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**A REVIEW OF THE OXIDATION AN REDUCTION PROCESSES IN ACID  
SULPHATE SOILS**

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## INTRODUCTION

About 13 million hectares of potential agricultural lands in tidal swamp areas are not developed because of acid sulphate soils (Table 1). These soils have pH values below 3.5 (if Entisols) or 4 (if Inceptisols) in the upper 50 cm. Except for their low pH, acid sulphate soils have other characteristics that suit them well for agricultural productions. The acid sulphate areas are usually well supplied with plant nutrients and water, and are otherwise topographically and hydrologically favourable for agricultural productions. There are about 5 million hectares of these soils in South and Southeast Asia, about 3.7 million hectares in Africa and about 2 million hectares in South America (VAN BREEMEN, 1980).

The high degree of acidity (or potential acidity) of acid sulphate soils makes reclamation liming economically unattainable in most cases. The only practical way to manage these soils is by proper drainage and water management. Maintaining high water table can control the oxidation of pyrite (the sulfur source in these soils). Where feasible, drainage and removal of acidity by leaching can be used. Proper water management and controlled drainage have made rice productions possible in large acid sulphate areas of Thailand and Vietnam. Any attempt to reclaim these soils for agricultural use should be exercised with great care.

This paper aims at reviewing research on the oxidation and reduction processes in acid sulphate soils. These pertinent information provide insights for the modeller to develop a simulation model of the oxidation and reduction processes.

Table 1. World distribution of acid sulphate soils<sup>1)</sup> (millions ha)

Region	Length of growing periods (days)				total
	< 90	90-180	180-300	> 300	
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	1.1	7.4	3.7	12.6

1) Adapted from BEEK et al. (1980), based on data from FAO/UNESCO soil map of the world. Growing period data according to FAO Agro-ecological zone project, Rome

## 1. SULPHUR COMPOUNDS IN UNDRAINED SOILS AND SEDIMENTS

Various sulphur compounds are present in undrained soils and sediments. Organic S is generally the most abundant form of S in non-sulphidic sediments, but it is quantitatively insignificant in pyritic sediments and in acid sulphate soils (BERNER, 1963; KAPLAN et al., 1963; VAN BREEMEN and HARMSSEN, 1975). Elemental S may be produced in large quantities under special conditions by chemical and microbial oxidation of  $H_2S$  (LJUGGREN, 1960; SILVERMAN and EHRLICH, 1964). In reduced marine sediments, elemental S is generally less than two percent of total S (BERNER, 1963; KAPLAN et al., 1963). Elemental S may be produced during the oxidation of FeS and  $FeS_2$ , but it is maintained at low concentration by microbial and chemical activity (BLOOMFIELD, 1972a).

According to RICKARD (1973) seven Fe sulphide forms are known: pyrite ( $FeS_2$  cubic), pyrrhotite ( $Fe_{1-x}S$ ,  $x = 0-0.126$  hexagonal), marcasite ( $FeS_2$  orthorhombic), mackinawite ( $FeS$  tetragonal), cubic FeS griegite ( $FeS_4$  cubic) and smythite ( $Fe_3S_4$  rhombic). Of these forms the most important in marine sediments and thus in undrained acid sulphate soils are mackinawite, griegite, and pyrite (MOHR et al., 1972). Mono iron sulphide may also be important, but it is rapidly transformed to one of these more stable crystalline forms. Hydrotroilite ( $FeS \cdot nH_{20}$ ) and melnikovite ( $FeS_2 \cdot nH_{20}$ ) have been reported in reduced acid sulphate soil (VAN BEERS, 1962).

In relation to the formation of acid sulphate soils, the residual and dominant form of iron disulphide is pyrite, but occasionally marcasite may also occur.

Pyrite may occur up to 5% in potentially acid muds, but amounts between 1 and 4% are most common (VIELLEFON, 1971; BLOOMFIELD, 1972). Other ferrous monosulphides generally comprise less than 0.01% and rarely exceed 0.6% of the soil (BLOOMFIELD, 1972b).

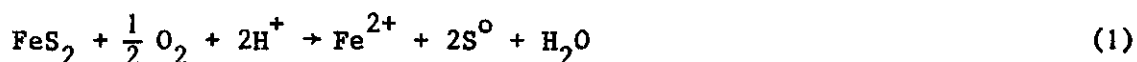
## 2. OXIDATION OF SULPHIDES

The oxidation of sulphides includes microbial and chemical reaction.

### 2.1. Microbial reactions

The micro-organisms involving in the oxidation of sulphides are the sulphur-oxidizing and iron-oxidizing micro-organisms. sulphur-oxidizing bacteria can be divided into the phototropic sulphurbacteria and the colourless sulphurbacteria.

The phototropic sulfur bacteria will not be important in the oxidation of pyrite because light cannot penetrate deeply enough into the soil and in the absence of light, these bacteria cannot oxidize reduced sulfur compounds (HANSEN, 1974). Colourless sulphur bacteria might be involved in the oxidation of elemental sulphur which is presumably formed in the soil from pyrite according to the equation (VAN BREEMEN, 1976):



The group of the colourless sulfur bacteria includes many genera of sulfur-oxidizing bacteria of which the representatives of the genus Thio-bacillus have been studied in detail (KUENEN, 1975). The different Thio-bacillus species under different environment were summarized by ARKESTEYN (1980).

