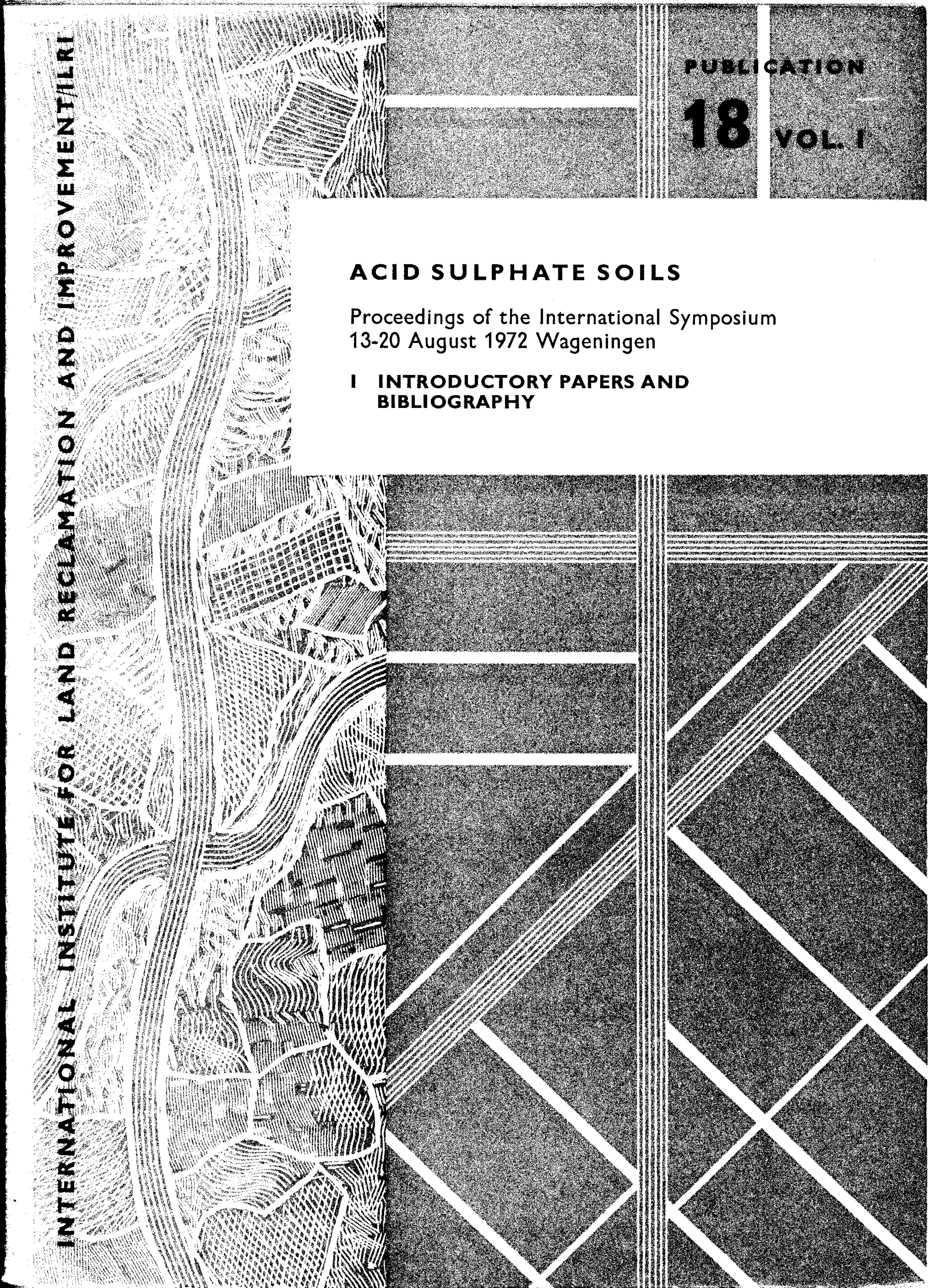


INTERNATIONAL INSTITUTE FOR LAND RECLAMATION AND IMPROVEMENT/ILRI

PUBLICATION
18
VOL. I

ACID SULPHATE SOILS

Proceedings of the International Symposium
13-20 August 1972 Wageningen

I INTRODUCTORY PAPERS AND BIBLIOGRAPHY

ACID SULPHATE SOILS

I INTRODUCTORY PAPERS AND BIBLIOGRAPHY

Publication 18 – *Vol. I*

ACID SULPHATE SOILS

Proceedings of the International Symposium on Acid Sulphate Soils
13-20 August 1972, Wageningen, The Netherlands

I INTRODUCTORY PAPERS AND BIBLIOGRAPHY

II RESEARCH PAPERS

Edited by: H. DOST

INTERNATIONAL INSTITUTE FOR LAND RECLAMATION AND IMPROVEMENT
P.O. BOX 45 WAGENINGEN THE NETHERLANDS 1973

CONTENTS

All figures and many tables are printed at the end of the relevant article

INTRODUCTION

The International Symposium on Acid Sulphate Soils was held at Wageningen, The Netherlands, from August 13th to 20th 1972. Its aim was to summarize all available information and to present recent advances in research on, and management of, acid sulphate soils.

The initiative for the Symposium was taken in 1970 by Mr.J.K.Coulter, Rothamsted Agricultural Experiment Station, United Kingdom, when he was visiting the Department of Regional Soil Science of the University of Agriculture, Wageningen. The idea was worked out by an Organizing Committee of the following composition:

CHAIRMAN	L.J.Pons, Department of Regional Soil Science University of Agriculture, Wageningen
VICE-CHAIRMAN	J.K.Coulter, Rothamsted Agricultural Experiment Station Harpenden, United Kingdom
SECRETARY	N.van Breemen, Department of Regional Soil Science University of Agriculture, Wageningen (until April 1st 1971). Since that date: H.Dost, International Institute for Land Reclamation and Improvement Wageningen
	and

REPRESENTATIVES OF

<u>University of Agriculture, Wageningen</u>

- Department of Irrigation
- Department of Land Improvement and Reclamation
- Department of Microbiology
- Department of Soil Fertility, Soil Physics and Chemistry

<u>Soil Survey Institute (Stiboka), Wageningen</u>

<u>University of Amsterdam</u>

- Physical, Geographical and Pedological Laboratory

The Organizing Committee obtained the indispensable support of various organizations: the International Society of Soil Science sponsored the Symposium; the University of Agriculture, Wageningen, gave financial support; the International Agricultural Centre, Wageningen, acted as executive agency; the Soil Survey Institute, Wageningen, the IJsselmeer Development Authority, Kampen, and the International Institute for Aerial Survey and Earth Science, Enschede, contributed to the organization of excursions; the International Soil Museum, Utrecht, lent an acid sulphate soil monolith from Thailand for display during the symposium; FAO, Rome, had a world map of acid sulphate soils prepared and presented;

the International Institute for Land Reclamation and Improvement, Wageningen, took upon itself the task of editing and publishing the Proceedings. The Organizing Committee thanks these organizations for their generous co-operation.
The program of the Symposium included two general and eight ad hoc sessions and two day-long excursions. One excursion was to the typical acid sulphate soils of the coastal lowland and the other to an interesting odd case of a fossil acid sulphate soil in an upland setting. The Symposium was opened by Dr P.Buringh, Chairman of the Board of the University of Agriculture, Wageningen. During the opening session Dr L.J.Pons, Chairman of the Organizing Committee, outlined the subject. The closing session centred upon the formulation of recommendations. The eight ad hoc sessions dealt with the following topics:

1. Formation and accumulation of sulphides
2. The genesis of Acid Sulphate Soils
3. The influence of acidity on ion exchange characteristics and the development of structure stability
4. The identification of potential Acid Sulphate Soils
5. Physiography, classification, and mapping
6. The effect of extreme soil acidity on the nutrient uptake and physiology of plants and microorganisms
7. The management of Acid Sulphate Soils and Pseudo-acid Sulphate Soils for agricultural and other uses
8. Reclamation and improvement of developed and potential Acid Sulphate Soils.

Taking part in the sessions and excursions were 87 participants from 25 countries. Their names are listed on page XIII. During the sessions the topics were introduced by lectures, supplemented by concise reviews of the relevant research papers presented for the Symposium+). Roughly half of the available time was reserved for discussions. The documentation available to the participants consisted of preprints of seven introductory papers and twenty-six research papers, an excursion guide, the FAO map showing the world distribution of acid sulphate soils, together with literature references, a draft for normalized nomenclature and various circulars pertaining to details of the program. During the sessions all speeches, lectures, summaries, comments and discussions were recorded on tape. Together the documentary material has outgrown by far the proportions of the space and means available for its editing and publishing. The present Proceedings therefore had to be limited to the content of the papers and the essentials of discussions and organizational data.

+) Reviews were presented by Mr.J.van Schuylenborgh (August 14th and 15th), Mr.C. Bloomfield (August 15th), Mr.J.Vieillefon (August 17th), Mr.F.R.Moormann and Mr.F.N.Ponnamperuma (August 19th).

The Proceedings are being published in two volumes. The first contains the introductory papers, the world map, a bibliography and information pertaining to the follow up of the Symposium - i.e. the text of the recommendations and the names and addresses of the members of the Working Party for Nomenclature and Methods, which was established during the final session. The second volume contains the research papers. Discussions are added in so far as they have been recorded in writing by the participants during the sessions.

The Bibliography in Volume I originates from the literature study on which A.Kawalec, FAO, based his map of the world distribution of Acid Sulphate Soils. The literature study itself was far too voluminous for complete publication in these Proceedings. Its literature references have been incorporated, in an adapted form, in the Bibliography and in the Geographical References that accompany the Map.

Since the establishment of the Working Party for Nomenclature and Methods, it has been augmented by three more members, representing Thailand and North and South America. The Working Party will devote itself to the selection and definition of generally acceptable criteria, methods and nomenclature for the study of Acid Sulphate Soils. At the same time it will function as a sequel to the present Organizing Committee, and the complete archives of the Symposium will remain in its care. +)

On completion of my editing job I should like to thank the Organizing Committee of the Symposium and the directorate and staff of the International Institute for Land Reclamation and Improvement for giving me the opportunity of doing this very instructive work. Special thanks I offer to N.van Breemen, my predecessor as Secretary of the Organizing Committee, for his continuing interest and support.

H.Dost
Editor and Secretary
of the Organizing Committee

+) The address of the secretariat of the Working Party on Nomenclature and Methods is: Department of Regional Soil Science, University of Agriculture, Duivendaal 10, Wageningen, The Netherlands.

RESOLUTIONS AND RECOMMENDATIONS

The participants of the International Symposium on Acid Sulphate Soils, convening at Wageningen, The Netherlands, August 13-20 1972, and considering the contents of the papers presented and the tenor of the discussions, recognize that Acid Sulphate Soils are problem soils which normally require expensive inputs for improvement, and that only in special circumstances should these soils be given a high priority in reclamation.

Nevertheless, they emphasize that where these special circumstances do occur, e.g. in areas where population pressure is demanding the cultivation of Acid Sulphate Soils or where such soils are already being cultivated, reclamation and improvement have to be considered.

Considering further that although certain clearly recognized principles are involved in the reclamation, management, and improvement of Acid Sulphate Soils, the application of these principles to suit the divers local conditions, in many instances requires further applied research.

In the context of the above considerations and recognitions, the participants recommend that during the coming years special attention be given to the following subjects and problems:

1. The relationship between pyrite formation and specific combinations of vegetation, flooding patterns, and types of deposits.

This subject is considered of special importance for both the use of remote sensing techniques in soil surveying and for soil and water management practices. It implies the study of what is often called the primary and secondary pyrite formation.

2. The relationship between the characteristics of sulphidic soil material and the dynamics of acid sulphate soils during development, in the field and after handling in the laboratory.

Sulphidic soil material is very sensitive to air oxidation and characteristics may change within days after sampling. Also for the comparison of laboratory experiments with field conditions, it is considered of importance that these experiments simulate field conditions more closely and that the results obtained with the laboratory models be correlated with those of controlled field experiments. Important factors that need consideration are: kinetics of pyrite oxidation,closed versus open systems, spatial differentiation of soil acidity on a microscale.

3. The dynamics of water soluble Fe and Al and of N, S, and pH in seasonally waterlogged acid sulphate soils, bearing in mind the wide differences in behaviour

of such soils in terms of pH changes, ferrous iron contents, etc. An effort should be made to relate these dynamics to soil properties measurable in the dry state.

This subject is of special importance in tropical areas where populations depend for their subsistence on rice growing on Acid Sulphate Soils.

4. Investigations of the behaviour of Al in respect to the structural stability of Acid Sulphate Soils and its interaction with such amendments as lime.

Such research is expected to be of particular benefit to agricultural production on drained Acid Sulphate Soils and also to contribute to a better understanding of the productivity of Para- or Pseudo-Acid Sulphate Soils.

5. Quantitative field methods for the identification of Potential Acid Sulphate Soils and for the evaluation of their potential acidity.

