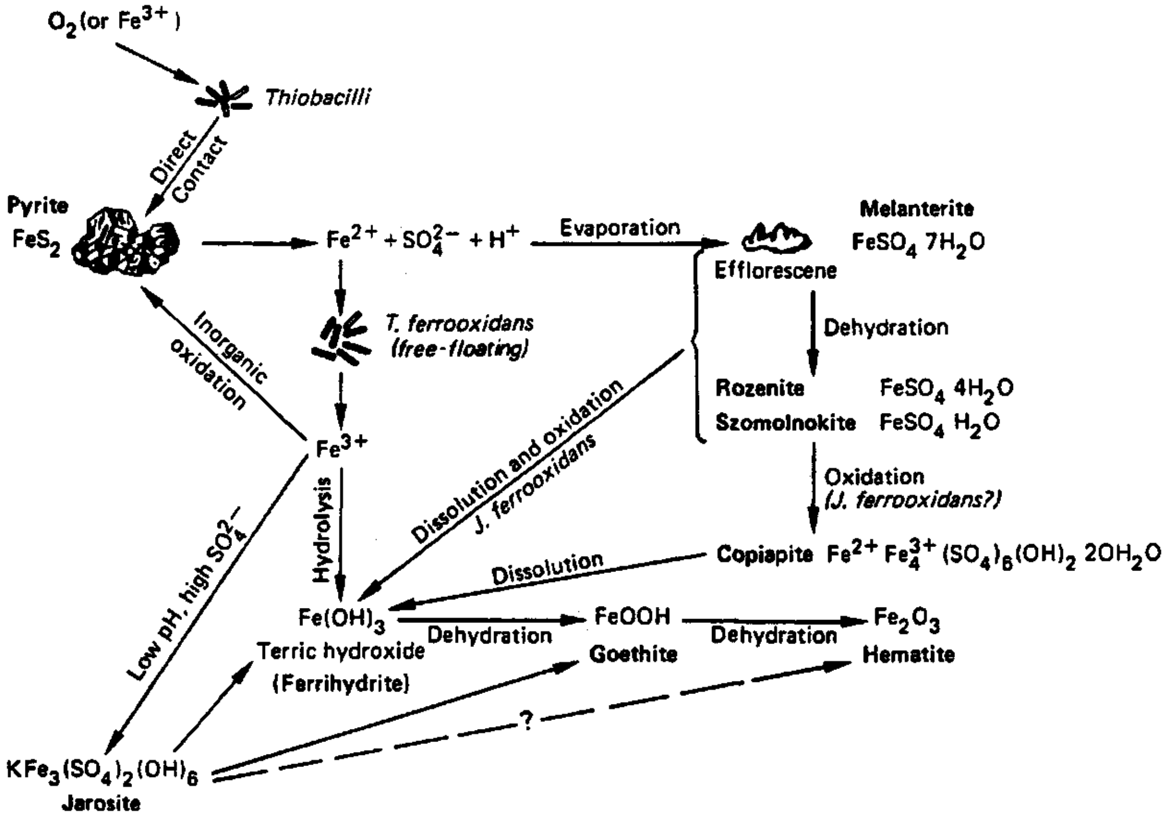

Figure 3. The overall sequence of mineral reactions for pyrite oxidation showing the relationships between oxidizing agents, catalysts, and mineral products (after NORDSTROM, 1982).

Once the pH of the oxidizing system is brought below 4, Fe^{3+} becomes appreciably soluble and brings about rapid oxidation of pyrite

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$$

In the presence of oxygen, the Fe^{2+} produced by these reactions is oxidized to Fe^{3+}. At pH values lower than 3.5, chemical oxidation is a slow process with a half time of the order of 1000 days (SINGER and STUMM, 1970). However, autotrophic bacteria, which seem to be ubiquitous in sulphidic and acid sulphate soils, overcome the kinetic barriers that exist in purely chemical systems. At low pH, Thiobacillus ferrooxidans oxidizes reduced sulphur species and also Fe^{2+}, thereby returning Fe^{3+} to the system (ARKESTEIJN, 1980).

$$Fe^{2+} + \frac{1}{4} O_2 + H^+ \xrightarrow{\text{Thiobacillus ferrooxidans}} Fe^{3+} + \frac{1}{2} H_2O$$

The rapid catalytic oxidation of pyrite by Fe^{3+} ions is limited by the pH, because Fe^{3+} is appreciably soluble only at pH values less than 4, and because Thiobacillus ferrooxidans does not grow at a higher pH. In calcareous soils, the oxidation of pyrite is probably slow. Fe^{3+} oxides and pyrite may be in intimate contact, but the rate of oxidation will be constrained by the insolubility of Fe^{3+}.