Table 1. The genus Thio-bacillus

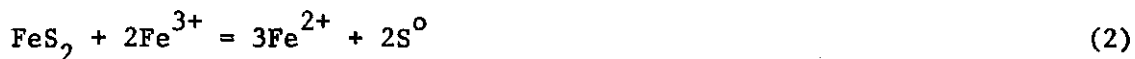
	Species	Habitat	References
Thio-bacillus	perometabolis	soil	LONDON and RITTENBERG, 1967
	novellus	soil	HUTCHINSON et al., 1969
	denitrificans	sea water, peat, mud, compost	"
	thio parus	water, mud, soil	"
	neapolitanus	soil, (sea) water	"
	thio-oxidans	soil	"
	ferro-oxidans	acid soils, acid waters	"
	acidifilus	acid soils, acid waters	GUAYAND SILVER, 1975

The Thio-bacilli are able to utilize several reduced sulphur compounds including  $S^0$ , as energy source. Thio-bacillus thio parus and several other thio-bacilli are able to grow at neutral pH, but thio-bacillus thio-oxidans, thio-bacillus ferro-oxidans and the recently isolated thio-bacillus acidophilus require a low pH for growth.

Hardly anything is known about the extent to which the colourless bacteria contribute to the oxidation of sulphur compounds in soils, only under extreme conditions, like low pH it has become more clear which bacteria were responsible for the oxidation of the reduced sulphur compounds, e.g. oxidation of pyrite by thio-bacillus ferro-oxidans in acid sulphate soils or acid mine-water.

Thio-bacillus thio-oxidans is autotrophic, obtaining energy from the oxidation of elemental sulphur or Thio-sulphate. It grows optimally at pH 2.0-3.5 and can tolerate conditions very much more acid than this (BLOOMFIELD and COULTER, 1973). LEATHEN and MADISON (1949) found T. thio-oxidans in all the mine effluents they examined, and it is understandable that this species should have been considered responsible for catalyzing the acidification reaction. However, although it promotes the oxidation of marcasite (LEATHEN et al., 1953), T. thio-oxidans has no direct action on pyrite, and an indirect mechanism based on the intermediate formation of elementary sulphur was proposed.

Pyrite is oxidized by  $Fe^{3+}$  according to the equation:



and sulphur thus formed could be the substrate for T. thio-oxidans, the oxidation of sulphur would decrease the pH and bring more  $Fe^{3+}$  into solution. This mechanism provides an explanation for the acidification, and it is significant that TEMPLE and KOEHLER (1954) found T. thio-oxidans to be more numerous at the site of oxidation than in the mine water.

Thio-bacillus ferro-oxidans is an autotroph that grows best at pH 2.0-3.5. It oxidizes  $Fe^{2+}$ , elemental sulphur or Thio-sulphate (UNZ and LUNDGREN, 1961). The upper limit for its growth is between 3.5 and 4.0, and it commonly occurs in acid sulphate soils and ochre deposits associated with pyritic soils (BLOOMFIELD, 1972).

The rate at which pyrite oxid is increased several fold in the presence of T. ferro-oxidans and is greatly accelerated once the pH

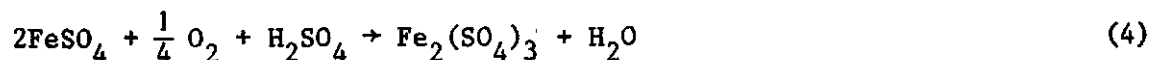
to within the range tolerated by T.ferro-oxidans (BLOOMFIELD, 1973).

The major influence of T. ferro-oxidans in promoting the oxidation of pyrite is probably indirect, operating via the catalysis of the oxidation of  $Fe^{2+}$ , but there is evidence for direct oxidation of sulphide sulphur.

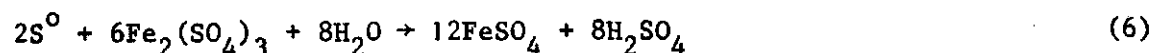
TEMPLE and DELCHAMP (1953) postulated an overall sequence of acid-forming reactions in coal-mine effluent which was adopted later by many other researchers. The first step is the non-biological oxidation of fine-grained pyrite to ferrous sulphate.



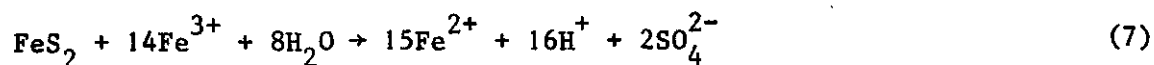
The ferrous sulphate is oxidized by thio-bacillus ferro-oxidans according to the equation:



The ferric iron formed reacts with pyrite yielding ferrous sulphate and elemental sulphur which is further oxidized to  $H_2SO_4$ .



The overall reaction is:



The validity of the above overall equation has been demonstrated even under anaerobic conditions whereas accumulation of intermediate elemental sulphur has not been shown hitherto. The role of thio-bacillus ferro-oxidans is to provide conditions of supply of ferric ions which in turn oxidize the pyrite yielding ferrous sulphate to complete a cyclic process.