Improvement of these methods is required to enable more precise and accurate soil survey and land classification.

6. The development and use of well defined and generally acceptable diagnostic criteria, descriptive and analytical methods, and nomenclature in research and in reporting.

This is urgently needed for world wide correlation of data and exchange of information. The convention agreed to the establishment of a working party to select and define such generally acceptable criteria, methods, and nomenclature. It was suggested that this working party present its results to the International Society of Soil Science in 1974.

7. The performance of vegetations, plant species and varieties important for reclamation and agriculture, with respect to the presence of major toxic components of Acid Sulphate Soils, i.e. Al, Fe, and S compounds.

Detailed study in this field is considered very important for widening the agricultural possibilities of these soils.

8. Long term, well monitored field experiments with various combinations of reclamation methods and soil-water-crop management systems.

These experiments should be conducted in at least two key areas i.e. in tropical rainy and in wet and dry tropical environments. The convention hopes through this recommendation to interrupt the long standing vicious circle of insufficient information and abortive trials.

9. The exchange of relevant data among field and research workers.

The convention recommends that the working party for methods and nomenclature, mentioned sub 6, promote this exchange for the time being and that in due course another International Symposium on Acid Sulphate Soils be organized, preferably in one of the tropical areas concerned.

Having recommended the above topics, the convention wishes to stress that these topics represent those aspects of Acid Sulphate Soil Research that merit special attention in studies and schemes in the majority of the world's large Acid Sulphate Soil Areas. At the same time it does not deny that, locally, other problems might well deserve higher priority. The present recommendations express a careful balancing of specificity against generality and as such they provide a frame of thought which may serve to guide soil scientists, agronomists and other persons involved in deciding on priorities in the specific areas under their consideration.

LIST OF PARTICIPANTS

BELGIUM

H.Eswaran
R.Tavenier

BRUNEI

A.W.Allen

COLOMBIA

F.Hanke

DENMARK

S.Elsnab Olesen
A.Fobian
J.P.Møberg

FINLAND

Raimo Erviö

FRANCE

J.Vieillefon

GERMANY

P.Ballmann
J.H.Benzler
H.P.Blume
H.Dümmler
H.Gebhardt
B.Meyer
E.Mückenhausen
H.Verhoeven

GUINEA

F.Bellon
A.Kawalec

INDONESIA

P.M.Driessen

IRAQ

Adnan Hardan

MALAYSIA

Hew Choy Kean
K.T.Joseph
K.Kanapathy
Poon Yew Chin

THE NETHERLANDS

J.P.Andriesse
P.S.E.F.Augustinus
H.de Bakker
T.A.El Baradi
H.van Baren
W.F.J.van Beers
W.A.Blokhuis
G.H.Bolt
N.van Breemen
R.Brinkman
P.Buurman
A.van Diest
H.Dost
P.J.Ente
J.Hofstee
A.F.van Holst
J.W.van Hoorn
F.W.Hilwig
A.F.Hunink
W.P.Locher
R.H.Messemaeckers
van de Graaff
Hebel W.Montagne
A.Muller
J.N.B.Poelman
L.J.Pons
H.Rogaar
R.M.Schelhaas
J.Schelling
W.Scheltema
J.van Schuylenborgh
W.A.Segeren
W.L.van Veen
B.Verhoeven
J.M.Verstraten
K.S.Voetberg
G.Voncken
C.van Wallenburg
G.J.W.Westerveld
I.S.Zonneveld

NEW ZEALAND

A.J.Metson

NIGERIA

F.R.Moormann

PHILIPPINES

F.N.Ponnamperuma

PORTUGAL

A.J.Sousa Alvim

SENEGAL

Gora Beye
V.Jacq

SIERRA LEONE

R.T.Odell

SPAIN

J.J.Davila Cremades
C.Roquero de Laburu
J.Torrent Castellet

SURINAM

W.van Vuure

SWEDEN

D.T.Rickard

THAILAND

W.van der Kevie

UNITED KINGDOM

D.Billing
C.Bloomfield
J.K.Coulter
R.J.W.Dight
M.Palmer
I.H.Rorison
P.Williams
J.A.Varley

U.S.A.

C.R.Frink

VENEZUELA

L.Bascones

WORKING PARTY ON NOMENCLATURE AND METHODS

ORGANIZING COMMITTEE

L.J.Pons
Professor of Soil Science
State Agricultural University
Duivendaal 10, Wageningen
The Netherlands

J.K.Coulter
Tropical Soils Liaison Officer
Rothamsted Experimental Station
Harpenden, Herts.
United Kingdom

H.de Bakker
Head, Dept.of Soil Classification
Netherlands Soil Survey Institute
Staringgebouw, Wageningen
The Netherlands

N.van Breemen
Staff member, Soils Department
State Agricultural University
Duivendaal 10, Wageningen
The Netherlands

H.Dost
International Institute for
Land Reclamation and Improvement
Staringgebouw, Wageningen
The Netherlands

CORRESPONDING MEMBERS

N.Ahmad
Professor of Soil Science
University of the West Indies
ST.AUGUSTINE
Trinidad W.I.

Gora Beye
Agropédologue
Centre de Recherches Agronomiques
Tropicales
B.P.34, Ziguinchir, Bambey
Sénégal

V.Jacq
Chargé de Recherches, Service
Microbiologique de ORSTOM
Centre de Bel-Air
B.P.1386, Dakar
Sénégal

K.T.Joseph
Head, Soils, Water & Engineering
Research Division MARDI
Jalan Swettenham, Kuala Lumpur
Malaysia

W.van der Kevie
Technical Officer, Soil Survey Dept.
P.O.Box 388
Wad Medani
Sudan

H.W.Patrick Jr.
Professor of Soils
Louisiana State University
Baton Rouge
Louisiana 70803
U.S.A.

F.N.Ponnamperuma
Soil Chemist
The International Rice Research Institute
Los Banos
Laguna
Philippines

S.Sombatpanit
Dept.of Land Development
Bangkhen
Bangkok
Thailand

INTRODUCTORY PAPERS
AND BIBLIOGRAPHY

OUTLINE OF THE GENESIS, CHARACTERISTICS, CLASSIFICATION AND IMPROVEMENT OF ACID SULPHATE SOILS

L.J.Pons
Department of Soil Science and Geology
University of Agriculture, Wageningen

Soil science and its various branches are rapidly extending. No wonder that for the last ten years we are witness to an increasing number of international symposia devoted to specific soil phenomena or categories of soils. The present Symposium on Acid Sulphate Soils illustrates this development. Also for these soils the fundamental research is progressing rapidly whereas at the same time they keep causing practical problems all over the world. I am very glad that you have joined this Symposium in such large number in order to exchange and to discuss experiences and to co-ordinate possible future efforts.

In the following outline of our subject I will try to sketch the development of research against the historical background of practical experiences. This sketch will be followed by discussions on the present state of problems and by speculations about possible solutions in the context of the specific topics listed in our program. But first some definitions.

Some definitions

For the subject of our symposium we choose the name "Acid Sulphate Soils" used in the widest sense of the expression. As such this expression pertains to all materials and soils in which as a result of processes of soil formation, sulfuric acids either will be produced, are being produced or have been produced in amounts that have a lasting effect on main soil characteristics. Traditionally the expression "Acid Sulphate Soils" is often used in a narrower sense for soils with cat clay phenomena. "Cat clay phenomena" are a combination of conspicuous straw-yellow jarositic mottles and a very low pH causing severe problems in agriculture. These phenomena come into existence after drainage and aeration of originally waterlogged and reduced parent material containing excessive amounts of sulphides, mainly pyrites. The oxidation of the sulphides readily produces acid sulphates, which are partly neutralized by readily neutralizing components and possibly partly leached; the remaining acid attacks the clay minerals, thereby causing the liberation of Aluminum ions in amounts toxic for plant roots and microorganisms. In the following we will precise the soils in which these processes actually are taking place by calling them "actual" or "developed acid sulphate soils" and the as yet totally reduced parent material will be indicated as "potential acid sulphate soils" or "sulphidic mud". Possible other precisions will be defined when they are introduced.

World wide distribution

Acid sulphate soils in the broad sense are occurring in all climatic zones of the earth. The map presented for this symposium by Kawalec, gives a good idea of their world wide distribution. This map also demonstrates that the majority of acid sulphate soils occurs in coastal areas and is developing in recent or subrecent marine sediments. Yet sulphidic materials, suitable to produce acid sulphate on oxidation are by no means restricted to recent marine sediments. They occur in many sedimentary rocks that may even date from Pre-cambrian times. The rare incidence of actual acid sulphate soils in continental environments can be explained by the close relation of acid sulphate soil phenomena with initial soil formation. In the history of older landsurfaces these soils are only transient phenomena. In fact the rare reports on inland acid sulphate soils pertain mainly to isolated phenomena, e.g. actual acid sulphate soils on sulphidic materials that obtained their sulphides from pyritic "rocks", or fossil acid sulphate soils developed on outcrops of the same kind of rocks. However, where, e.g. near lignite quarries or coal mines, pyritic material is brought to the surface actual sulfuric acidification may become a serious problem for restauring vegetation on spoil areas, or it may cause pollution of rivers with sulfuric acids. These are real cases of acid sulphate soil formation and belong to our sphere of interest. For the present outline however, I would like to restrict myself to the prevalent acid sulphate soils of coastal areas, and I would like to start with those of The Low Countries.

Historical notes on nomenclature

In The Netherlands acid sulphate soils have been known for ages and since the 18th century they have drawn scientific interest. According to Poelman, who is well acquainted with the older literature as may also appear from his contribution to this Symposium, the famous Linnaeus was the first to describe our acid sulphate soils. This was in 1735 when Linnaeus was working on a classification of rocks, minerals and soils of our country. He used the expressions *argilla vitriolacea*, meaning clay with sulfuric acid, and *argilla mixta fusca*, *vitriolico salsa*: mixed clay, brown, with the taste of sulfuric acid salts.

In 1771 Le Franc van Berkhey published a natural history of Holland in which he distinguishes two kinds of cat clay: "black peaty cat clay" and "blue cat clay". At this time "cat" was used in Dutch vernacular as a prefix connotative of harmful, mysterious influences or qualities. People dredging peat for fuel and farmers using mud for fertilizing soils used the term "cat-clay" for sulphidic mud, but also for various other kinds of infertile, waterlogged or markedly mottled soils, including actual acid sulphate soils. The exclusive use of the Dutch "kattekleigronden" or "cat clay soils" in English, for acid sulphate soils dates only from the time when the first regional soil investigations were carried out (Hissink, 1923) and especially when the soil survey started in The Netherlands (Edelman, 1948).

Mystery and evil is at the origin also of the vernacular names used in Northern Germany. Benzler (this Symposium) reports the name "Maibolt" for clay with jarositic mottles, "Mai" stending for "Maifelder" or hay fields and "bolt" for "Kobolt" a kind of evil ghost. No doubt similar expressions of unfavourable opinions on acid sulphate soils must exist in many other languages, because it is a curious fact that all over the world these unfavourable soils with their striking morphological features did attract farmers and subsequently deceived these farmers in their expectations. In this respect the early occupational history is very much the same for many coastal alluvial plains and deltas.

Occupational history of coastal low lands

Actual and potential acid sulphate soils are occurring in areas that are flat, badly drained and suffering from saline, brackish or fresh water floods. They consist largely of swamps and marshes. Vast depressions may be filled in with peat, their mineral soils being permanently waterlogged, reduced and unripe. River levees or beach ridges are often the only culminations. Early occupation concentrates frequently on such culminations that adjoin vast tracts of even herbaceous fresh water marshes. Initially these sites provide ample fish, fowl and game, and relatively fertile naturally drained soils. In the marshes there is ample room for extensive rice cultivation or cattle raising. Often the rivers provide also plenty fresh irrigation water whereas tidal amplitudes enable some drainage by simple devices. The farmers start with using these natural advantages of the estuaries and coastal marshes. At that time the possible presence of potential acid sulphate soil in the marshes is not apparent and does not bother the farmers as they do not drain intensively. Actual acid sulphate soils are avoided or in case of inadvertent development, abandoned for new land. Then, as new land becomes scarce, the farmers gradually learn to live with possible acid sulphate soil problems, often at the cost of enormous sacrifices, which rarely are assessed. Various contributions to this Symposium describe very interesting instances of traditional adaptation of agricultural systems to acid sulphate soil conditions.

Better known were until now the instances that large scale reclamation or improvement of coastal marsh land with the aid of modern techniques of water control and drainage, resulted unexpectedly in actual acid sulphate soil phenomena and inproductive soils. Unexpectedly, because the waterlogged and reduced sediments to be reclaimed, to the responsable engineers seemed to be very homogeneous and similar to sediments reclaimed successfully earlier. By now we know the causes of this problem and in some cases its remedy, and we claim that acid sulphate soil conditions can be predicted. This knowledge, however, is relatively novel, and in many cases the only safe advice we are able to give is: leave it alone. To the venerable acid sulphate soil problem such advice is at best only half an answer. The history of the polders in Holland offers some instructive examples in this respect.