The different stages of oxidation do not necessarily occur at exactly the same localisations in soil. Field and micromorphological examination of acid sulphate soils shows distinct seperation of pyrite and its oxidation products: jarosite, iron oxides, and gypsum. In horizons where there is a reserve of pyrite to be oxidized, this is confined to the cores of peds, whereas jarosite and iron oxides and gypsum are closely associated with pores and ped faces. VAN BREEMEN (1976) suggests that oxygen reacts with dissolved Fe^{2+} before it can reach the pyrite and that Fe^{3+} is the immediate oxidant (see figure 4).

Under a climate with pronounced wet and dry seasons, oxidation of pyrite may continue after flooding, using the oxidative capacity that was stored as Fe^{3+} oxide during the dry season. Ever so, the supply of oxygen appears to be the rate-limiting factor in the oxidation of pyrite under acid conditions in the field. Excavated pyritic material is oxidized very much faster, and suffers a much lower pH than the same material in situ. As long as there is a reserve of pyrite to be oxidized, deepening of drainage or an unusually dry season invariably leads to increased production of acidity.

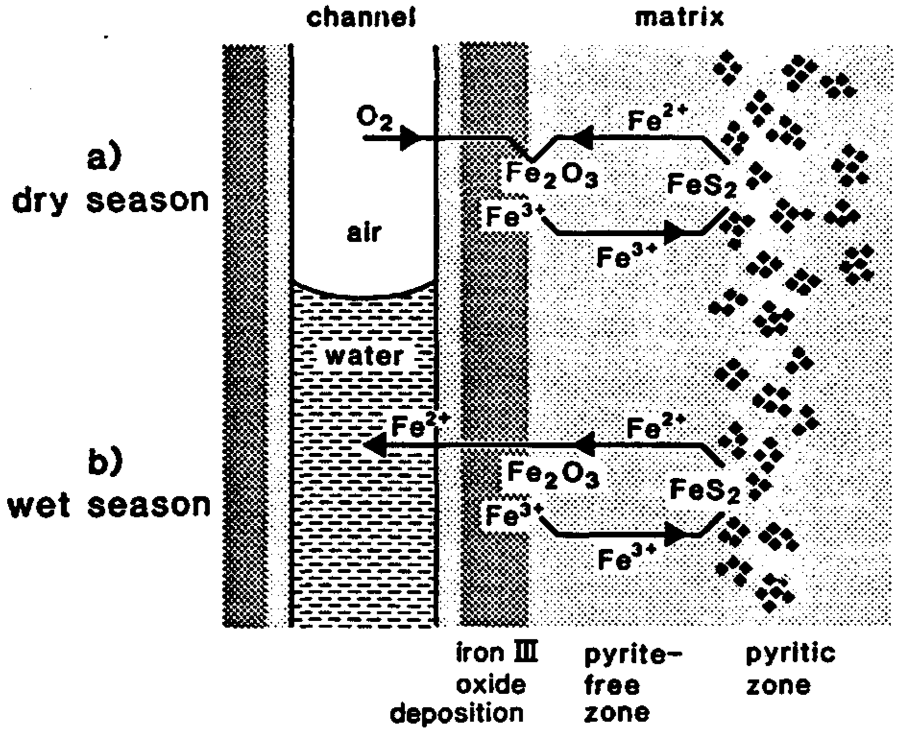

Figure 4. Model of pyrite oxidation in an acid sulfate soil (after VAN BREEMEN, 1976).

a) During the dry season, oxygen diffuses into the soil from pores and fissures. Fe^{2+} ions in solution are oxidized to Fe^{3+} ions or oxides. At low pH, some Fe^{3+} remains in solution, diffuses to the pyrite surface where it is reduced to Fe^{2+}, liberating acidity. Fe^{2+} diffuses back towards the oxidation front where it is oxidized, liberating more acidity.

b) Some oxidation of pyrite can continue under acid, waterlogged conditions, using the reserve of iron III oxides. In this case, Fe^{2+} ions migrate out of the soil into drainage or floodwaters before being oxidized.