The only other micro-organisms associated with the oxidation of pyrite are Metallogenium and Leptospirillum ferro-oxidans. The latter organism catalyses the oxidation of pyrite when grown in mixed cultures with sulphur oxidizing thio-bacilli, indicating that microbial oxidation of the sulphur as well as the iron moiety must be involved (BALASHOVA et al., 1974; NORRIS and KELLY, 1978). The oxidation of pyrite by a

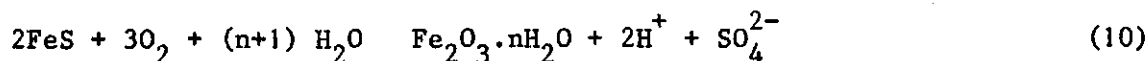
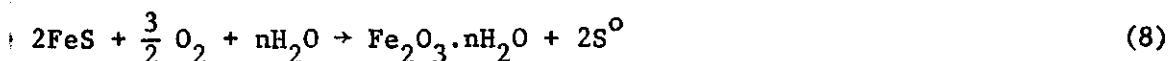


mixed culture of *Leptospirillum* and members of the genus *thiobacillus* was more extensive than that brought about a pure culture of *thiobacillus ferro-oxidans* (NORRIS and KELLY, 1978).

## 2.2. Chemical reactions

### 2.2.1. Oxidation of FeS

Oxidation of FeS proceeds quickly in the presence of  $O_2$ , yielding elemental S and ferric oxide (VERHOOP, 1940, BERNER, 1962); BLOEMFIELD, 1972) observed rapid formation of  $SO_4^{2-}$  during aeration of a suspension of FeS-containing soil, but found that most of the FeS was recovered as elemental S upon quick air-drying. If microbial conditions were favourable, elemental S was rapidly oxidized to  $SO_4^{2-}$ . The sequence of reactions can be written as follows:

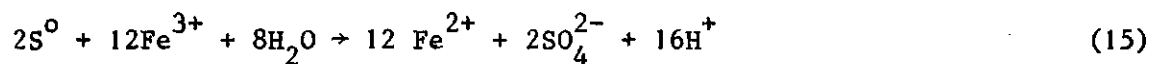
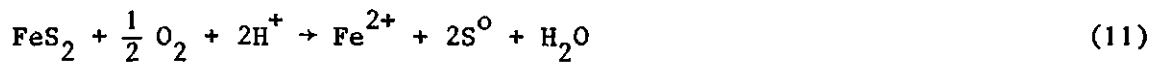


### 2.2.2. Oxidation of pyrite ( $FeS_2$ )

When pyritic sediments are exposed to air due to drainage, a complex sequence of reactions is started. Initially, when the pH of the soil is near neutrality, pyrite oxidation is purely chemical. Once the pH drops below 4.0 *Thiobacillus ferro-oxidans* starts its contribution to the further oxidation of pyrite as discussed earlier.

Using pyrite stability diagrams, VAN BREEMEN (1973) concluded that  $O_2$  and  $Fe^{3+}$  are the only two oxidants active in pyrite oxidation under natural conditions. Some investigators (HART, 1962; VAN BREEMEN, 1973) indicated that the initial products of pyrite oxidation are elemental S and  $Fe^{2+}$  while others (BLOOMFIELD, 1972b, GARRETS and THOMPSON, 1960; SILVERMAN, 1967) reported that  $SO_4^{2-}$  is released essentially instantaneously during pyrite oxidation by  $Fe^{3+}$ . Elemental S is released at higher pH values for this oxidation pathway.

If  $O_2$  and  $Fe^{3+}$  are the oxidants, and  $S^0$  is the initial oxidation product, the following reactions characterize the processes accompanying pyrite oxidation (VAN BREEMEN, 1973).



Reaction (10) describes the purely chemical oxidation of pyrite by  $\text{O}_2$ . Although this is a relatively rapid reaction, SINGER and STUMM (1970). TEMPLE and CHAMPS (1953) demonstrated that it is a slow process due to the sluggishness of pyrite oxidation in a sterilized moist, aerated medium where  $\text{Fe}^{3+}$  was absent. At low pH, when conditions are favourable for  $\text{Fe}^{3+}$  to remain in solution reaction (11) takes place very slowly - of pH value from 3 to 3.5  $\text{Fe}^{3+}$  is precipitated as  $\text{Fe}(\text{OH})_3$  having insignificant amounts of  $\text{Fe}^{3+}$  in solution to react with pyrite. Therefore, very little of the Fe released by pyrite oxidation would occur as free  $\text{Fe}^{3+}$ .

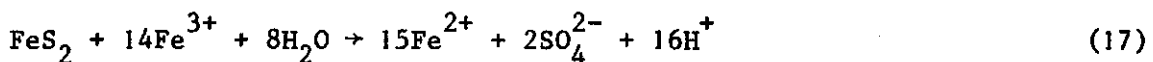
If the pH is below 3.5 the chemical oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  reaction (11) is very slow. The rate is independent of the pH:

$$-\frac{d(\text{Fe}^{2+})}{dt} = K(\text{Fe}^{2+})(\text{O}_2)$$

where  $K = 1.0 \times 10^{-7} \text{ bar}^{-1} \cdot \text{min}^{-1}$  (SINGER and STUMM, 1970).

At atmospheric  $\text{O}_2$ , only 5% of the ferrous iron in a solution originally containing  $9 \times 10^{-4} \text{ MFe}^{2+}/\text{l}$  was oxidized in 150 days (SINGER and STUMM, 1970).

In the presence of  $\text{Fe}^{3+}$ , both pyrite and elemental sulphur are rapidly oxidized according reactions (13 and 14). The combined process of these reactions:



takes place rapidly at room temperature (GARRELS and THOMPSON, 1960; SINGER and STUMM, 1970).