The reclamation of lake-bottoms in The Netherlands

In the lower parts of Holland modern drainage techniques were introduced in the 17th century. At that time it became possible to reclaim marshes and lakes with the aid of windmills. Some of the polders reclaimed from lakes were reported a complete success because, as we know now, the lake bottoms contained highly calcareous sediments. However, in the majority of the reclaimed lakes areas of actual acid sulphate soils appeared shortly after drainage, causing grave disappointments and important losses of investments both for the reclaiming companies and for the individual settlers. The farmers tried to minimize losses by maintaining very high groundwater tables, thus preventing further oxidation of sulphidic muds. They had to concentrate on grassland and dairy farming but with the prevailing high watertables productivity remained low.

In spite of the difficulties with the majority of lake bottom reclamations the reclamation went on until 1852 when the largest of the lakes became the Haarlemmermeerpolder (Polder Lake Haarlem). Large parts also of this lake bottom consisted of sulphidic muds and during the first ten years after reclamation high groundwater tables were maintained. All the same the grass suffered both from acidity and waterlogging and for the first generation of settlers disaster seemed unavoidable.

In 1856 a soil scientist, named Van Kerckhoff, was called in. He concluded, after chemical investigations that the infertility was caused by the presence in the soil of ferric vitriol originating from the weathering of ferrous sulphide. In fertile soils ferric vitriol was found absent but these contained calcium carbonate and therefore Van Kerckhoff recommended lime as an amendment for the cat clay soils. Then some farmers discovered that ploughing only to 30 cm depth brought up so much lime that the acids could be completely neutralized. Apparently relatively shallow sulphidic layers were underlain by highly calcareous sediments. From then on it became a regular practice in the Haarlemmermeerpolder to bring up calcareous subsoil layers and this, together with improved drainage, turned this polder into one of the most productive agricultural districts of Holland.

Van Kerckhoff's positive contribution to the solution of the acid sulphate soil problem in the Haarlemmermeerpolder promoted further scientific investigations. In 1886 Van Bemmelen completed a report in which he explains the reduction-oxidation cycle by which marine sulphates are accumulated under reduced conditions as sulphides and the sulphidic sediments turn into acid sulphates on aeration. Other studies followed, but it was not until the 1930's that with the reclamation of the first of the Zuiderzee Polders, Lake Wieringen, sulphidic muds were drained intentionally and improved according to plan. To this reclamation we owe the detailed studies of Zuur (1936) including the first detailed soil maps ever made in our country. The present situation in the Wieringermeerpolder is reported on by Verhoeven in his paper for this symposium. It shows that the reclamation and improvement of the "cat clays" was a complete and lasting success. In fact the resulting soils are, 40 years after first drainage, for the farmers equal to adjacent originally calcareous soils. In Holland the mystery of the "cat clays" has been reduced to a technical problem due to a fruitful combination of farmers' common sense and a scientific approach and, thanks to the specific sedimentary conditions that provided a common occurrence of calcareous deposits close to the sulphidic muds.

Improvement of acid sulphate soils in The Netherlands and elsewhere

As you will see on the excursions and as is reported in various papers, in Holland improvement of acid sulphate soils involves a lot of earth moving. Calcareous soil material may be dumped by ship on lake bottoms even before empolderment, it is also spread by trucks or brought up from the subsoil by deep ploughing or spading. This is expensive and for economic application in principle the bulk of the acid formed after drainage should be leached down and out, whereas the calcareous soil material serves to build up a new top soil on top of the least acid surface layers.

If no calcareous soil material is available neutral soil may be brought on the surface in larger amounts and limed subsequently. This is even more expensive, but in the economic setting of The Netherlands it may be feasible. You can see an interesting sample of this latter case on the excursion to the eastern part of

The Netherlands. Here weathering of exposed Tertiary Sulphidic clays, releases sulphates which via seepage water move towards marshy valley bottoms, where they give rise to sandy and peaty sulphidic soils, which latter at present are being reclaimed with the aid of drainage, and dressings of pure sand and lime. Several of the symposium's papers pertain to this sequence of inland Acid Sulphate Soils i.e. Buurman c.s., Poelman, Westerveld c.s.

I mentioned the above case to demonstrate that calcareous soil material is not the only natural asset to be applied in improving drained acid sulphate soils. Its presence surely simplifies the solution of the problem but other solutions do exist. This is also intimated by various papers reporting on successfull, traditionally developed agricultural practices using seasonal sea water flushing as in West-Africa, or building ridges as in Malaysia. In the resulting soils acids have been leached, neutralized or otherwise inactivated to the extent that microbiological activity and root development are not hampered any more. Similar situations may occur in natural conditions as I myself have observed in the Guyanas and in Thailand. I suggested the name "Pseudo- or Para Acid Sulphate Soils" for these soils. Only in some of the cases calcium carbonate was active in eliminating acids. With many of the improved acid sulphate soils in Holland these tropical soils have in common that they still show jarositic mottles and high soluble sulphate contents and that they have a high percentage saturation of Aluminum but no toxic amounts of free Aluminum. Later on I will come back on these Para Acid Sulphate Soils.

What is interesting us here is that the development of actual acid sulphate soils is not determined only by the pyrite/lime proportion of the parent material, but that there is quite some room for modifications due to variations in environmental conditions, including various systems of reclamation and soil management. In this respect the case histories of the Dutch, inland polders are interesting, not just because they demonstrate calcareous soil material to be an effective amendment, but much more because they show that mastery of the local acid sulphate soil problem evolved from the more passive prevention of acid sulphate soil formation towards actively modifying it by modification of the environmental conditions. This was only possible through a thorough understanding of the whole chain of dynamic phenomena from sedimentation to soil formation and to the reactions of plant roots, always in relation with prevailing environmental conditions.

The same chain of processes we have tried to cover with the topics of our Symposium. I would like now to review shortly which are the characteristic questions and problems for each of these topics and try to evaluate to which extent we know already some answers.

The main topics of the present symposium

The topics of our symposium seem to revolve around two basic questions:

- what is the natural history of acid sulphate soils?
- what could their function be in the human environment?

The first question falls apart into:

- from which kind of parent materials are acid sulphate soils developing?
- what kind of acid sulphate soils exist and what are their characteristics,
- how proceeds their pedogenesis?

The second into:

- what are the assets, what the deficiences of the various acid sulphate soils?
- where do they occur and how can they be recognized,
- how can their possible agronomic assets be realized,
- in which conditions should this be done.

All the above questions are intimately interrelated and in principle none of them can be considered to have a definite priority. The sequence of the topics listed in our program is reflecting merely an arrangement from more fundamental towards more practical subjects, or if one wishes: from genesis, through characteristics and classification to application or improvement.

Pyrite accumulation

Topic 1: formation and accumulation of sulphides pertains to the component that embodies the potential acidity in the parent material of acid sulphate soils. We know that the formation of sulphides by microbiological sulphate reduction is a very common event wherever sulphates and organic matter occur in reduced natural environments. During this process the organic matter is partly oxidized by which oxidation bi-carbonates are produced. The peculiarity of microbiological sulphate reduction in marine sediments, is that the sulphides precipitate and may accumulate in considerable amounts as pyrite, whereas the bi-carbonates form no insoluble products with the cations of the sea water and together they are removed. The amount of pyrites fixed in wet marine sediments is generally directly proportional with organic matter content. In reduced tidal deposits very large amounts of pyrites can be concentrated in the organic matter produced by a telmatophytic vegetation. Most sulphidic muds, in the sense of parent material for acid sulphate soils, originated that way.

The distribution, concentration, size and shape of pyrite cristals in such sulphidic muds show large irregular variations on a small scale as well as on a large scale. These variations may influence strongly the subsequent soil formation. The variability is an obstacle to sampling, classifying and mapping sulphidic muds and to predicting their possible soil formation. Therefore we would like dearly to recognize and understand its patterns particularly in relation to external environmental features e.g. type of telmatophytic vegetation, hydrological regime etc. and in relation to subsequent processes of soil formation.

In this context it is important to distinguish between primary and secondary pyrite accumulation. Primary accumulation of pyrite takes place in the seawater/ sediment interface without the influence of vegetation in contrast to secondary accumulation which occurs in the vegetated tidal mud flats and is sustained by the organic matter produced by the vegetation. The patterns of primary pyrite accumulation are relatively simple as to distributional variations, and we might well start with studying the fundamentals of primary pyrite accumulation in order to come to a better understanding of the intricacies of secondary pyrite accumulation. We are therefore happy to have among us an outstanding specialist in this field: Dr Rickard, who will give us an introductory lecture on sedimentary pyrite formation.

The content in primary or syn-sedimentary pyrite of marine muds shows important zonal differences. It is much higher in temperate than in tropical climates. This difference is related to the lower amounts of syn-sedimentary organic matter in the tropical deposits. The potential acid sulphidic Littorina deposits around the Bothnic Gulf in Scandinavia for instance, contain only primary pyrite. For the largest part of the globe, and particularly for the tropics, it takes secondary pyrite accumulation to produce the surplus in pyrites that characterizes potential acid sulphate soil material. The zonality in the world distribution of acid sulphate soils, apparent from a definite concentration within the 20 °C isotherms (as shown on the map presented by Kawalec), therefore, is not related to the zonality in primary pyrite content. On the contrary, it is the expression of the overruling influence of secondary pyrite accumulation produced by the tropical mangroves, the distribution of which is limited by the 20 °C isotherm.

Syn-sedimentary buffering minerals

The emphasis on pyrites as an essential component of the sulphidic muds should not distract us from the other components which may influence the pathways and the ultimate results of the subsequent soil formation. We already mentioned calcium carbonate and bi-carbonate as important neutralizers of acids. Less conspicuous, because they react relatively slow, but nevertheless very important neutralizing or buffering components are the clay minerals and various magnesium- and magnesium-iron-silicates e.g. glauconites, chamosites, etc.

As primary pyrite, these neutralizing components are syn-sedimentary minerals and as such their occurrence and proportions are characteristic for specific sedimentary units. To a certain extent the laws governing their distribution have been elucidated by sedimentologists and geochemists. Most important determinants for the presence of these minerals in specific sediments are the geology and weathering conditions in nearby continents and the load of the rivers and ocean currents that contribute to the coastal deposits.

In this respect it is interesting to note that in the humid tropical regions most rivers supply very small amounts of calcium carbonate and montmorillonite, the exceptions creating favourable conditions for the deposition of muds with a relatively high acid-buffering capacity.

But for the most important of the buffering minerals, for calcium carbonate, the primary content is subject to secondary modifications, mainly decalcification. Decalcification is particularly rapid in marshes. In marine muds it may proceed simultaneously with, although independantly from secondary pyrite accumulation.

Both these secondary processes are conducive to increasing the total potential acidity of the muds, and to overruling the primary homogeneity of the sedimentary unit in respect to the very properties which we wished to relate to that sedimentary unit. This implies that in deducing soil patterns from primary sedimentological patterns we have to be very careful particularly if it comes to distinguishing acid sulphate soils from other alluvial soils. The complexity of the relationships involved forces us to link sediments and acid sulphate soils through at least two steps.

One step is to establish the regular relationships between primary and secondary mineral content of the muds, and the other step concerns relating the muddy parent material to the subsequent modifications due to soil formation per se. It is particularly for the first mentioned step that we need the help of sedimentology, geochemistry, microbiology and plant ecology and we are greatly appreciating that these disciplines are represented at our symposium. As for the other step, here we touch on the second topic of our program: the genesis of acid sulphate soils.

The genesis of acid sulphate soils. Ripening

Soil formation in fresh marine muds starts when tidal floods make place for drainage and atmospheric exposure of the mud. Initial soil formation is characterized by ripening. Early ripening and the last phases of deposition may overlap, but once deposition has terminated, ripening in normal muds proceeds consequently from the surface downward, first quickly, then slowing down to reach a limit when an equilibrium has been reached with the new environmental conditions. Meanwhile in the ripened soil material soil horizons are coming into existence in a characteristic sequence.

The influence of excess pyrites in the fresh mud starts to show during the ripening process. Ripening of mud is marked by increase of consistency, shrinking, cracking, structuration, oxidation, weathering and biotic activity, primarily as a result of the irreversible drying of the wet sediment. The loss of water due to surface evaporation and gravity drainage is initially proceeding superficially and slow, until it is greatly intensified by evapotranspiration through the suction of penetrating plantroots. In normal muds the roots of pioneer vegetations are able to penetrate and to remove excess water to depths far beyond those reached by gravity drainage and surface evaporation alone. In sulphidic muds however, the physiological functions of the plantroots are inhibited as soon as oxigen penetrates the superficial mud layers, oxidizes pyrites and produced acids in intensities beyond the instantaneous buffering possibilities. Because pyrite oxidation is progressively accelerated at pH's below 4, the bulk of the pyrite in sulphidic muds will oxidize within a period of a few weeks once moisture content comes near field capacity for the first time. The resulting acids will attack the clayminerals and Al kations will be liberated in amounts toxic to the very plantroots that promoted the oxidation by their physiological drainage of the mud.