Conversely acid production is stopped by raising the watertable. The overall sequence of reactants, products, and catalysts for pyrite oxidation is shown in the schematic illustration of figure 3 (after NORDSTROM, 1982). The picture attempts to tie together the roles played by:

- the oxidizing agents ferric iron and oxygen
- the catalyzing agent Thiobacillus ferrooxidans which utilizes oxygen for respiration, and
- the mineral products

5. KINETIC ASPECTS OF PYRITE OXIDATION

Pyrite oxidation is a time dependent process. Factors that influence the rate of pyrite oxidation are the supply of oxygen and ferric iron, the temperature and the total surface area of pyrite per unit of soil.

Several authors tried to define rate laws in order to calculate and predict the decrease in pyrite (and the consequently increase in sulfuric acid) as a result of the oxidation of pyrite by dissolved oxygen or by ferric iron in soils.

5.1. Pyrite oxidation by ferric iron

WIERSMA en RIMSTIDT (1984) measured rates of reduction of ferric iron by pyrite and marcasite in chloride solutions. Preparation of grain surfaces to avoid anomalous rapid initial rates was not reported. The pyrite was suspended in solution by stirring, so any rate effects due to abrasion of colliding grains are unknown in their experiments. Wiersma and Rimstidt assumed a first-order rate law (see table 3), and determined rate constants by integrating the rate over time according to the assumed law. However, they noted that the derived rate constants decreased with decreasing initial ferric iron concentration.

In nearly identical series of experiments, SINGER AND STUMM (1969) noted the same behaviour when they calculated rate constants from an assumed first-order rate law. They consequently rejected a first-order rate law as invalid. For these reasons it is not acceptable to assume a first-order rate law and rate constants caculated from such a law as valid.

Table 3. Rate laws for oxidation of pyrite by ferric iron in low temperature (30°C) acidic solutions.

Study	pH range	T range	Rate law
McKibben & Barnes (1986)	1 - 2	25-30°C	$(Fe^{3+})^{0.58}(H^+)^{-0.50}$
Wiersma & Rimstidt (1984)	2	25-50°C	$*(Fe^{3+})$
Mathews & Robins (1972)	0 - 1.5	30-70°C	$*(Fe^{3+})(Fe^{3+} + Fe^{2+})^{-1.0}(H^+)^{-0.44}$
Garrels & Thompson (1960)	0 - 2	30°C	$*(Fe^{3+})(Fe^{3+} + Fe^{2+})^{-1.0}$

*Rate dependence on ferric ion assumed rather than derived

MATHEWS and ROBINS (1972) studied the oxidation of pyrite-marcasite mixtures by ferric sulfate solutions. They also assumed a first order dependence on ferric iron to derive their rate constant. They concluded that the rate was proportional to the ratio of ferric to total iron, but gave no supporting data. According to their rate law, oxidation in solutions containing no ferrous iron should be independent of ferric iron concentration. Such behaviour does not agree with the data given by McKIBBEN and BARNES (1986). MATHEWS and ROBINS (1972) rate dependence on pH is nearly identical to that determined in the study of McKIBBEN and BARNES (1986), although the ionic strenght may also have been varied with pH in the experiments carried out by MATHEWS and ROBINS (1972).

GARRELS and THOMPSON (1960) studied the reduction of ferric iron by pyrite in ferric sulfate solutions. They reported that pH did not affect rates. On the basis of a qualitative analyses of Eh versus time plots, they concluded that the rate was dependent on the ratio of ferric to total iron concentration, due to competitive adsorption between ferric and ferrous ions.