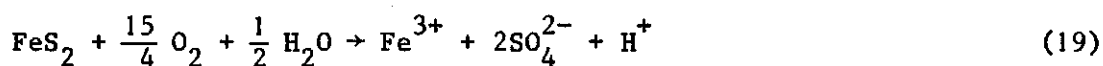
From data of GARRELS and THOMPSON (1960), 50% of  $2 \times 10^{-3}$  m solution of ferric sulphate was reduced by pyrite in 5 hours. SINGER and STUMM (1969) carried out a similar experiment over a wider range of conditions and showed the first order dependence of both  $\text{Fe}^{3+}$  and  $\text{FeS}_2$ :

$$-d[\text{Fe}^{3+}]/dt = K[\text{Fe}^{3+}][\text{FeS}_2] \quad (18)$$

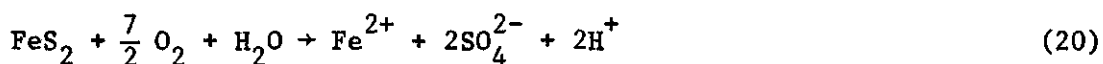
where  $[\text{FeS}_2]$  represent the molar concentration of pyrite. The presence or absence of oxygen makes no difference to the oxidation rate by ferric iron (SINGER and STUMM, 1969).

For the inorganic pyrite oxidation, four possible cases have been identified:

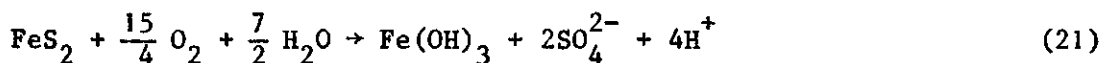
1. All iron is oxidized and remaining in solution as  $\text{Fe}^{3+}$



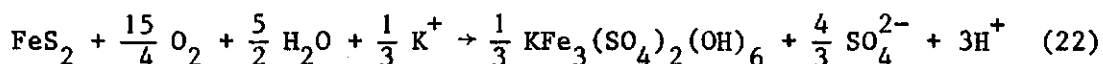
2. Iron is released as  $\text{Fe}^{2+}$



3. All iron is oxidized and hydrolyzed to ferric iron hydroxide



4. Formation of Jarosite



The amount of acid produce during pyrite oxidation and the amount of lime require for neutralization under different reactions are shown in Fig. 1.

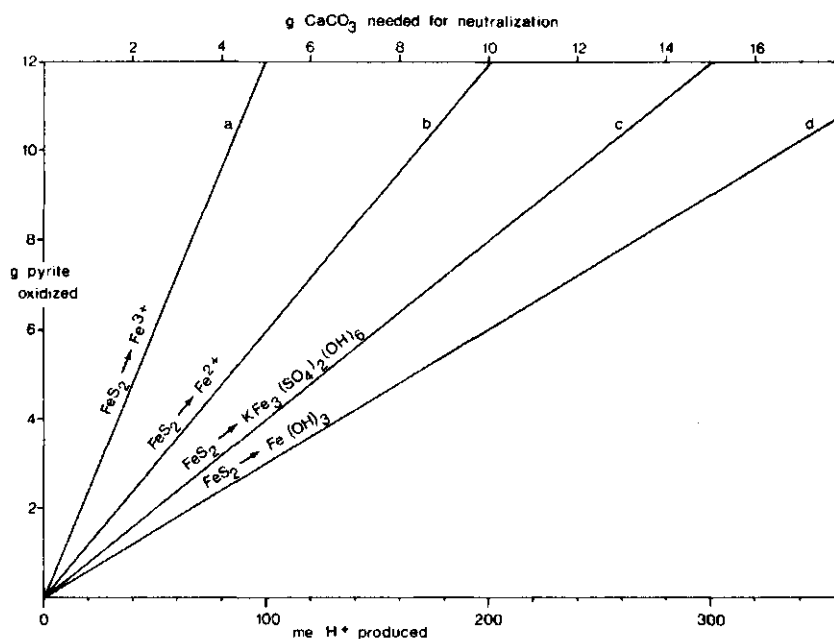


Fig. 1. Acid production during pyrite oxidation (from VAN BREEMEN, 1973)

### 2.2.3. Factors affecting pyrite oxidation

Factors influence the rate of pyrite oxidation are the supply of oxygen, ferric iron, temperature, surface area of pyrite, the presence of impurities minerals such as trace metals and the presence of other minerals such as chalcopyrite, speralerite, calcite, etc.

#### Oxygen

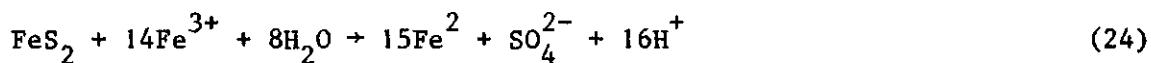
The rate of pyrite oxidation based on the oxygen concentration differs among researchers (SHUMATE et al., 1971). They reported a rate expression based on an adsorption equilibrium hypothesis:

$$r = (K[O_2]) / (1 + K_1[O_2] + K_2[I]) \quad (23)$$

where  $r$  is the rate of pyrite oxidation in micromoles pyrite per hour per gram of sample,  $K$  is the rate constant,  $K_1$  is the adsorption equilibrium constant for oxygen on pyrite,  $K_2$  is the adsorption constant for an inert gas,  $I$ , on pyrite.

#### Ferric iron

As the ferric concentration increase with increasing acidity, the role of ferric iron becomes more important as an oxidizing agent. Pyrite is rapidly oxidized by ferric iron in the absence of oxygen and at low pH values according to the following equation: (GARRELS and THOMPSON, 1960 and SMITH et al., 1968):



### Temperature

Temperature causes doubling of the oxydation rate of pyrite by oxygen for every 10°C rise (SHUMATE et al., 1971).