If the acids and the soluble Al ions are not leached out or eliminated quickly, e.g. by tidal floods or by riverfloods containing calcium carbonate then the roots die off and depending on external conditions, the ripening process is either interrupted all together or slowed down to the rate that moisture can be removed from the soil merely by gravity drainage and surface evaporation.

With this obstruction of the ripening process the genesis of acid sulphate soils breaks away from the regular soil development in marine muds. With other soils, as ripening continues, the vegetation remains instrumental in draining excess water and, by opening up the massive mud by root penetration and cracks, in leaching excess salts. The soil is developing gradually properties suitable for a wider variety of plants, which latter in the ripened soil regulate further drainage and leaching by recycling moisture and minerals and by building up and maintaining structures for the storage of these soil components. Thus with normal soil, an equilibrium between biotic and physico-chemical processes, between soil profile and environment is gradually reached.

With acid sulphate soil on the contrary, ripening remains shallow and soil development tends to proceed spasmodically towards a soil profile in which the upper part soon becomes strongly weathered and acid, whereas at small depth the subsoil remains unripened. Small changes in environmental conditions are likely to cause both in the acid ripened topsoil as in the unripened subsoil, large fluctuations in chemical properties, often beyond the tolerance limits of natural vegetation or possible crops.

Soil profile development

The overruling role of the chemical aspects in the genesis of acid sulphate soils in comparison to the role of vegetation, is reflected in the major morphometric characteristics of the well developed profiles which are pretty much the same all over the world. The rate of development is however, strongly determined by the degree to which external conditions favour drainage and leaching. In humid climates profile development is in many cases arrested when on accretion of the shoreline, the shallowly ripened muds come into the position of backswamps. There they may be covered by peat and be conserved for centuries, the major changes being re-reduction, some compaction, desalinization, renewed root penetration by telmatophytes and possibly decalcification. After natural drainage the soil development proceeds spasmodically in the earlier described general direction. In dryer climates ripening and profile development proceed faster and deeper as the dry season becomes more important.

The main features that accompany initial ripening, oxidation and acidification are a strong segregation of brown iron oxides followed by the appearance of pale yellow jarosite mottles, in and around cracks, rootchannels and other apertures in the partly aerated coarsely prismatic sulphidic mud, which itself changes in colour from bluish or brownish black to grey. At the same time the pH drops and Electric Conductivity rises, and possibly gypsum cristal may appear in the already ripened parts.

Initially the downward moving oxidation and acidification frontier is irregularly shaped. When it reaches depths of 40-60 cm, it tends to take a more regular horizontal shape. At this time, normally enough acids have been leached or eliminated from the surface layer, at least during wet periods, to allow the seasonal establishment of a shallow rooting herbaceous vegetation, contributing to the formation of a granular or subangular blocky, often umbric epipedon. During dry seasons, on the bare surface a powdery or crusty salt concentration may accumulate. Below the epipedon the upper part of the prismatic jarositic zone turns into a blocky or fine prismatic cambic horizon with brown or red mottles, while the lower part continues to follow the oxidation and acidification frontier which now marks the lowest groundwater levels.

Depending on climate and groundwater relations this horizon sequence may be reached after a few years or a few decennia.

A permanent vegetation cannot establish itself as long as seasonally fluctuating acidity and soluble Al in the upper 40-60 cm keep transgressing the tolerance limits of most plants. Normally in natural acid sulphate soils, this unfavourable condition is only ending, either when the soils become permanently flooded again, or when all potential acidity and excess actual acidity in at least the upper 100 cm has been eliminated. Without external mineral supply the elimination of acidity can be achieved in the long run only through leaching and by neutralisation at the expense of plantnutrients, clayminerals and other weatherable silicates.

The resulting soils are extremely poor in plantnutrients and generally not ripened beyond about 75-200 cm depth. Only if external conditions continue to favour drainage and leaching for very long periods, e.g. on pleistocene marine terraces with eustatic sea level changes, deeper soils may develop, which by their solum cannot be distinguished any more from other thoroughly weathered and leached soils.

Development of transitional soils

This generalized sketch of acid sulphate soil formation pertains to natural developments in massive homogeneously sulphidic material without interference of mineral supply from floods or shallow non-sulphidic subsoils. In these latter situations or with very heterogeneous pyrite occurrence the acid sulphate soil phenomena may occur only locally or temporary and the resulting soils may acquire properties transitional to other soil types. Such transitions are of great practical interest because they often have favourable agricultural properties in contrast to typical acid sulphate soils and in some respect also in contrast to many non-acid-sulphate marine soils. In the present context the transitional soils are of particular interest because they affirm the notion that acid sulphate soil-formation deviates from normal soil genetical processes by a marked antagonism between geochemical and biotic processes. With acid sulphate soil-formation the pioneer vegetation is first instrumental in building up a high acidity potential. Then by boosting the ripening process, the vegetation is instrumental in releasing the acidity and toxic reaction products to intensities beyond its own tolerance. Thus the chemical reactions are inhibiting the regulating activities of the vegetation that with normal soil formation, would lead to a relative stable dynamic equilibrium between vegetation and soil. In acid sulphate soils this equilibrium is only reached after these soils have lost their excess acidity and as a result, their strong dynamism, which implies that they have acquired characteristics of other soil types.

Research methods

This anomalic chemical dynamism is at the root of all the difficulties that acid sulphate soils present to agriculture, reclamation, and land classification. On the other hand it is this anomaly that allows us to witness the formation of complete soil profiles within a few years. This means that the genesis of acid sulphate soils is within the scope of controlled field experiments, which might greatly facilitate the verification by inductive analytical methods of hypothetical relations deduced from assumed genetical field sequences.

Various papers demonstrate, that for the time being also without controlled field experiments important contributions can be made to better understanding of fundamental genetical processes.

This takes however very careful selection of unequivocal chrono-, hydro- or litho-sequences, detailed morphometric descriptions, sustained by micro-morphological and microscopical observations, and specially adapted sampling techniques, analytical procedures and correlative methods. Of particular interest in this respect are normative mineralogical calculations of chemical composition and analyses of interstitial water. But I will not elaborate on these aspects as Van Breemen in his lecture on the genesis of acid sulphate soils will give us a thorough and up-to-date review of the geochemical background as it has developed during the last years in close cooperation of laboratory- and fieldworkers.

There remain of course many phenomena observed in the field which as yet we cannot fully satisfactorily place in our genetical and dynamic theories, and reversily, many of the fundamental processes that have been recognized cannot as yet be applied satisfactorily to concrete situations.

Among these remaining problems figure the effects of alternative drying and wetting by rains and flooding in various frequencies and intensities, the effects of various kinds of organic matter, the effects of physical properties such as size and distribution patterns of mineral and organic particles, or structural stability.

We might well mention all phenomena that are liable to influence the mobility of oxigen and oxidation products and the intensity of acidification, and which thereby might possibly modify the pathways of the soil formation. These and other problems affect directly the predictability of soil formation in specific environmental conditions, the design of reclamation and of course the plant soil relationship as we will see further on.

Al chemistry and structural stability

At this point I would like to give some more attention to the problem of structural stability more particularly in relation to Aluminium. It has been observed frequently that well developed acid sulphate soils have a remarkably stable structure. This is partly due to iron coatings on the surfaces of peds and root channel walls. For an important part it is also caused by the potentially high structural stability of the clay, which latter in acid sulphate soils is characterized by a high concentration of absorbed Al. Al-clays prepared in the laboratory show the same structural stability, and moreover they resist relatively strongly to replacement of the Al-ions by mono-valent ions. As we know, in acid sulphate soils the Al-clay is the result of the acids attacking the clay minerals and thereby liberating Al-kations in such concentrations that they not only replace originally absorbed kations but also remain in the soil solution in amounts toxic for most plants. On subsequent leaching for instance with sea water, the soluble Al may be removed whereas absorbed Al-kations resist a proportional replacement. In the leached soil the Al-toxicity has disappeared but the structural stability remained.

Such soils do actually occur and they may have excellent agricultural properties as for instance the para-acid sulphate soils on which I will come back later in an other context. Here I wish to stress that Al plays an ambiguous role in acid sulphate soils. Until now the emphasis of soil studies has been too much concentrated on only its negative chemical aspect: toxicity, its positive influence on structural stability - i.e.its physical aspects, deserves at least as much attention. This is all the more so as this positive aspect of Al is not affecting only acid sulphate soils but other acid soils as well.

I am thinking here particularly of heavy textured soils developing in humid tropical regions on non-calcareous recent marine muds without excess pyrites. These soils show weak internal structure stability because of their low primary organic matter content and further because of swelling and shrinking clay minerals with a high rate of adsorbed bases, dominated by Mg and may be by Na, this latter possibly in many cases now completely leached. As a result of these disadvantages, these soils show soon after reclamation structural decline causing serious drainage problems. Preliminary trials in Surinam, some of which are reported in the paper by Scheltema and Boons, have shown that in principle the structural stability of these soils can be improved by artificial acidification, without harming essentially their chemical fertility. These trials were paramount to forcing soil properties to resemble more closely those of acid sulphate soils and in fact, are contrasting alternatives for trials aimed at improving soil stability with lime.

The role of Al in acid sulphate soils thus suggests that these much despised soils have some properties that present alternatives for liming and other conventional methods aimed at improving soil structure. If this idea could be worked out positively then it might well change the attitude of the agricultural sciences and practices towards acid soils in general. This is one of the reasons why the Organizing Committee put the influence of acidity on ion exchange characteristics and the development of structure stability as a separate topic in the program next to soil genesis.

We are glad that we could persuade the well known specialist in this field, Dr Frink, to present an introductory lecture. We hope that it will stimulate many of the participants to give the above expressed suggestions considerations in their future working programs.

Identification and prediction of acid sulphate soil conditions

An other subject closely related to the genesis of acid sulphate soils is the identification of potential acid sulphate soil-material, topic number 4 on our program.

Mr.Brinkman will present a critical review of the various methods that have been developed to recognize sulphidic material with a view to predicting actual soil development following drainage. I will restrict myself here to relating this subject to the other topics of our program.

It is obvious that the identification of sulphidic muds in relation to their future development is directly dependent on the knowledge of the fundamental soil genetical processes and their modifications under the specific environmental conditions under consideration. Existing identification methods therefore reflect our genetical knowledge including its deficiences. The ideal in this respect is that we can indicate explicitly that parent material in a certain site following specific environmental changes will yield particular kinds of soil.

In The Netherlands we have come quite close to this ideal as the papers of Van Wallenburg, Westerveld and others will demonstrate. For most other parts of the world we must content ourselves with such statements as: in a specific environment or in muds with an equivalent excess of pyrites over calcium carbonate, intensive drainage will yield acid sulphate soils sometimes, frequently, nearly always, hardly ever or never.

The relative precision and accuracy of the Dutch technique is due to the fact that it is based not only on general genetical principles but also on a long experience with reclamations and above all on detailed surveys of soils in the context of their historical physiographic setting, including the reconstruction of mineralogical, sedimentary, hydrological and land-use history. For concrete situations elsewhere the Dutch identification methods therefore cannot be applied formally, with the same chance of success.

If we wish to achieve more than merely giving a conservative warning for possible disasters then we should take into account for each physiographic area, the characteristic modifying factors. This implies regional investigations that combine analytical methods, experiments and soil surveys. These latter should not be merely aimed at registration of soil profiles but, in fact should be by themselves cartographic correlative studies of soils and physiographic history.

The complicated character of physiographic history in deltaic regions should not be underestimated and I would like to warn against relating soils explicitly to external phototypic physiographic features. Particularly vegetation types are likely to be misleading in this respect. I am thinking of swamp vegetations that often are merely indicative of flooded conditions and in combination with peat may disguise all underlying topography. Also the phototypic aspects of ephemerous herbaceous vegetations may be very alike for acid or non-acid saline soils. Moreover for shallowly ripened acid sulphate soils the rootchannel systems of past vegetations may be more significant for further development than the actual vegetation.

Given the complexity of many coastal lowlands it is probably advisable to select for detailed integral studies, primarily relatively simple physiographic situations with unequivocal, genetically significant soil sequences. If traditional agricultural systems are present, these might be included as historical experiments. Finally controlled field experiments could be combined with reconnaissance soil surveys.

This is often preferable to extensive detailed surveys. But here I have entered already far into the field of our fifth topic: physiography, classification and mapping.

Physiography, classification and mapping

On this vast subject we will have an introductory lecture by Van der Kevie and the many other papers in this category will be reviewed by Vieillefon. Special mention goes also to Kawalec of FAO for his preparation of a map showing the world wide distribution of acid sulphate soils.