According to McKIBBEN and BARNES (1986), it is difficult, given the discrepancies above, to come to a consensus on the rate law and mechanism of oxidation of pyrite by ferric iron. The data of WIERSMA and RIMSTIDT (1984); RIMSTIDT et al. (1986) and SINGER and STUMM (1969) clearly do not support a first-order dependence on ferric ion. Rate laws expressing the rate as a function of ferric to total iron are likewise dubious, because they are derived on the basis of an assumed first-order dependence on ferric ion. They also violate the recent data given by McKIBBEN and BARNES (1986), which yield a square-root rate law for the effect of ferric ion and a negligible dependence on ferrous ion concentration. Square-root rate laws generally imply dissociation of a species on the mineral surface, but this is obviously unlikely in the case of ferric ion. Using theoretical arguments, LASAGA (1981) has demonstrated how non-integer rate laws for non-dissociating species may be the result of rate-limiting desorption of products on heterogeneous mineral surfaces. It is likely that studies of adsorbed complexes on oxidized pyrite surfaces using high-resolution spectroscopic techniques will provide the most useful insight into oxidation mechanisms. Techniques such as Fourier transform infrared, Auger electron and X-ray photo-electron spectroscopy may be particularly promising (PERRY et al., 1983; TAYLOR, 1984).

5.2. Pyrite oxidation by dissolved oxygen

In table 4 different rate laws describing the oxidation of pyrite by dissolved oxygen are shown.

MATHEWS AND ROBINS (1974) studied the oxidation of mixtures of pyrite and marcasite by dissolved oxygen, using the same techniques as in their previous study of oxidation by ferric ion. They measured total, ferric and ferrous iron concentrations with time. They found no pH-effect, but conducted their study over a very limited, acidic range. Their experiments yielded a 0.81-order dependence on dissolved oxygen concentration.

SMITH and SHUMATE (1970) did not specifically determine a rate law, but presented enough data for McKibben and Barnes to derive the one shown in table 4.

Table 4. Rate laws for oxidation of pyrite by dissolved oxygen in low temperature (30°C) acidic solutions.

Study	pH range	T range	Rate law
McKibben & Barnes (1986)	2 - 4	20-40°C	$(O_2)^{0.49}$
Mathews & Robins (1974)	-0.1 - 1.2	30-70°C	$(O_2)^{0.81}$
Smith & Schumate (1970)	2 - 10	20-35°C	$*(O_2)^{0.70}(H^+)^{-0.10}$

*Rate law calculated from their data for $P_{O_2} < 1$ atm.

To determine rates of oxidation, they measured oxygen consumption rates and assumed that the stochiometry of this reaction can be applied at all pH values. Recently MOSES (1982) and GOLDHABER (1983) show this assumption to be invalid, because of the persistence of metastable sulfur oxyanions at pH values above about 4. Consequently, some of the rate data of SMITH and SHUMATE (1970) are subject to question. McKIBBEN and BARNES (1986) suggest that a complete reinvestigation of the rate of pyrite oxidation by oxygen is warranted above pH 4. The fact that elemental sulfur or metastable sulfur oxyanions are not observed as products of pyrite oxidation below pH 4 suggests that the sequential electron transfer reactions forming sulfate from pyrite sulfide are rapid at low pH. However, acccording to McKIBBEN and BARNES (1986), elucidation of the exact pyrite oxidation mechanisms will probably require high-resolution spectroscopic studies of adsorbed complexes formed on pyrite surfaces. Nevertheless, experimental determined relations describing the rate of pyrite oxidation as a function of dissolved oxygen, ferric iron and/or H^+ concentrations can be a useful tool in modelling the chemical processes taking place in (potential) acid sulfate soils. So far no integrated hydro-chemical model exists describing all the processes taking place in acid sulfate soils accurately.

LITERATURE

ALLER, R.C., 1980. Quantifying solute distributions in the bioturbated zone of marine sediments by defining an average micro-environment. In: Geochimica et Cosmochimica Acta, Vol. 44, 1955-1965.

ARKESTEIJN, G.J.M.W., 1980. Contribution of micro-organisms to the oxidation of pyrite. Thesis, Agricultural Univeristy Wageningen, The Netherlands.

BERNER, R.A., 1972. Sulfate reduction, pyrite formation, and the oceanic sulfur budget. In: The changing Chemistry of the Oceans: Nobel Symposium 20 (Eds. D. Dyrssen and D. Jagner). Almqvist and Wiksell, 347-361.