### Grain size and morphology

Pyrite can vary significantly in grain size and morphology. The most reactive form of pyrite is framboidal having a size of less than a micrometer (CARUCIO et al., 1976). The reaction rate increased by a factor of 1.5 as the surface area of pyrite doubled (PUGH et al., 1984).

### Trace metals

Trace metals appear to have no significant effect on the oxidation rate, but the co-existence of other sulphates such as chalco pyrite and sphalerite tends to decrease the oxidation rate.

## 2.3. Oxidation products

### 2.3.1. Acid production

The amount of acid produced by pyrite oxidation is shown in Fig. 1. The acid production varies with oxidizing conditions. Generally, samples oxidized under moist laboratory conditions resulted lower pH values than soil oxidized in the field. pH lower than 2.5 was observed in laboratory oxidation experiments (CHENERY, 1954; VAN BREEMEN, 1973). Under field conditions pH was in between 3 and 4.0 (CALVERT and FORD, 1973; CHENERY, 1954; CLARK et al., 1961; COULTAS and CALHOUN, 1976; FLEMMING and ALEXANDER, 1961; VAN BREEMEN, 1973; VAN BREEMEN and HARMSSEN, 1975).

The pH depends both on the amount of sulphuric acid produced and on the pH buffering characteristics of the soil materials. WIND and STEEGHS, (1964) found a pH lower than 2 in a sandy soil. The buffering capacity includes the interaction of acid with alkalinity in soil solutions, exchangeable bases, soil minerals and clay minerals.

### Alkalinity

The interstitial waters in non alkaline soils can contribute to the neutralization of 1 me acidity produced per 100 g of soil by pyrite oxidation at the most under moisture content up to 100% (VAN BREEMEN, 1973).

### Exchangeable bases

Exchangeable bases may be replaced by  $H^+$  as the pH decreases, resulting in the formation of non-exchangeable acidity. The pH-dependent CEC is influenced by the nature and the quantities of clay and organic matter present in soils. Comparing CEC at pH at 7.0 with CEC at pH 3.5 to 4.0 of several acid sulfate soils, SOMBAPANIT (1970) concluded that 10 to 30 meq of acidity were absorbed in the exchange complex.

Exchangeable  $Al^{3+}$  appears in appreciable amount if the pH drops below 5 or 4 (COULTER, 1969), ALLBROOK, 1972), but a considerable amount of non-exchangeable acidity is formed already at higher pH.

### Weatherable minerals

There is no sharp boundary between ion exchange reactions and mineral transformations. Kaolinite are poor in bases, but at low pH it can buffer the acid produced (VAN BREEMEN, 1973). Micas and feldspars may remove acidity from the soil by reaction of lattice OH groups. The most important minerals in buffering acidity are carbonates such as calcite and aragonite. These minerals are dissolved by strong acids to produce divalent metal cations,  $CO_2$  and  $H_2O$ . As long as carbonate materials remain in the immediate environment, the reactions of the soil remain close to pH 7.0. As more acid is produced,  $Ca^{2+}$  and  $SO_4^{2-}$  may either remain in solution or precipitation as gypsum  $[CaSO_4 \cdot 2H_2O]$ , depending on the moisture content of the soil.

### 2.3.2. Minerals

#### Iron minerals

Iron minerals found in acid, unsaturated pyrite-rich soils have a wide range of properties from very insoluble iron hydroxides to very soluble iron sulphate hydrates. The more soluble sulphate are most commonly formed during dry periods as evaporation promotes the rise of subsurface waters to the upper most soil layer surface by capillary action. As these waters reach the upper layers of the soil, they become progressively more concentrated and finally various salts precipitate in an efflorescence.

Weathering pyrite gives the maximum acidity when all the iron is oxidized and hydrolyzed to solid ferric oxide ( $Fe(OH)_3$ ). But the reaction does not normally go to completion due to the absence of sufficient bases to neutralize the acid, basic iron sulphates formed. The most widely iron sulphate form is jarosite. There has been a large

number of investigations into the formation of jarosite by the oxidation of pyrite and these have been summarized by VAN BREEMEN (1973). Another form of iron sulphate is natrojarosite which is formed only on depletion of all available potassium. Jarosite is more stable at lower pH values than ferric hydroxide (BROWN, 1971). Jarosite is pale yellow, insoluble in water and commonly found along root channels, on ped faces, and on draining spoils (BLOOMFIELD and COULTER, 1973). It is stable only under strong oxidizing and acid conditions.

#### Sulphates

An addition to jarosite, sulphate of sodium, magnesium, calcium and aluminium are formed. Sodium and magnesium sulphates leach readily from the profile as soon as adequate drainage provided. Calcium sulphate is somewhat less soluble, but leaches in wetter conditions. Gypsum accumulates as nests of crystals in drier areas and has been recorded in rice soil in Malaysia (BLOOMFIELD and COULTER, 1973).

Under strongly dry conditions, some soluble aluminium sulphate may appear as efflorescences on the surface of the soil. Sodium alum  $\text{Na Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and tamargite,  $\text{Na Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  as well as gypsum and sodium chloride were detected in surface crusts from Thailand (VAN BREEMEN, 1973). Alunite,  $\text{KAl SO}_4(\text{OH})$ , was found on the surface of acid sulphate soil in Vietnam (HERBILLION et al., 1966).