The combined contributions present an impressive amount of new facts. They also confront us with a large variety of descriptive methods and nomenclature. Under these circumstances it is reassuring that the majority of the authors correlate their soil descriptions with the soil classification system of FAO and/or with the American Soil Taxonomy. In both these international systems the acid sulphate soils have been recognized on high categorical levels, as will be explained in detail by Van der Kevie. In my opinion Soil Taxonomy in particular provides an excellent extensible frame for world-wide classification and a sound basis for normalization of methods and terminology in soil profile description.

The problem of normalization has become urgent, and this convention seems to be the right occasion to tackle it in respect to our specific subject. The Organizing Committee therefore has formulated some suggestions for normalized nomenclature and reserved time in our program for a discussion.

We might extend this discussion to include the central concepts and the distinguishing criteria for taxonomic and possibly mapping units. With the present body of knowledge in respect to processes and morphometric characteristics it probably will not be difficult to reach agreement for the well developed acid sulphate soils. If it comes to relating soil units and agricultural potential I am afraid however, that we will be confronted again with the deficiencies in our knowledge that I mentioned before in my remarks on the topic of identification and prediction.

Soil Survey can contribute to closing this gap in our knowledge by selecting soil sequences in which the typical course of acid sulphate soil formation is interrupted or changed to the effect that the resulting conditions for plantgrowth are superior to those that normally develop. Integrated detailed correlative studies of these sequences and controlled field experiments might teach us to which extent and by which efforts we might reach the same effects. The soil sequences have to be looked for primarily in areas with traditional agricultural practices and with transitions towards non-acid sulphate soils.

Para acid sulphate soils

In this context I would like to ask once more your attention for the para acid sulphate soils which I referred to earlier in relation to Al chemistry and structural stability. These soils were first described in Surinam where they occur together with typical acid sulphate soils and normal acid soils (Umbric tropaquepts) apparently all developed from the same sedimentary unit, a non-calcareous heavy textured marine clay.

These para acid sulphate soils are ripened to depths of 100-200 cm. The profile has a stably granular umbric epipedon, a prismatic cambic horizon with brown and jarositic mottles in a grey matrix and with many distinct iron-coated open rootchannels, the latter extending into the subsoil and giving the profile a high vertical permeability. The soil is acid, pH 4-5, has a Al-dominated adsorption complex, but no toxic amounts of soluble Al in the soil solution.

The soil properties, soil sequence and the physiographic setting indicate that the solum developed from muds which were at least partly sulphidic, went through intensive acidification in an early phase of ripening and subsequently were leached by seawater. Laboratory experiments sustain this interpretation. Apparently the acidification did not last to be able to interrupt the ripening as is the case in comparable typical acid sulphate soils. This might have been due to a relatively small or locally concentrated excesses of pyrites in the sulphidic mud combined with external conditions that favour drainage and leaching.

In Surinam these para acid sulphate soils are not just odd transitional soils, they are recognized for being very productive for a variety of crops. This productivity they owe directly to their excellent physical properties and indirectly to the transient phase of acid sulphate development, the toxic chemical effects of which were subsequently moderated by leaching. This means that, provided the leaching of soluble Al can be realized, moderate acid sulphate soil phenomena are not only acceptable but might even be considered a positive asset in reclamation of non-calcareous and sulphidic muds, particularly in situations were no lime is available for the formation of Ca-clays and complete neutralization of acids. Para acid sulphate soils therefore could stand model for reclamation and improvement of the majority of tropical acid sulphate soils.

In my opinion para acid sulphate soils are naturally occurring in many coastal plains, particularly developed from transitional sulphidic muds, that is, in marine muds with moderate excess of pyrites over readily neutralizing components. Incorporating these soils in detailed studies is of great practical interest as these studies can provide the keys for reclamation and management practices that are not merely aimed at eliminating the unfavourable effects of acid sulphate soil phenomena but also try to make the best possible use of the positive effects in respect to the physical soil properties.

Plant response to acid sulphate soil conditions

The potential for favourable physical properties in acid sulphate soils should of course not distract our attention from the harsh fact that this potential cannot be realized satisfactorily without living plants, and that in typical acid sulphate soils the chemical disadvantages that inhibit root development remain the immediate crucial problem. This is also expressed in the large number of papers that treat the toxicity problem as a given fact.

The contributions that specifically deal with toxicity as a problem to be solved are however relatively few in number. We have the paper of Ponnamperuma on the chemical dynamics of acid sulphate soils that affect rice production, and the paper of Jacq on interrelation between roots, microbes and sulphur compounds. Further, in relation with the topics of improvement, soil management and reclamation, the lecture of Coulter, and other papers touch toxicity problems of specific crops. It is obvious that most work in this field is done by agronomists and soil fertility specialists without considering that soil-genetical processes and the dynamics of soil-plant systems are related. As we have seen earlier, with acid sulphate soils in particular, the two can hardly be separated because of close interrelationships. The Organizing Committee has therefore also introduced the topic of plant response to soil acidity in the program of our symposium.

We will have an expert lecture by Dr Rorison on the physiological aspects of this subject. We hope that this lecture will lead to a closer co-operation with physiologists in our future research. I may well add here that in my opinion the same is necessary in relation to microbiologists.

At this moment I will not elaborate this subject systematically and restrict myself to mentioning some other aspects of plant soil relationships which in my opinion need further consideration.

Some further remarks on plants and acid sulphate soils

Earlier I expressed some doubt about the explicit indicative value of phototypic vegetations for interpretative mapping of acid sulphate soils particularly as such methods might distract the attention from the historical aspects of vegetation-soil relationships. The present situation should be seen against the background of this historical aspect. In many cases this takes an expertise beyond the know-how of usual soil survey teams. I would recommend therefore the cooperation with plant ecologists and sedimentologists. I might well add once more, that studying the root channel systems of both past and present vegetations in reduced muds is very useful for historical reconstructions as well as for judging the internal drainability of the mud.

Directly related to this latter remark is the open question whether we might facilitate future drainage and leaching of sulphidic muds, which at present are in swamp condition, by controlling the swamp vegetation, for instance by furthering the growth of species with coarse, but dense, deep reaching rootsystems. In the same line of thought one might consider to keep the pyrite content of sulphidic muds low by reducing telmatophytic vegetations and thereby pyrite accumulation during the last phase of sedimentation.

The last aspect of soil-plant relationships that I had liked to recommend for further consideration is the selection of crop varieties for their acidity tolerance. Here I am thinking of pH values of 4-5, within which range stability of Al-clays can be combined with a reasonable chemical fertility potential in improved acid sulphate soils.

Reclamation, improvement and management of acid sulphate soils

Herewith we have come to the practical topics of our symposium: reclamation, improvement and management of acid sulphate soils. We will have lectures and summaries on these subjects by Coulter, Ponnamperuma and Moormann. They will provide us with quite a number of factual data and cases, mainly pertaining to the unfavourable aspects of acid sulphate soils and to the various efforts to correct them to create rooting conditions that are favourable for specific crops.
I will only add some general remarks on the nature of the problems involved.

The negative assets generally ascribed to acid sulphate soils partly pertain to the physiographic setting partly to the inherent dynamical instability of these soils. The environmental problems are either poor external drainability and permanent flooding or large seasonal fluctuations in groundwater levels. Correction of these environmental conditions by drainage and/or irrigation causes radical changes in the soil. Drainage evokes catastrophic acidification and toxic concentrations of Al^{+++}, Fe^{++} and often of Mn^{++}, poor microbiological activity and deficiencies in macro- and micro-nutrients. Subsequent flooding reverses only partly the acidification and its side effects but, on the other hand brings risks of Fe^{++} and H_2S toxicity and salinity. The salts originate either from the local groundwater, from adjacent soils or from the sea.

In older well developed acid sulphate soils the dynamic reactions and the toxicities become weaker due to thorough leaching but these soils are acid and have a poor potential and actual fertility. After flooding reduction in these well developed soils proceeds very slowly due to low organic matter content and retarded microbiological activity. By the time that toxicities have been eliminated by leaching, nutrient deficiencies have become a permanent feature.

These negative assets are obviously enormous handicaps for agriculture. In many instances to overcome them it will take great efforts aimed at detailed studies, experiments, design, construction and organization. The problems of reclamation, improvement and management of acid sulphate soils, therefore might be considered mainly of theoretical interest if it were not for the fact that large populations in developing countries, under demographic and economic pressures have become dependent for their very subsistence of a more intensive use of these soils. Confronted with this "fait accompli" our main problem is not any more how to prevent the inadvertent reclamation of acid sulphate soils but very definitely how to make the best of it once they are occupied. This social-economical context gives urgency to our technical problem: how to apply theories to concrete situations.

Agricultural situations with acid sulphate soil problems

Let me shortly review the main categories of situations involved. There are four of them. The first of these pertains to shallowly developed acid sulphate soils in nearly permanent flooded conditions. The farmers maintain the wet conditions, often with primitive means, in order to safeguard their rice crops or marshy grassland against the toxicities that accompany alternative aeration and flooding of these soils. This situation is occurring in all regions were climate and hydrological conditions support also natural swampconditions.

The second category is that of acid sulphate soils developed unexpectedly following drainage of swamps. The reclamation was often aimed at drainage of overlying peatsoils and of associated non-sulphidic or transitional muds, with a view to dry crop production. The developed acid sulphate soils suffer from stagnating ripening processes, extreme acidity in the topsoil and various toxicities in near-surface layers due to uncontrollable groundwater fluctuations. This situation occurs in moderate humid and in alternatively wet and dry tropical climates.

The third type of situation in which acid sulphate soils are occupied for farming are the irrigable, naturally developed acid sulphate soils of regions with an outspoken dry season. On these soil irrigated rice cultivation is practised. In these soils Al toxicity is not readily reduced after flooding, the retardation being due to low organic matter content and poor microbiological activity. Rice transplantation therefore has to be postponed and, before the rice plants have grown sufficiently, other toxicities are likely to appear.

In the fourth and last category fall the shallowly or deeply developed acid sulphate soils which have already been improved with naturally available amendments, or for which such an improvement could be realized easily. I am primarily thinking of a situation as in The Netherlands where sulphidic deposits alternate with layers containing calcium carbonate. Then here are the areas within reach of irrigation water rich in calcium carbonate as in parts of the Thailand coastal plain. Another case are the acid sulphate soils in tidal regions where a combination of outspoken dry and very wet seasons allow first shallow ripening, then leaching with seawater and subsequently desalinization and irrigation with rain water. These situations occur among other places in Sierra Leone and Guinea in West Africa. The elimination of excess acids, aluminium, iron, sulphates, etc. in the soils of this category is not always equally successful, much depends on the external drainability and the effectiveness of water management. Moreover nutrient status remains a problem.

Soil-genetical considerations applied to concrete situations

Overlooking the range of technical problems that the various acid sulphate soils present to agriculture one recognizes that they are an accumulation of the general problems of coastal lowlands and the acid sulphate soil formation. Limiting oneself to these latter, one realizes that as in natural conditions, also in agriculture root development in these soils is liable to being inhibited as long as the mineral composition of the soil material is conducive to extreme chemical changes following small changes in groundwaterlevel or moisture content. This situation will only terminate when the mineral composition has changed in the sense that potential acidity and excess sulphates, aluminium, iron, etc. have been eliminated to levels tolerable to plantroots. This change can, according to our genetical theories, only be effected by combined drainage, leaching, buffering and possibly fixation. The less drainage and leaching can contribute the more has to be left to suitable buffering minerals. If these minerals are not supplied from external sources, then the buffering will proceed by acid hydrolysis at the expense of the minerals present in the soil, including clayminerals and by precipitation at the expense of reserves of plant nutrients. Drainage without adequate leaching and external mineral supply therefore not only increases acutely excess acidity and related toxicity but moreover results in lasting nutrient deficiences.

It is obvious that most traditional farmer communities lack the resources for realizing drainage, leaching, liming and fertilizing in the required proportions if natural conditions are not providing particularly favourable conditions. On the basis of soil genetical considerations it is therefore perfectly understandable why farmers often prefer shallowly developed acid sulphate soils and also why modern drainage methods, that are suitable for other lowland soils, when applied to acid sulphate soils are adding more new problems than they are solving.

Also the traditional solutions can be understood in soil-genetical terms. For instance the agricultural systems aimed at keeping groundwater levels high with minimal fluctuations are paramount to containment of the unstable dynamic equilibrium inherent to the early phases of acid sulphate soil development. At the same time they try to arrest this soil development or at least to prevent it to proceed catastrophically towards irreversible acidification and mineral depletion.

Very instructive in this context is the application of ridges for growing dry crops in some humid areas were drainage of acid sulphate soils cannot be effected adequately. These ridges are being built to create topsoils out of reach of groundwater fluctuations. The material used is often prepared from sulphidic mud that has been exposed to aeration and rain and subsequently fertilized with ashes and organic mulch. Results are normally mediocre but favourable results are reported by Kanapathy for Malaysia where similar methods are combined with light applications of lime and moderate improvements of water management. This system shows that enforced and consequent leaching can replace lime to a large extent for the timely elimination of acids following drainage. The paper of Verhoeven demonstrates the same complementary relation between leaching and liming for a Dutch polder.