BERNER, R.A., 1980. Early diagenesis: A theoretical approach. Princeton, 241 pp.

BERNER, R.A., 1984. Sedimentary pyrite formation: an update. In: Geochimica et Cosmochimica Acta. Vol. 48, 605-615.

BERNER, R.A. and R. RAISWELL, 1983. Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory. In: Geochimica et Cosmochimica Acta. Vol. 47, 855-862.

BEEK, K.J., W.A. BLOKHUIS, P.M. DRIESSEN, N. VAN BREEMEN, R. BRINKMAN and L.J. PONS, 1980. Problem soils: their reclamation and management. In: Land reclamation and water management: developments, problems and challenges. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands. Publ. 27, 43-72.

BREEMEN, N. VAN, 1973. Soil forming processes in acid sulfate soils. In: Dost. Vol. 1, 66-130.

BREEMEN, N. VAN, 1976. Genesis and solution chemistry of acid sulfate soils in Thailand. Pudoc, Wageningen.

BRINKMAN, R., 1982. Directions of further research on acid sulfate soils. In: Dost and Van Breemen, 12-20.

CHENERY, E.M., 1954. Acid sulfate soils in Central Africa. In: Trans. 5th International Congress of Soil Science. Leopoldville, 4 pp, 1958.

DENT, D., 1984. Acid sulfate soils: a baseline for research and development. Institute for Land Reclamation and Improvement. Publ. 39, Wageningen.

FISHER, I.S.J., 1986. Pyrite formation in bioturbated clays from the Jurassic of Britain. In: Geochimica et Cosmochimica Acta. Vol. 50, 517-523.

GARRELS, R.M. and M.E. THOMPSON, 1960. Oxidation of pyrite by iron sulfate solutions. In: American Journal of Science. Vol. 258, 57-67.

GOLDHABER, M.B., 1983. Experimental study of metastable sulfur oxyanion formation during pyrite oxidation at pH 6-9 and 30°C. In: American Journal of Science. Vol. 283, 193-217.

JØRGENSEN, B.B., 1982. Ecology of the bacteria of the sulfur cycle with special reference to anoxic-oxic interface environments. In: Phil. Trans. Roy. Soc. London. B298, 543-561.

KAPLAN, I.R., K.O. EMERY and S.C. RITTENBERG, 1963. The distribution and isotopic abundance of sulfur in recent marine sediments of southern California. In: Geochimica et Cosmochimica Acta. Vol. 27, 297-331.

LASAGA, A.C., 1981. Rate laws of chemical reaction. In: Kinetics of geochemical processes. Eds. A.C. Lasaga and R.J. Kirkpatrick, Min. Soc. Amer. Rev. in Min. Vol. 8, 1-68.

MATHEWS, C.T. and R.G. ROBINS, 1972. The oxidation of ferrous disulfide by ferric sulfate. In: Austr. Chem. Eng., Aug., 21-25.

MATHEWS, C.T. and R.G. ROBINS, 1974. Aqueous oxidation of iron disulfide by molecular oxygen. In: Austr. Chem. Eng., Nov.-Dec., 19-24.

McKIBBEN, M.A. and H.L. BARNES, 1986. Oxidation of pyrite in low temperature acidic solutions: rate laws and surface textures. In: Geochimica et Cosmochimica Acta. Vol. 50, 1509-1520.

MOSES, C.O., 1982. Kinetic investigations of sulfide mineral oxidation in sterile aqueous media. M.S.thesis, University of Virginia, 100 pp.

MUNSELL, 1954. Munsell soil color chart. Munsell Color Company, Baltimore.

NORDSTROM, D.K., 1982. Aqueous pyrite oxidation and consequent formation of secondary iron minerals. In: Acid sulfate weathering. Soil Science Soc. Am. Special Publ. 10, Madison, Wisc., 37-56.

PERRY, D.L., L. TSAO and K.A. GAUGLER, 193. Surface study of HF- and HF/H_2SO_4-treated feldspar using Auger electron spectroscopy. In: Geochimica et Cosmochimica Acta. Vol. 47, 1289-1292.

PONS, L.J. and N. VAN BREEMEN, 1982. Factors influencing the formation of potential acidity in tidal swamps. In: Dost and Van Breemen, 37-51.