### 3. REDUCTION PROCESS

During the period of flooding or submergence, the oxygen supply of the soil is virtually cut-off. Soil microbes rapidly use up the trapped oxygen, rendering a flooded soil practically devoid of oxygen within a day or two of flooding (PONNAMPERUNA, 1964). In the absence of molecular oxygen, anaerobic bacteria utilized oxidized compounds such as nitrate, manganese oxides, ferric oxides and sulphate which are reduced in this order. After the disappearance of nitrate, the concentration of  $Mn^{2+}$  and some what later, of  $Fe^{2+}$  generally increase to distinct peaks during the first weeks flooding, and then decrease to fairly constant values. If reduction becomes sufficiently intense, sulphate is reduced to sulphide.

The requirements for soil reduction are the absence of oxygen, the presence of decomposable organic matter, and anaerobic bacterial activity. The course, rate and degree of reduction are influenced by the nature and content of organic matter, temperature, the nature and content of electron acceptors, and pH. Also, air drying a wet soil intensifies reductions after submergence (AOMINE, 1962; YOSHIZAWA, 1966) and N, P, K fertilizers accelerate reductions in soils deficient in these nutrients (CHIAN and YANG, 1970).

The sequence of soil reduction under submergence was reviewed by PONNAMPERUNA (1972).

Soil reduction is accompanied by important chemical and physico-chemical processes:

1. decrease in redox potential (Eh) or pE
2. changes in pH
3. changes in specific conductance
4. denitrification
5. accumulation of ammonium and fixation of nitrogen gas
6. reduction of Mn (IV)
7. reduction of Fe (III)
8. reduction of sulphate
9. production of organic acids
10. accumulation of carbon dioxide
11. changes in concentration water-soluble iron, manganese, phosphorus, silicon, boron, copper, molybdenum and zinc



### 3.1. Redox potential

When an aerated soil is submerged, its redox potential decreases during the first few days and reaches a minimum, then it increases, attains a maximum, and decreases again asymptotically to a value characteristic for the soil after 8-12 weeks of submergence (PONNAMPERUMA, 1955, 1965; MOTOMURA, 1962; YAMANE and SATO, 1968). The course, rate, and the magnitude of the Eh decrease depend on the kind and amount of organic matter, the nature, and content of electron acceptors, temperature and the duration of submergence. The influence of various factors on the redox potential on submerged soils was reviewed by PONNAMPERUMA (1972).

### 3.2. Carbon dioxide

Saturating a soil with water drastically cut down the escape of soil gases just as it excludes air from the soil. Carbon dioxide and other gasses produced in the soil thus accumulate, build up pressure and escape as bubbles. The partial pressure of  $\text{CO}_2$  in a soil increases after submergence, reaches a peak of 0.2-0.8 atm after 1-3 weeks, and declines to a fairly stable value of 0.05-0.2 atm (IRRI, 1964). The pattern of  $\text{PCO}_2$  kinetics depends on soil properties and temperature (CHO and PONNAMPERUMA, 1971). The following are the patterns of  $\text{PCO}_2$  of different soils:

a. Alkaline neutral soil	$\text{PCO}_2$ (atm) max	Peak (weeks after flooding)
low organic matter (OM)	0.2-0.3	4-6
b. Slightly acid soil		
low to moderate (OM)	0.2-0.4	2-3
high Fe, Mn		
c. Strongly acid latosolic soil	0.6-0.8	1
moderate OM, high Fe, low Mn		
d. Soil high OM low Fe, Mn	0.3-0.6	1

Carbon dioxide profoundly influences the chemical equilibria in a reduced soil with its high content of divalent cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ :

$$pH = pK - \frac{2}{3} \log PCO_2 \quad (MCO_3 \text{ present}) \quad (25)$$

$$pH + \frac{1}{2} \log M^{++} = pK' - \frac{1}{2} \log PCO_2 \quad (MCO_3 \text{ present}) \quad (26)$$

$$pH = pK'' - \frac{1}{3} \log PCO_2 \quad (M(OH)_2 \text{ present}) \quad (27)$$

$$Eh = E_o + 2.303 \frac{n'RT}{nF} \log PCO_2 - 2.303 \frac{n''RT}{nF} pH$$

(MCO<sub>3</sub> present) (28)

where: Eh is the potential difference between the normal hydrogen electrode and the soil system

E<sub>o</sub> is a constant for a particular soil, soil system such that it is zero when reductant and oxidant are present in equal proportions

'R is the gas constant

T is the absolute temperature

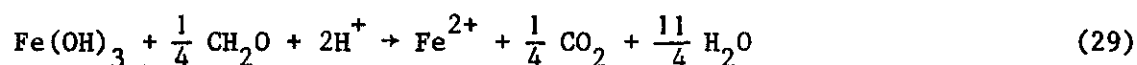
F is 96,500 coulombs

n is the number of electrons transferred in the reaction

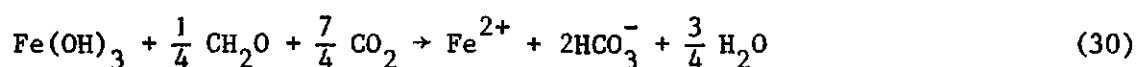
According to the above equations, the partial pressure of CO<sub>2</sub> in a reduced soil will determine its pH, Eh, and solubility of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup> and Mn<sup>2+</sup> and influence indirectly specific conductance and cation exchange reactions.