For situations where external supply of buffering minerals, particularly of lime is difficult the crucial problem therefore is how to control the movement of water in the soil. This holds as well for leaching after drainage as for prevention of groundwater fluctuations. This problem cannot be solved by mere improvement of water control in ditches but requires high permeability of the soil material itself, particularly of the sulphidic mud. For sulphidic mud a high intrinsic permeability can be expected to be produced naturally only by open root channels from former swamp vegetations, permeable layers of peat or sand, or a particular potential of the sulphidic mud to form irreversible cracks. In considering improvement these physical aspects of the sulphidic muds are extremely important. They should be investigated carefully in relation to the mineralogical composition of the mud and to the external conditions that determine drainability, availability of water and buffering minerals.

The above stipulations stress once more the necessity for preparing reclamation and improvement projects by careful local and regional investigations. For acid sulphate soils there are no simple solutions or generally applicable formulas.

At the very best we may conclude that the various concrete situations and experiences as well as the theoretical considerations lead to the conclusion that sites with acid sulphate soils can be used profitably for agriculture only if the natural processes of acid sulphate soil formation either can be arrested in an early phase of development, or if they can be deviated to result in the formation of transitional or totally different kinds of soil.

Technically this can be achieved by forcefully overruling or replacing soils and environmental conditions. Agriculture, however, is based on making an optimal use of naturally occurring processes and resources. From this latter point of view reclamation, improvement and management of acid sulphate soils is basically a problem of better understanding the genetical relations of concrete acid sulphate soils in relation to their specific physiographic setting. The solution of this problem requires, I repeat it, specific information provided by integral regional studies, focussing on all the aspects represented in the program of our symposium.

Ladies and gentlemen,
I realize that my remarks on the practical topics must sound like an anti-climax. They reflect the fact that acid sulphate soils remain to be problem soils. I want to stress however, that they are at the same time scientifically extremely interesting soils, that by the very dynamic character of their processes of formation come within reach of human controls much more than other soils. Acid sulphate soils thereby help us understanding general soil genesis.

I hope that this interesting aspect of acid sulphate soil will encourage us in finding the solutions for the urgent concrete problems these soils present to millions of people in the tropical coastal low-lands. Thank you.

Summary

This lecture outlines the nature and scope of acid sulphate soil phenomena and the problems they present to agriculture. It starts with a sketch of the development of research against the historical background of agricultural experiences and proceeds with reviewing the present state of fundamental and applied research in the context of the Symposium's program. Special emphasis is laid on the relation of acid sulphate soil phenomena to other soils developing in recent marine deposits. Some methodological approaches are criticized and possible alternatives are discussed.

Résumé

Cette conférence donne un aperçu du caractère et de l'étendu des phénomènes de sol sulfaté acide et des problèmes agronomiques connexes. Elle dépeint d'abord le développement historique des recherches scientifiques en rapport avec l'utilisation des terres basses et puis, l'état actuel des connaissances théoriques et appliquées dans le cadre du programme du Symposium. Le rapport entre les phénomènes de sol sulfaté acide et des autres types de sol formés dans les dépôts marins recents, a été accentué. Quelques points de vue méthodologiques sont critiqués et des méthodes alternatives sont discutées.

Resumen

Esta conferencia resena la indole y la extención de los fenómenos de suelo ácido sulfático y de los problemas agrícolas conciernientes. Se bosqueja a grandes rasgos en primer lugar el desarrollo histórico de las investigaciones en relación con el uso de las tierras bajas y pués, el estado actual del conoscimiento teorético y aplicado al respecto de los temas en el programa del simposio. Se hace hincapié en la relación entre fenómenos de suelo ácido sulfático y la formación de otros tipos de suelo en arcillas marinas recientes. Se nota unos puntos de partida metodológicos y métodos alternativos son expuestos.

Zusammenfassung

Mit dem Vortrag wird ein Abriss der Natur und des Umfangs der Phänomene in sulfatsauren Böden und der damit verbundenen Agrarprobleme gegeben. Zuerst wird die historische Entwicklung wissenschaftlicher Untersuchungen im Bezug auf die Bodenverwendung erörtert. Dann folgt eine Übersicht der heutigen Lage der theoretischen und praktischen Kenntnisse im Rahmen des Symposiumsprogramms. Besonders hervorgehoben werden die Verhältnisse zwischen sulfatsauren Böden und anderen Bodentypen, die sich im jungen Meereston gebildet haben. Es werden einige methodologische Gesichtspunkte und alternative Methoden diskutiert.

SEDIMENTARY IRON SULPHIDE FORMATION

David T. Rickard
Research Fellow, Swedish Natural Science Research Council
Geological Institute, Stockholm University, Stockholm, Sweden

Sulphur is removed from the oceans by two processes: evaporite formation and fixation in sediments as iron sulphide minerals. It has been suggested (14) that sedimentary iron sulphide formation is the more important quantitatively at present. In the past, evaporite formation has been periodically widespread, and there is about twice as much sulphur bound up in ancient evaporites as in other sediments (34).

However, there is evidence that iron sulphides have been formed in sediments since earliest Precambrian times. Most ancient organic sediments contain authigenic iron sulphide minerals, usually pyrite, and it has been identified from some of the oldest known rocks.

Sulphur is present in seawater mainly as sulphate. The fixation of marine sulphate as iron sulphides in sediments therefore involves a reduction process. Seawater sulphate is virtually inert towards inorganic reduction under present environmental conditions, and the reaction is carried out through the activities of biologic mediators.

It is possible that in the past sulphide was occasionally fixed in sediments as non-ferrous metal sulphides. However, only extremely limited amounts of authigenic non-ferrous sulphide minerals have been observed in recent sediments.

The two major factors in sedimentary sulphide fixation are thus the sources and forms of iron and sulphur. These are discussed in this paper, together with details of the chemistry and environmental limitations of sedimentary iron sulphide formation.

The sources of iron

The relative stability of various common dissolved and solid iron species in low temperature aqueous environments has been widely illustrated in terms of redox potential and pH (57, 27, 58). These diagrams, of which Fig. 1 is an example, demonstrate that under the oxidized, neutral to alkaline conditions of the marine environment α Fe_2O_3, hematite, is the equilibrium iron phase.

These diagrams, apart from only reflecting the situation at equilibrium, are only valid for the species considered.

Iron species not considered include $Fe(OH)_3^0$ (aqueous), α - FeOOH (goethite), and iron silicates.

The relationship between goethite, $\alpha FeOOH$, and hematite has been studied (69, 65, 26, 10, 43). Although earlier studies had indicated that goethite was stable with respect to hematite at temperatures less than 130°C in the presence of an aqueous phase, these results had not demonstrated the reversibility of the reaction. More recently, Berner (10) and Langmuir (43) have independently shown that hematite is essentially stable with respect to goethite under all geochemical conditions. Berner obtained a value of -0.66 $kcal.mole^{-1}$ for the standard free energy change (ΔF^o) at 25°C for the reaction

$$\underset{\text{goethite}}{2\ FeOOH} \rightarrow \underset{\text{hematite}}{Fe_2O_3\ /} \ + \ / \ \underset{\text{liquid}}{H_2O}$$

in the presence of small (several hundred angströms) goethite crystals. The very small ΔF^o value for this reaction would intuitively indicate that goethite might persist metastably in the natural environment. In fact it does seem that the rate of conversion of goethite to hematite is slow at low temperatures, possibly because of the relative insolubility of the iron oxides (26).

Stumm and Morgan (73) give the rate expression for the reaction of dissolved oxygen and ferrous iron as

$$-\frac{d(Fe^{2+})}{dt} = k(Fe^{2+})(OH^-)^2 P_{O_2}$$

or, more conveniently,

$$-\frac{d\ \ln(Fe^{2+})}{dt} = \frac{k_H(O_2\ aq)}{(H^+)^2}$$

The constant $k_H = 3 \times 10^{-12} min^{-1} ek.mole^{-1} liter^{-1}$ at 20°C. The rate expression shows that the rate increases 100 times for unit pH increase. Although the system considered is artificial compared with real conditions, the magnitude of the rate constant suggests that significant quantities of dissolved ferrous iron would only persist in solutions with a pH less than 6.

Catalysts, such as Cu^{2+} and Co^{2+} in trace quantities as well as Fe^{3+}-complexing anions, such as HPO_4^{2-} and a variety of organic compounds, increase the reaction rate considerably. Stumm and Morgan (73) point out that these organic substances, such as cysteine, phenols, polyphenols, gallic acid and tannic acid, also reduce Fe^{3+} synthetically in a matter of hours. They suggest that reactions sequences occur such as

$$Fe^{2+} + 1/4\ O_2 + org \rightarrow Fe^{3+}\text{-org complex}$$
$$Fe^{3+}\text{-org complex} \rightarrow Fe^{2+} + \text{oxidized org}$$
$$Fe^{2+} + 1/4\ O_2 + org \rightarrow Fe^{3+}\text{-org complex}$$

Thus relatively high steady state concentrations of dissolved Fe^{2+} may occur in environments where the rate of oxygenation of Fe^{2+} is slow compared with the Fe^{3+} reduction rate by organic matter. The organic matter then retards the overall Fe^{2+} oxidation while it speeds up the Fe^{2+} oxygenation step.

The oxidation of ferrous iron is followed by hydrolysis to insoluble ferric hydroxides, oxides and oxyhydroxides. At least at lower pH values, the hydrolysis of Fe^{3+} is much faster than the oxidation of Fe^{2+} (73). Ferric hydroxo complexes have a pronounced tendency to polymerise. The process involves the formation of dimers which are hydrolysed to form additional hydroxides, which can ultimately form bridges and finally metastable colloidal iron hydroxo polymers (72). Ultimately, insoluble ferric oxyhydroxide precipitates are formed. At pH values lower than the zero point of charge of the oxyhydroxide precipitate, positively charged metal hydroxo polymers prevail; at more alkaline pH values anionic hydroxo polymers and negatively charged colloids exist. These ferric ion hydrolysis species are strongly adsorbed at solid-solution interfaces. Stumm and Morgan (73) note that adsorption of polyhydroxo metal complexes can occur against electrostatic repulsion forces. The transportation of iron in natural waters as adsorbed ferric oxyhydroxide on clays (17), living diatoms and plankton and organic debris (31) has been widely reported. Adsorbed ferric oxyhydroxides and oxides also give the yellow to red coloration of sand grains (13).

The extremely small size of ferric oxyhydroxide particles in natural solutions makes it difficult to distinguish between dissolved and particulate Fe^{3+} species even by membrane filtration. Hutchinson (35) also notes that the addition of colorimetric reagents, such as dipyridyl, to solutions containing suspended ferric oxyhydroxides, disturbs the Fe^{3+}/Fe^{2+} equilibrium and leads to spurious Fe^{2+} values. For this reason, it is probable that the reports of dissolved Fe^{2+} iron from analyses of surface seawater are exaggerated. In the absence of other ligands than OH^-, the solubility of Fe^{3+} cannot exceed about $10^{-8}M$ within the pH range 6-9. Stumm and Morgan (73) suggest that statements claiming that decaying vegetable matter, such as humic acids which carry carboxyl and hydroxyl functional groups, forms soluble chelates in natural waters must be taken with reservation. Although such substances can unquestionably chelate and bind ferric iron, prohibitive concentrations are required to prevent precipitation at pH values from 6-9 (58). It is more probable that the ferric iron-organic complexes are present as highly dispersed colloids.

In contrast, organisms possess compounds capable of strongly chelating ferric iron. Of particular note are the ferrichromes which are apparently the strongest Fe^{3+} complex forms presently known (73). The ferric iron remains in solution even at great dilutions and high pH. Although these ferrichromes are widely distributed in microorganisms, their significance in the geochemical mobilisation of iron in the natural aqueous environment is unknown.

Ferric iron has a strong tendency to interact with phosphate. The solubility of pure $FePO_4$ is minimal at pH = 5.5 but increases rapidly with increasing pH. Hutchinson (35) reported that an oxidized mud surface does not merely hold phosphate but prevents diffusion of phosphate and Fe^{2+} from deeper layers because the Fe^{2+} is always in excess and, when oxidized, precipitates all the phosphate. The extent of complex formation of Fe^{3+} with HPO_4^{2-} or PO_4^{3-} depends on the $(HPO_4^{2-})/(OH^-)$ or $(PO_4^{2-})/(OH^-)^3$ ratios. Thus with decreasing pH, phosphate substitutes more readily than (OH^-) on the surface of the Fe^{3+} iron. Rosenquist (63) reported vivianite, $Fe_3(PO_4)_2.8H_2O$, from holocene clay sediments of lacustrine origin. Associated marine and lagoonal sediments did not contain vivianite. Rosenquist showed that vivianite tended to form under extreme reducing conditions, with low pH values (7.4) where the stoichiometric solubility of hydroxyl apatite was greater than $10^{-4.5}$ mole $litre^{-1}$. Higher pH values, Ca/Fe ratios of more than 10, and higher CO_2 partial pressures explain why vivianite is not abundant in modern marine sediments.