RIMSTIDT, J.D., J.A. CHERMAK and W.D. NEWCOMB, 1986. The oxidation of sulfide minerals. In: Fifth Intern. Symp. on Water-Rock Interaction, Reykjavik, Iceland, 8-17 Aug. Extended Abstracts, 471-474.

SINGER, P.C. and W. STUMM, 1969. Oxygenation of ferrous iron. Water Pollut. Control Res. Ser. Rept. 14010-06-069. Fed. Water Quality Admin., U.S. Dept. of the Interior, 150 pp.

SINGER, P.C. and W. STUMM, 1970. Acidic mine drainage: the rate determining step. In: Science. Vol. 167, 1121-1123.

SMITH, E.E. and K.S. SHUMATE, 1970. Sulfide to sulfate reaction mechanism. Water Pollut. Control Res. Ser., Rept. 14010 FPS 02/70, Fed. Water Quality Admin., U.S. Dept. of the Interior, 115 pp.

TAYLOR, J.A., 1984. An X-ray photoelectron and electron energy loss study of the oxidation of lead. In: Jour. Vac. Sci. Technol., A2(2), Apr.-June, 771-774.

USDA, 1970. Selected chapters from the unedited text of the Soil Taxonomy of the National Cooperative Soil Survey. SCS, USDA, Washington.

WESTRICH, J.T., 1983. The consequences and controls of bacterial sulfate reduction in marine sediments, Unpubl. Ph.D. dissertation, Yale University, 530 pp.

GEOGRAPHICAL REFERENCES

BEYE, G., M. TOURÉ and G. ARIAL, 1975. Acid sulfate soils of West Africa, problems of their management for agricultural use. In: IRRI, Rice Conference, Los Baños, Philippines.

BREEMEN, N. VAN, 1976. Genesis and solution chemistry of acid sulfate soils in Thailand. Pudoc, Wageningen.

BREEMEN, N. VAN, 1977. Acid sulfate soils and rice. In: IRRI. Soils and Rice conference, Philippines.

BREEMEN, N. VAN, 1978. Landscape, hydrology and chemical aspects of some problem soils in the Philippines and in Sri Lanka. A terminal report submitted to the International Rice Research Institute, Philippines.

BLOOMFIELD, C. and D.S. POWLSON, 1977. The improvement of acid sulfate soils for crops other than padi. In: Malayan Agricultural Journal 51.

COLLIER, W.L., 1979. Social and economic aspects of tidal land development in Indonesia. The Australian National University, Development Studies Centre, Occasional Paper no. 15.

CONTINET, S. and J.H. DURAND, 1966. Les sols de mangroves de la cote nordouest de Madagascar, Region d'Ambanja. In: Agron. Trop. (Paris). Vol. 21, 347-360.

DIDI ARDI, S., I. ABDULLAH ABAS and PERMADY SUDEWO, 1986. Soil properties of agricultural land in Karany Agung Ulu Transmigration Project, South Sumatra, Indonesia. In: Lowland Development in Indonesia. Symp. Papers, Jakarta, Indonesia. Supporting Papers, 113-126.

DIEMONT, W.H. and H. VAN REULER, 1984. Physiography and pyrite formation in Berbak, Sumatra, Indonesia. RIN Contributions to research on management of natural resources 1984-2. RIN, Arnhem, The Netherlands.

DRIESSEN, P.M. and ISMANGUN, 1972. The influence of tidal fluctuations on soil formation and agriculture in the Coastal Region of Southern Kalimantan. In: H. Dost (Ed.) Acid Sulfate Soils; Proceedings Int. Symp., Wageningen, ILRI Publ. 18.

DRIESSEN, P.M. and ISMANGUN, 1972. Pyrite containing sediments of Southern Kalimantan, Indonesia. Their soils, management and reclamation. In: H. Dost (Ed.) Acid Sulfate Soils.; Proceedings Int. Symp., Wageningen, ILRI Publ. 18.

DRIESSEN, P.M. and M. SOEPRAPTOHARDJO, 1974. Soils for agricultural expansion in Indonesia. Soil Research Institute Bogor. Bull. 1, 63 pp.