### 3.3. Reductions of Fe<sub>2</sub>O<sub>3</sub>

For the reduction of ferric oxide by organic matter, protons are required:



In most normal paddy soils, carbon dioxide is the main proton donor in equation (29), since HCO<sub>3</sub><sup>-</sup> appears along with Fe<sup>2+</sup> and cations displaced by Fe<sup>2+</sup> at the exchange complex (IRRI, 1965), leading to the total reaction:



In acid sulphate soils, however, ferrous sulphate is formed instead of ferrous carbonate.

The intensity of reduction in acid sulphate soils is low compared to that of normal paddy soils (NHUNG and PONNAMPERUMA, 1966; PARK et al., 1971; PONNAMPERUMA et al. 1973, VAN BREEMEN, 1976). KAWAGUCHI and KYUMA (1969) observed from anaerobic incubation test text surface samples from some acid sulphate soils (pH 4.3 - 4.5) underwent rapid reduction whereas other did not. Some of the factors responsible for slow reduction may be a) low content of easily reducible  $Fe_2O_3$  (PONNAMPERUMA et al., 1973); b) a low content of easily oxidizable organic matter; c) a poor nutrient status (SOMBATPANIT and WANGPAIBOON, 1973); and d) an adverse effect of low pH, either directly or indirectly, on the activity of microbes.

The concentration of ferrous iron,  $Fe^{2+}$  increases greatly under reduced conditions. NHUNG and PONNAMPERUMA (1966) report that the concentration of  $Fe^{2+}$  reached 800 ppm after 6 weeks submergence. TANAKA and NAVASERO (1966b) also reported very large increases in the iron contents of leachates in flooded conditions, with or without incubation, values of 800 to 1700 ppm being obtained. Ferrous iron concentrations of 5000 ppm, 2 weeks after submergence, were reported by PONNAMPERUMA et al. (1973) but values of 500 - 1000 ppm are more common; however, some soils apparently give very little. However, not all acid sulphate soils give large amount of iron on reduction; this can be attributed to small iron contents, or the absence of easily reducible iron oxides, an ill defined term.

According to JAMES (1966) the iron concentration in aerobic seawater is largely determined by amorphous ferric hydroxide and averages  $6 \times 10^{-9}$  mol/l. In anaerobic conditions more iron might be dissolved as  $Fe^{2+}$ . However, as soon as sulphate reduction occurs, the  $Fe^{2+}$  concentration will again decrease as a result of the formation of ferrous sulphides

The increase in concentration of water-soluble  $Fe^{2+}$  is caused by the reduction of ferric hydroxide and can be described quantitatively by the equation:

$$Eh = a - b \log Fe^{2+} + 0.18 \text{ pH} \quad (31)$$

Thus  $Eh + 0.18 \text{ pH}$  should be a linear function of  $\log \text{Fe}^{2+}$  with  $a = 1.03$  and  $b = -0.06$ .

### 3.4. pH

1. The increase in pH of a soil on flooding is caused by reduction of Fe and Mn.
2. pH after reduction in acid soils or throughout submergence in calcareous soils is regulated by the partial pressure of  $\text{CO}_2$ .
3. The higher pH values of suspensions of reduced soils than those of the equilibrium solutions is due to loss of  $\text{CO}_2$ .
4. pH values of the soil solution of reduced soils lie between 6.5 and 7.0 regardless of initial pH values and other soil properties.

TANAKA and NAVASERO (1966b) leached small samples of acid sulphate soils from Vietnam and Malaya, with initial pH of about 3.5, and found that the first leachate had pH of 3.7 and contained 70 ppm of aluminium; rice plant grown in this leachate died, but normal growth was obtained in the filter successive leachate, which had a pH of 9.8 and contained 21 ppm of aluminium.

Increases in pH, after submergence many of them greater than those reported by Tanaka and Navasero, have often recorded. PONNAMPERUMA et al (1973) reported rises from about pH 3.5 to 6.1 in 12 weeks flooding of acid sulphate soils from Vietnam, much of the increase taking place in the first 2 weeks. NHUNG and PONNAMPERUMA (1966) reported an increase from pH 3.6 to 4.7 in 16 weeks' floodings, whereas TOMLINSON (1957) reported an increase from 2.7 to 6.2 when mangrove soils in Sierra Leone were flooded with rainwater.

KANAPATHY (1973) gave an increase from pH 2.6 to 6.3 in 60 days' waterlogging. BEYE (1973) found an increased that varied with soil treatments. In some polders the pH increased from 3.8 to 5.7, in others to less than 4.0. Soils in pots might be expected to behave differently from those in fields, especially if soluble salts were leached in the field.

The application of three independent criteria, via  $\text{pH} = f(\text{PCO}_2)$ ,  $\text{Mn}^{++} = f(\text{PCO}_2, \text{pH})$  and  $Eh = f(\text{PCO}_2; \text{pH})$  to the soil solutions of 31 soils strongly suggests:

- a. the presence of  $\text{MnCO}_3$  in reduced soil, and
- b. the precipitation of  $\text{MnCO}_3$  as the cause of the decrease in  $\text{Mn}^{++}$  in the soil solution, after the initial increase following flooding.

### 3.5. Manganese

The concentration of soluble Mn at a given time represents a dynamic balance between the release of  $\text{Mn}^{++}$  by the reduction of the insoluble higher oxides on the one hand, and cation exchange and precipitation reaction on the other. The release of  $\text{Mn}^{++}$  depends on the amount of active Mn and the redox potential of the soil. Removal of  $\text{Mn}^{++}$  by cation exchange and precipitation is governed by the cation exchange capacity of the soil and the presence of other cations, pH and  $\text{PCO}_2$ .