Thermodynamic data are not available for natural iron silicates such as glauconite. Boström (15) presented hypothetical stability diagrams for ion species which included iron silicates. He argued that these silicates, which had apparent stability fields in reduced environments, would limit the upper pH stability of other iron species. Garrels and Christ (27) showed that pure iron metasilicate, $FeSiO_3$, would usurp the magnetite stability field in the presence of aqueous solutions saturated with amorphous silica. It is probable that natural iron silicates, which commonly contain high Fe^{3+}/Fe^{2+} ratios, would be stable under a wider range of conditions, especially in these more oxidized environments normally occupied by hematite or goethite. Cloud (20) showed that glauconite tends to form today in the presence of both organic matter and dissolved oxygen and at the sediment-water interface, probably in zones of fluctuating redox potential. H_4SiO_4 interacts with ferric iron in a similar way to phosphate. Soluble Fe^{3+}-silicate complexes have similar stabilities to soluble Fe^{3+}-phosphate complexes, and considerable amounts of silica can be removed by ferric oxide precipitation at pH 5-7 in the laboratory (73).

It is noteworthy on Fig.1 that siderite, $FeCO_3$, has only a very limited stability field, under stringent reducing conditions and with the virtual absence of sulphide. Berner (11) demonstrated a further limitation to siderite formation, namely that siderite cannot form in calcium-rich solutions. For siderite to be stable relative to calcite in the reaction

$$\underset{\text{siderite}}{FeCO_3} \quad + \quad \underset{\text{aqueous}}{Ca^{2+}} \quad \rightleftarrows \quad \underset{\text{calcite}}{CaCO_3} \quad + \quad \underset{\text{aqueous}}{Fe^{2+}}$$

the iron concentration must be at least 5% of the calcium concentration. In seawater and marine sediments it is normally less than 0.1%, and thus siderite is thermodynamically unstable.

The source of iron available for pyritisation is further limited by the low reactivity of sulphide with many detrital iron minerals under the low temperatures and pressures of the marine environment. Very fine-grained detrital iron minerals are the most reactive. Magnetite and ferromagnesian silicates are particularly resistant to sulphide attack in these environments, although Menon (46) has reported diagenetic pyrite being formed through the sulfidation of biotite iron.

Summarizing, the source of iron for sulphidation is mainly the ferric oxides, oxyhydroxides and oxides. These compounds are commonly supplied to the pyritisation environment adsorbed on organic and inorganic particulate matter and living organisms. Subsequent reactions with organic matter in the sediment may release dissolved ferrous iron. Dissolved organic complexes of ferric iron seem of less importance, although the significance of organisms in the mobilisation of iron, in ferrichrome complexes for example, may not be fully appreciated. Iron silicates, and possibly phosphates and carbonates, may be of local importance.

The source of sulphur

Sedimentary sulphide production occurs almost entirely as a result of dissimilatory sulphate-reduction by bacteria. From Fig.2 it would seem possible for inorganic sulphate-reduction to take place in many natural environments. However, the low temperature reduction of sulphate is kinetically slow. For example, the addition of Zn metal to sulphuric acid solutions results in the evolution of hydrogen, and yet the remnant solution still contains sulphate. No inorganic sulphide source is known in any modern non-volcanic environment, and sulphate may be regarded as inorganically inert with respect to reduction at low temperatures.

The biologic and abiologic decomposition of natural organic sulphur compounds may also result in the release of sulphide. Fish protein contains about 2% dry weight sulphur and thus the decomposition of some 2600 g of this material could produce up to 32g sulphide. In contrast, dissimilatory sulphate-reducing bacteria may produce the same amount of sulphide from 96 g of aqueous sulphate at the expense of only 180 g lactate.

Skopintsev (68) has shown experimentally that the bacterial decomposition of biogenic organic matter in seawater results in dissolved sulphide concentrations quantitatively equivalent to the disappearance of dissolved sulphate, with no significant contribution from the organic sulphur compounds. Berner (12) has further noted that marine sediments often contain amounts of pyrite sulphur in excess of that which could theoretically be provided by 100% organic matter.

The most conclusive evidence as to the importance of sulphate-reducing bacteria comes from the studies of Japanese near-shore waters. In particular, the microbial flora of Karogara Bay contain some 37.3% sulphate-reducers, making up by far the largest proportion of microorganisms (66). Furthermore, studies in Hiroshima Bay demonstrated that the weight of sulphide per gram mud was directly proportional to the number of sulphate-reducing bacteria (39).

The bacteria responsible for dissimilatory sulphate-reduction belong to the genera *Desulfovibrio* and *Desulfotomaculum*. An electronmicrograph of a typical *Desulfovibrio* species is shown in Fig.3 and the major characteristics of these organisms are summarised in Table 1.

Sulphate-reducing bacteria are normally heterotrophic. They facilitate overall reactions of the type

$$2\ CH_2O + SO_4^{2} \rightarrow HCO_3^- + HS^- + CO_2 + H_2O$$

Using a known metabolizable substrate such as lactate, the reaction would be written

$$2\ CH_3.CHOH.COOH + SO_4^{2-} \rightarrow 2\ CH_3.COOH + HCO_3^- + CO_2 + HS^- + H_2O$$

The bacteria perform the reduction through a series of reactions involving ATP (adenosine triphosphate), APS (adenosine-5-phosphosulphate), at least two enzymes (ATP-sulfurylase and APS-reductase), and an electron donor (38). A cytochrome (c_3 in Desulfovibrio) is involved in electron transfer during these operations (54). The reduction is accompanied by an enrichment in the faster-reacting, lighter ^{32}S isotope over ^{34}S. This is an ecologically and geochemically important phenomenon which itself has been the subject of a symposium (37).

The bacteria are obligate anaerobes but otherwise they tolerate a wide range of conditions. Species may be found that will withstand pH = 5 - 9.5, Eh = +80 - 400 mv, 0 - 70 °C and 0 - 12% NaCl concentrations. The author has worked with one strain (Canet 41, N.C.I.B. 8393) which could grow in NaCl-free solutions as well as in solutions containing 12% NaCl. Zobell (81) isolated a strain from a deep-sea environment which was able to reduce sulphate at 1000 atm. pressure and 104 °C.

These wide physico-chemical tolerances are reflected in the ubiquity of their presence in the anaerobic parts of almost all natural aqueous environments. The presence of an anaerobic sulphide-containing zone beneath the oxidized surface is the normal situation in marine, brackish and fresh water sediments, as well as in many soils.

The limits of the sulphate-reducing environment are controlled by the tolerances of the sulphate-reducing bacteria. Baas Becking et al. (3) assembled the results of 477 pH and Eh measurements from regions where sulphate-reduction occurs. The results are shown in Fig.4. The lower limit of sulphate-reduction occurs at about pH 5, although there is one measurement (from 1934) of apparent sulphate-reduction at pH 4.2 from a peat bog. The upper pH limit is just above pH 9, although one measurement from the alkaline Searles Lake, California, gave pH 9.9. The measured Eh limits of the sulphate-reducing environment are less meaningful, and probably at best represent mixed potentials. Morris and Stumm (49) note that significant reduction of SO_4^{2-} to H_2S at pH 7 requires $p\varepsilon < -3$, and that the biological enzymes that mediate this reduction with organic matter oxidation must operate at or below this value. Sulphate-reduction occurs within the cell and it is possible for the bacteria to develop with a significantly higher $p\varepsilon$ value in the growth medium. Even so it is customary to add cysteine, Na_2S or thioglycollic acid to at least $p\varepsilon = -3$ in batch culture media. A standard method for counting sulphate-reducing bacteria involves the insertion of an iron needle for the same purpose.

The uppermost Eh noted by Baas Becking et al. (3) was over +100 mV, whilst the lowermost limits were on the boundary given by the equilibrium

$$\begin{array}{lllllll} 2\ H_2O & + & 2\varepsilon & = & H_2O & + & 2\ OH^- \\ \text{liquid} & & & & \text{gas} & & \text{aqueous} \end{array}$$

at 25 °C and where $\underline{P}_{H_2}$ = 1 atm. All these measurements are rather meaningless, Zobel (80) noted an Eh of -580 mV in one sediment, and hydrogen producing organisms are known from sediments. No temperatures are given by Baas Becking et al. (3), and thus no correction can be made for variations in temperature.

Apart from the prevalence of mixed potentials, the sulphate-reducing environment within a sediment may be extremely small. The organisms involved are minute and a cubic centimetre of water can contain more than 10^9 of them. The insertion of electrodes into such an environment not only involves the risk of introducing oxygen, but also means that the electrode is often recording the average potential of a number of such oxidized and reduced microenvironments.

Furthermore, since the reproductive cycle of these microorganisms is extremely short, a reducing microenvironment may be established for very short time periods. Scippel et al. (64) have estimated natural doubling times for these organisms in Baltic near-shore muds to be about 84 hours. Hallberg (29) has calculated a doubling time of only 8 hours in laboratory continuous cultures at 25 °C. Thus in a sediment, a period of days is sufficient to produce a meaningful amount of hydrogen sulphide which may be permanently fixed as metal sulphide.

In summary, the pH and Eh redox tolerances of sulphate-reducing bacteria are not sharply delineated. It is probable that the bacteria are active between approximately pH 5-9, and that observations much different from this range result from other factors. In particular the sporulating Desulfotomaculum species can exist in their vegetative stage under extreme pH conditions. Redox tolerances are less definable. No lower limit has yet been discovered, and the bacteria can grow in a hydrogen atmosphere. The upper limit is probably ultimately dependent on the oxygen concentration. However, symbiosis between aerobes and anaerobes, resulting in the removal of oxygen as fast as it is introduced, can mean that oxygen may exist together with sulphate-reducers in certain ecosystems. Hallberg (28) claimed to have recorded oxygen at all depths in a reduced Dutch tidal sediment.

The sulphate-reducing bacteria are normally heterotrophic, and thus their development depends on a supply of utilizable organic matter. Kimata et al.(39) demonstrated that the number of sulphate reducers was directly proportional to the weight of organic matter per gram mud in Hiroshima Bay.

The supply of utilizable organic matter to sulphate-reducing bacteria depends on the relative rate of total organic matter supply to its rate of oxidation by aerobic microorganisms.

According to Hargrave (30) the major factor controlling aerobic development in bottom communities is temperature, the mechanical properties of the sediment being less important. As long as decomposable organic matter is supplied to the sediment surface faster than aerobic microorganisms can oxidize it, oxygen will be used up faster than it can be supplied. High rates of organic matter supply are only indirectly dependent on the primary production, since a major part of the destruction of the primary production occurs in the uppermost water layers. The supply is optimum where the waters are not disturbed and where the remnant organic detritus can settle most efficiently. Since fine silts and clays are deposited under these conditions, this explains the common relationship between anaerobic conditions and fine-grained sediments.

Berner (13) showed that this relationship between the total sulphate-reducing bacterial activity and organic matter supply means that the rate of sulphate-reduction can be treated mathematically to a good approximation. Berner (13) assumed a first order rate law for the reduction, which is in good agreement with the observations of Kimata et al. (39).

$$\frac{dc}{dt} = -LkG$$

where dc/dt is the rate of charge of sulphate concentration with time, L is the stoichiometric coefficient relating sulphate reduced to carbon oxidized, k is the bacterial rate constant and G is the concentration of available organic carbon. If diffusion is the only factor affecting sulphate concentration then

$$\frac{dc}{dt} = D_s \frac{\delta^2 c}{\delta x^2} - LkG - \omega \frac{\delta c}{\delta x}$$

where D_s is the whole sediment diffusion coefficient for sulphate, x is the depth and ω is the sedimentation rate. Solving for steady state conditions produces a concave downward curve for c versus x which approaches an asymptotic value. The application of this model to muds of Southern California gave reasonable values of dc/dt (-1.8×10^{-14} moles S.cm^{-3} .sec^{-1} at x = 0) and D_s (0.3×10^{-5}cm.sec^{-1}). The model is however very approximate, and observed depth distributions of sulphate from the Gulf of California gave only one concave down curve. The other four distributions were concave up, indicating a decrease in sulphate reduction on the relative rate of total organic matter supply to its rate of oxidation by aerobic microorganisms.

According to Hargrave (30) the major factor controlling aerobic development in bottom communities is temperature, the mechanical properties of the sediment being less important. As long as decomposable organic matter is supplied to the sediment surface faster than aerobic microorganisms can oxidize it, oxygen will be used up faster than it can be supplied. High rates of organic matter supply are only indirectly dependent on the primary production, since a major part of the destruction of the primary production occurs in the uppermost water layers. The supply is optimum where the waters are not disturbed and where the remnant organic detritus can settle most efficiently. Since fine silts and clays are deposited under these conditions, this explains the common relationship between anaerobic conditions and fine-grained sediments.