EDELMAN, C.H. and J.M. VAN STAVEREN, 1958. Marsh soils in the United States and in the Netherlands. In: Journal Soil and Water Conservation. Vol. 13, 5-17.

EELAART, A.L.J. VAN DEN, 1982. Problems in reclaiming and managing tidal lands of Sumatra and Kalimantan, Indonesia. In: H. Dost and N. van Breemen (Ed.). Proceedings of the Bangkok Symposium on Acid Sulfate Soils, ILRI Publ. 31, 272-290.

EELAART, A.L.J. VAN DEN and W. BOISSEVAIN, 1986. Evaluation and improvement of water management for potential acid sulfate soils in tidal lands of South Kalimantan. In: Lowland Developmenmt in Indonesia. Symp. Papers, Jakarta, Indonesia. Supporting Papers, 227-241.

EVAN, H., 1966. Toxic sulfate soils in Gyana and their improvement for sugar cane cultivation. Proceedings of the British West Indies Sugar Technology Conference held in Guyana.

FISHER, I.S.J., 1986. Pyrite formation in bioturbated clays from the Jurassic of Britain. In: Geochimica et Cosmochimica Acta. Vol. 50, 517-523.

GRANT, C.J., 1973. Acid sulfate soils in Hong Kong. In: Proc. Int. Symp. on Acid Sulfate Soils, Wageningen. Vol. II, 215 -228.

ISMANGUN and P.M. DRIESSEN, 1968. The acid sulfate soils of Indonesia. Agricultural Cooperation Indonesia. Netherlands Research Reports 1968-74. Section 4 Technical Contributions. Ministry of Agriculture, Jakarta. Ministry of Foreign Affairs, the Hague.

JORDAN, H.D., 1964. Relation of vegetation and soil development of mangrove swamps for rice growing in Sierra Leone. In: Journal of Applied Ecology, no.1.

KAWASAKI, H. and T. MEKARU, 1978. Characteristics of acid sulfate soils in the Okinawa Islands. Bulletin of the Kyushu Agricultural Experimental Station.

KIVINEN, E., 1950. Soil sulfates and their management in Finland. In: Trans. 4th Int. Congr. Soil Sci., Amsterdam. Vol. II, 259-262.

KUNG, T.T. and S.L. CHOU, 1964. On the genesis of strongly acid salty paddy soils of S. Kwanytung. In: Chinese Acta Pedol. Sinica. Vol. 12, 183-191.

LEVENTHAL, J.S., 1983. An interpretation of carbon and sulfur relationships in Black Sea sediments as indicators of environments of deposition. In: Geochimica et Cosmochimica Acta. Vol. 47, 133-138.

MARSH, D.F.M., 1966. Reclamation of saline swamps in the Niger Delta. In: Proc. of the 2nd Nigerian Forestry Conference.

METSON, A.J., E.J. GIBSON, J.E. COX and D.B. GIBBS, 1977. The problem of acid sulfate soils with examples from North Auckland, New Zealand. In: N.Z. Journal of Science. Vol. 20, 371-394.

MOORMAN, F.R., 1961. Researches on acid sulfate soils and their amelioration by liming. In: Agronomic Library. Ministry of Rural Affairs, Saigon.

NOORSYAMSI, H. and O.O. HIDAYAT, 1974. The tidal swamp rice culture in South Kalimantan. Contr. Centr. Res. Inst. Agric. Bogor 10, 1-8.

OENEMA, O., 1986. Pyrite accumulation in salt marshes of the Eastern Scheldt, the Netherlands. In: Trans. of the XIII Congress of the Intern. Soc. of Soil Science, Hamburg.

OOSTERBAAN, R.J., 1982. Natural and social constraints to polder development in Guinea-Bissau. In: Polders of the World. Intern. Symp., Lelystad, the Netherlands. Vol. I, 1465-160. ILRI, Wageningen.

PONS, L.J., 1965. Pyrites as a factor controlling chemical ripening and formation of cat clay, with special reference to the coastal plain of Surinam. In: Agric. Exp. Stat. Paramaribo. Bull. no. 82, 141-162.

POSTMA, D., 1982. Pyrite and siderite formation in brackish and fresh-water swamp sediments. In: American Journal of Science. Vol. 282, 1151-1183.