### 3.6. Changes in specific conductance

Flooded soils build up high concentration of soluble ions in the early stages of submergence because of:

- a) the release of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  by reduction of the insoluble oxides
- b) mobilization of  $\text{Ca}^{++}$  and  $\text{Mg}^{2+}$  by the solvent action of  $\text{H}_2\text{CO}_3$  in calcareous soils
- c) the production of  $\text{NH}_4^+$  and
- d) the displacement of  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  from soil colloids by  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ .

After precipitation part of the  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  and the accompanying reversion of cations to the exchange sites, the concentration of ions in the solutions decreased.

The kinetics of specific conductance varies widely with the soils. A specific conductance exceeding 4 mmhos/cm indicate the presence of too much salt for the healthy growth of rice (IRRI, 1967). Values considerably in excess of 4 mmhos/cm are possible in submerged soils that have low cations exchange capacity and are high in organic matter (especially if they are fertilized) and in acid sulphate soils.

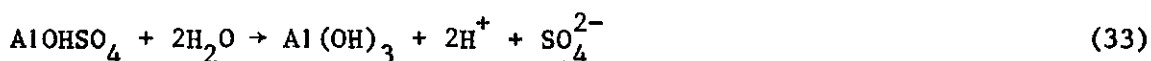
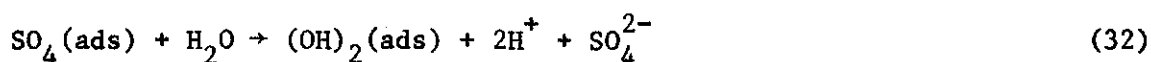
#### Sulphate

In acid sulphate soils the concentration of dissolved sulphate nearly always fluctuates between  $1 \times 10^{-2}$  and  $3 \times 10^{-2}$  mol/l

(NHUNG and PONNAMPERUMA, 1966; VAN DER SPEK, 1950; YONEDA and KAWADA, 1954; HORN and CHAPMAN, 1968). Even at extremely low pH values (1.9) only a slightly higher  $\text{SO}_4$  concentration was found ( $7 \times 10^{-2}$  mol/l; WIND and STEEGHS, 1964). In leached acid sulphate soil (pH 4-6)  $\text{SO}_4$  concentration of approximately  $2 \times 10^{-3}$  mol/l occurred (VAN DER SPEK, 1950). Even under reduced conditions the  $\text{SO}_4^{2-}$  concentration remains constant over a long period (NHUNG and PONNAMPERUMA, 1966).

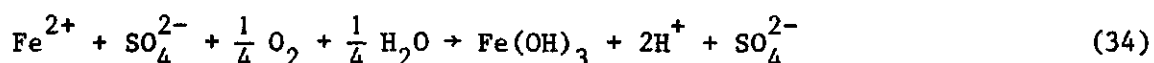
It takes months before sulphate reduction takes place in the surface horizon of acid sulphate soils (pH < 4). NHUNG and PONNAMPERUMA (1966) found that only after 37 weeks after inundation of an acid sulphate soil (pH 3.5)  $\text{SO}_4$  reduction was noticeable. By increasing the pH of the same soil to pH 5.6 by liming all sulphate disappeared within 24 weeks after inundation. Most soils obtain pH values between 6.0 and 7.0 within few weeks after inundation (PONNAMPERUMA et al., 1966) as a result of reduction of other components (e.g.  $\text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}^+ + \text{e} \rightarrow \text{Fe}^{2+} + 3\text{H}_2\text{O}$ ); under those conditions the sulphate is usually entirely reduced within 3 to 5 weeks (IRRI, 1964, 1965).

The change in dissolved sulphate must be due to hydrolysis of basic sulphates or desorption of sulphate (NHUNG and PONNAMPERUMA, 1966). The desorption of  $\text{SO}_4^{2-}$  or hydrolysis of basic sulphate ( $\text{AlOH}_2\text{SO}_4$ ) provides protons necessary for iron reduction:



Under conditions too acid for appreciable dissociation of  $\text{CO}_2$ , these protons thus have the same role as those supplied by carbon dioxide at higher pH. The disappearance of exchangeable and water-soluble aluminium and the simultaneous appearance of exchangeable  $\text{Fe}^{2+}$  in flooded acid sulphate soils (PARK et al., 1971, SOMBAPANIT and WANGPAIBOON, 1973) show that the protons formed during hydrolysis of aluminium are also involved in the reduction of iron but these are not associated with an increase in dissolved sulphate.

The ferrous sulphate that reached the soil water interface by diffusion will produce sulphuric acid upon oxidation of  $\text{Fe}^{2+}$  to ferric oxide:



## SUMMARY

The purpose of this paper is to review research on the oxidation and reduction processes in acid sulphate soils. Acid sulphate soils are soil materials in which during the soil formation, sulphuric acid was produced, is being produced, or will be produced in amounts that have lasting effect on the main soil characteristics. Various sulphur compounds in undrained soils and sediments are presented. Oxidation processes include microbial and chemical reactions. Factors influencing pyrite oxidation are: the supply of oxygen, ferric iron, temperature, surface area of pyrite, the presence of impurities minerals and other minerals. Products of the oxidation comprise acidity alkalinity, exchangeable bases, weatherable minerals, iron minerals and sulphate. Reduction process takes place during the period of flooding or submergence where the oxygen supply of the soil is virtually cut-off.

The important chemical and physico-chemical processes during the soil reduction are reviewed in detail.

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