QUADIR, A., 1951. The Kosh soils of the Chittagong coastal area, East Pakistan.

RAYCHAUCURI, S.P. and P.V. ANANTHRAMAN, 1960. Characteristics of some Indian acid soils growing paddy. In: Journal of Indian Soc. Soil Science. Vol., 8, 223-228.

RICHMOND, T.A., J. WILLIAMS and K. DATT, 1975. Influence of drainage on pH, sulfate content and mechanical strength of a potential acid sulfate soil in Fiji. In: Tropical Agriculture. Vol. 52, no.4.

ROELSE, K., S.A. VERWEIJ, J. STUIP, I. DE VRIES, D.J.M. KERSSENS and SURYADI, 1986. Water quantity and quality aspects of Kolam systems in Kalimantan. In: Lowland Development in Indonesia. Symp. Papers, Jakarta, Indonesia. Research Papers, 35-54.

ROQUERO DE LABURU, C. and J. GRACIA-CASAL, 1973. Suelos de sulfatos acidos del "Banhado do Taim", Rio Grando do Sul, El Brazil. In: Proc. Int. Symp. on Acid Sulfate Soils, Wageningen. Vol. II, 229-242.

SIOLI, H., 1964. Scientific problems of the humid tropical zone deltas and their implications. In: Proc. Dacca Symp. UNESCO, Paris, 89-96.

SOEPRAPTOHARDJO, M. and P.M. DRIESSEN, 1976. The lowland peats of Indonesia, a challenge for the future. Soil Research Inst. Bogor. Bull. no.3, 11-19.

SOEPRAPTOHARDJO, M. and H. SUHARDJO, 1977. Rice soils of Indonesia. In: IRRI Symposium on soils and rice, the Philippines, session 'rice soils of the world'.

STEENWINKEL, C.H., 1982. Policy and settlement aspects of tidal swamp land development in Indonesia. In: Polders of the World. Symp. Papers, Lelystad, the Netherlands. Vol. II, 552-561.

SUDJADI, M., 1984. Problem soils in Indonesia and their management. In: Problem soils in Asia, FFTC Book Series No. 27, 58-73.

TAN, K.H., 1968. The genesis and characteristics of paddy soil in Indonesia. In: Soil Sci. and Pl. Nutr. Vol. 14(3), 117-121.

THOMAS, P., J.A. VARLEY and J.E. ROBINSON, 1979. The sulfidic and associated soils of the Gambia Estuary. Project Report 89, Land Resources Development Centre, Tolworth Tower, Surbiton, Surrey, UK.

THOMPSON, J.G., 1972. Occurrence of acid sulfate soil in Rhodesia. In: Rhodesian Journal of Agricultural Research. Vol. 10, 153-157.

VIEILLEFON, J., 1977. Les sols des mangroves et des tannes de Basse Casamance (Sénégal). Mémoires ORSTROM 83, Bondy.

VIRMANI, S.S., 1978. Some results of varietal screening for tolerance to iron toxicity in Liberia. In: IRRI, Rice Conference, Los Baños, Philippines.

WESTERHOUT, J., 1982. Agricultural development in tidal lands in Indonesia. In: Polders of the World. Symp. Papers, Lelystad, the Netherlands. Vol. II, 267-275.

WIERSINGA, R.Th. and S. SUDIBJO, 1982. Land and water management in tidal swamp land developement projects in Indonesia. In: Polders of the World. Symp. Papers, Lelystad, the Netherlands. Vol. I, 532-539.

WIJK, C.L. VAN, 1951. Soil survey of the tidal swamps of South Borneo in connection with the agricultural possibilities. Contr. Gen. Agr. Res. Sta. No. 123, Bogor, Indonesia.

WIKLANDER, L., G. HALLGREN, N. BRINK and E. JONSSON, 1950. Studies on gyttja soils. II. Some characteristics of northern Sweden. In: Ann Royal Agric. College Sweden. Vol. 17, 24-36.

WILLIAMS, C.N., 1980. Effects of lime, drainage, maganese dioxide, and seedling condition on rice in acid sulfate soils in Brunei. In: Expt. Agriculture. Vol. 16, 313-320.