Berner (13) showed that this relationship between the total sulphate-reducing bacterial activity and organic matter supply means that the rate of sulphate-reduction can be treated mathematically to a good approximation. Berner (13) assumed a first order rate law for the reduction, which is in good agreement with the observations of Kimata et al. (39).

$$\frac{dc}{dt} = -LkG$$

where dc/dt is the rate of charge of sulphate concentration with time, L is the stoichiometric coefficient relating sulphate reduced to carbon oxidized, k is the bacterial rate constant and G is the concentration of available organic carbon. If diffusion is the only factor affecting sulphate concentration then

$$\frac{dc}{dt} = D_s \frac{\delta^2 c}{\delta x^2} - LkG - \omega \frac{\delta c}{\delta x}$$

where D_s is the whole sediment diffusion coefficient for sulphate, x is the depth and ω is the sedimentation rate. Solving for steady state conditions produces a concave downward curve for c versus x which approaches an asymptotic value. The application of this model to muds of Southern California gave reasonable values of dc/dt (-1.8×10^{-14} moles $S.cm^{-3}.sec^{-1}$ at x = 0) and D_s ($0.3 \times 10^{-5} cm.sec^{-1}$). The model is however very approximate, and observed depth distributions of sulphate from the Gulf of California gave only one concave down curve. The other four distributions were concave up, indicating a decrease in sulphate reduction rate with time at the sediment-water interface and non-steady state conditions (13).

Organic matter supply is normally the factor limiting sulphate-reduction. Sulphate, which is essential to most species of sulphate-reducing bacteria, is generally in excess. Exceptions include waters containing little or no sulphate, such as lakes and the high moor bog waters of Tasmania (3), and environments with excessive organic matter, such as may result from pollution (13). In these latter cases, the rate of diffusion of sulphate becomes the limiting factor. The effect is noticeable geologically where the iron sulphide content of such organic-rich ancient sediments as oil shales and coals, is proportionally lower than would be expected.

The role of minor elements in the development of sulphate-reducers has been widely discussed but much conflicting evidence is available (33,32,40,54). It is probable that trace element requirements are interdependent through the ability of one element to substitute for another, and may differ for individual strains. It has been established that there is a minimum iron requirement for optimum growth for D. desulfuricans, but this is far below the minimum iron concentrations of the natural environment.

Base metal toxicity has been discussed, but, as has been shown in the case of copper by Temple and Leroux (75), these elements are not normally sufficiently concentrated in a mobile toxic form in natural waters. Hydrogen sulphide toxicity has been determined by Miller (48) and Rickard (59) and has been shown to be effective only at hydrogen sulphide concentrations in excess of 3 $g.l^{-1}$.

Iron sulphide formation chemistry

Since the classic work of Allen et al. (2), there have been several studies of iron sulphide formation chemistry in low temperature aqueous solutions. Berner (8), Korolev and Kozorenko (41), Rickard (60) and Roberts et al. (62) have described inorganic experiments on iron sulphide formation. Rickard (59), Freke and Tate (25) and Hallberg (29) investigated the mineral products from cultures of sulphate-reducing bacteria.

Prior to these studies only three iron sulphide minerals were known, and subsequent discoveries have so complicated this group that earlier investigations are of limited usefulness and have not been quoted.

The major iron sulphide forms are listed in Table 2. Marcasite, mackinawite, griegite and cubic FeS have apparently no thermodynamic stability at any temperature with respect to pyrite and pyrrhotite. Smythite may be stable below 75°C. Apart from the forms listed, a number of other iron sulphides have been synthesised or found naturally, but have not been well defined. Of particular note are the hexagonal FeS described by Hallberg (29) from continuous cultures of sulphate-reducing bacteria, and the apparently monoclinic highly unstable Fe_2S_3 synthesised by Rickard (58) from aqueous solutions at 25°C.

All these various iron sulphides may be involved to a greater or lesser extent in sedimentary pyrite formation. Our knowledge about many of the processes involved is still incomplete but the broad lines have been established.

The overall reaction for sedimentary pyrite formation may be written

$$< FeS > \ + \ < S > \ \rightarrow \text{pyrite}$$

where < FeS > represents one or more metastable iron sulphides and < S > represents a sulphur species.

The relative importance of the various metastable iron sulphides in < FeS > is uncertain. However, mackinawite and griegite are commonly the first minerals identified in wet low temperature reactions involving ferrous or ferric iron and aqueous sulphide, except under special conditions. The cubic FeS of Takeno et al. (74) has been reported to transform to mackinawite after about a month, in a reaction that has not been reversed. The mackinawite-griegite transformation is apparently reversible (60,79). Hallberg's hexagonal FeS was apparently one of the first phases formed from continuous culture of sulphate-reducing bacteria, and Rickard's monoclinic Fe_2S_3 spontaneously decomposed to black ferrous sulphide (identified as partially mackinawite) and sulphur.

On the pyrite formation scheme shown in Fig.5, "black FeS" is queried. As yet there are no data that any phase other than mackinawite and griegite occurs in black sedimentary iron sulphide (8, 36, 52, 77). The primary black iron sulphide received from laboratory synthesis is virtually x-ray amorphous, but usually gives one or two broad bands approximately coincident with the mackinawite strongest lines. It is non-magnetic (60) and has an Fe/S ratio of about 1 independent of pH in the range 5-9 (60, 6). These observations would indicate that it is not finely crystalline griegite.

As shown by Rickard (60) griegite tends to form more rapidly at more acid pH values. Berner's (9) thermodynamic data imply that mackinawite is only stable with respect to griegite at extremely low $p\varepsilon$ values at pH less than 7. Since the transformation of mackinawite to griegite is an oxidation, and since this is easily performed in the absence of dissolved oxygen and primary ferric iron, Rickard (60) proposed that the mechanism was an autooxidation involving water, in a similar way to the transformation of $Fe(OH)_2$ to Fe_3O_4.

The reaction

$$\underset{\text{mackinawite}}{3\ FeS} \quad + \quad \underset{\text{aqueous}}{S^{2-}} \quad = \underset{\text{griegite}}{Fe_3S_4} + 2\varepsilon$$

is plotted in terms of pε, pH and pS on Fig.6. A high total dissolved sulphur activity (pS = 1) is included, in order to demonstrate the extent of the elemental sulphur stability field. This field retracts into high pε, low pH values at higher pS values. Note that even at pS = 1, the reaction

$$\underset{\text{mackinawite}}{3\ FeS} \quad + \quad \underset{\text{elemental}}{S^{O}} \quad = \underset{\text{griegite}}{Fe_3S_4}$$

is improbable, even though theoretically possible ($\Delta F^{O} = -2.5$ kcal.mole^{-1}), because of the limited S^{O} stability field. The SO_4^{2-} stability field is plotted on the diagram as a dashed line since it is effectively irreversible in the natural aqueous environment in the absence of biological mediators. The inorganic oxidation of aqueous sulphide by oxygen results mainly in the formation of sulphate, and is very fast (50, 19). Furthermore, both mackinawite and griegite are very susceptible to air oxidation, and griegite may undergo a pyrophoric reaction. Thus the SO_4^{2-} stability field limit may indicate the upper stability limit for mackinawite and griegite in the presence of oxygen.

The reaction

$$< FeS > \ + \ < S > \ \rightarrow \text{pyrite}$$

has been studied by Berner (8), Rickard (60) and Roberts et al. (62). The solid state mechanisms are thermodynamically possible

(i) $< FeS > \ + < S^{O} > \rightarrow$ pyrite

(ii) griegite $\rightarrow$ pyrite + mackinawite

In reaction (i), < FeS > can be either mackinawite or griegite. The reaction has $\Delta F^{O} = -16.0$ kcal.mole^{-1} for mackinawite and $\Delta F^{O} = -45.5$ kcal.mole^{-1} for griegite (9). Both reactions have been observed at temperatures around 100°C and above (58, 69). At lower temperatures, down to 60°C, the reaction is slower, and results in greater percentages of marcasite, the dimorph of pyrite. Reaction (ii) has not been observed although griegite has been observed to dissociate into pyrite + pyrrhotite at higher temperatures (42). In general, it would be expected that solid-solid reactions involving iron sulphides would be geologically slow at low temperatures and pressures. They may have some greater importance in late diagenesis, but observations demonstrate that pyrite is formed rapidly in the upper layers of the sediment.

Roberts et al. (62) and Berner (12) failed to detect pyrite in the reaction between ferrous salts and pure aqueous polysulphide solutions. However, Rickard (60) added aqueous ferrous sulphate to an impure polysulphide solution which also contained sulphur and sulphide, and obtained pyrite and ferrous sulphide, possibly mackinawite.

Experiments on the kinetics and mechanisms of pyrite formation are in progress (Rickard, unpublished work). The preliminary results indicate a half order dependence of the rate of pyrite formation on sulphide concentration, in the reaction between < FeS >, sulphur and aqueous sulphide at 40°C. The < FeS > is the typical fine black iron sulphide received on the sulphidation of a ferrous salt. It is non-magnetic, and thus probably not griegite. It shows a few broad mackinawite peaks on x-ray analysis, but is otherwise x-ray amorphous.

This rate dependence on sulphide concentration would be expected if one of the rate controlling reactions in pyrite formation involved a dissolved sulphur species. Optical observations of the precipitate show no close spatial relationship between the fine pyrite grains and the sulphur. The sulphur used was commercial "flowers of sulphur" which is formed by a sublimation process. It has been identified as rhombic sulphur during the present investigation and is easily identifiable optically since the individual crystallites are flocculated in uniform spheres, of the order of 10μ in diameter. Pyrite seems to be associated with the black < FeS >, which indicates that some transport process is involved. The half order dependence would be in agreement with a dissolution process of the sulphur spherules.

These observations indicate that it is highly probable that aqueous polysulphides are involved in pyrite formation. Sulphur is known to dissolve quite rapidly in alkaline sulphide solutions to give polysulphides, and pyrite itself is an iron polysulphide.

The probable reaction for pyrite formation in aqueous solution is thus of the form

$$< \mathrm{FeS} > \quad + \quad S_n^{2-} \rightarrow \text{pyrite}$$

with the immediate oxidants being polysulphide anions. Various stoichiometrics for this reaction can be calculated based on the relationship

$$S_n^{2-} \quad + \quad (n-2)S^{2-} \quad = \quad (n-1)S_2^{2-}$$

where n = 2-5. However, in the absence of more detailed evidence such calculations are meaningless.

This mechanism was proposed by Rickard (58, 60) and Roberts et al. (62). Rickard also discussed the relationship of marcasite and pyrite formation, which has been usually overlooked by other investigators, since marcasite tends to form from the same reaction mixture as pyrite, that is $< FeS > + S^o + S^{2-}$, but at acid pH values. At acid pH values polysulphide anions are highly unstable and instantaneously dissociate into sulphide + sulphur. Thus Rickard proposed that marcasite formed through the reaction between < FeS > and sulphur, whilst polysulphide anions are involved in pyrite formation. It is further interesting to note that at acid pH values, < FeS > is more soluble, and thus the reaction may not be a solid state reaction entirely. The presence of sulphur is thus an integral factor in pyrite and marcasite formation, even though it may not react directly with ferrous sulphide to form pyrite. Several processes may form elemental sulphur in the natural environment. The sulphidation of ferric oxyhydroxides is particularly important in this context because the elemental sulphur is produced spatially near the ferrous sulphide. Both abiologic and biologic sulphide oxidation may also result in sulphur formation.

Pyrite formation chemistry in low temperature aqueous solutions is summarised in Fig.5. Basically a black < FeS > precipitate is formed, which may contain other phases than mackinawite and griegite. Subsequently this reacts with sulphur, through polysulphide intermediaries, to form pyrite. Solid state reactions, which are slow at low temperatures, may become more important during the later stages of diagenesis.

The environment of iron sulphide formation

The factors limiting the environment of iron sulphide formation are the production of sulphide and the distribution of reactive iron minerals.

Since sulphide production is almost entirely a result of the activities of sulphate-reducing bacteria,the tolerances of these microorganisms are coincident with the limitations to sulphide producing environments. These tolerances have been discussed above.

It has been pointed out, however, that the sulphate-reducing environment within a sediment may be extremely small, since 10^9 bacteria may be contained within a single cubic centimetre of water. The doubling time for these bacteria is measured in days rather than weeks, and thus a relatively short time is required to produce sufficient hydrogen sulphide for permanent fixation as a metal sulphide. Thus the presence of dispersed sulphide grains within an ancient sediment does not necessarily mean that the sediment was a sapropel or even that bacteriological sulphate-reduction was widespread, since the individual reduced microenvironments which produced the sulphides could have been both chronologically and spatially infinitesimal from a geologic viewpoint.

The microenvironment may support the growth of anaerobic sulphate-reducers without being entirely anoxic, since small fluxes of oxygen could be removed by aerobic microorganisms developing symbiotically with the sulphate-reducers. Sulphide-oxidizing microorganisms in particular develop readily in the presence of both sulphide and oxygen.

The occurrence of sedimentary metal sulphide grains reflects the conditions of preservation of the sediment as much as the conditions of formation. The author has observed black sedimentary iron sulphides in both sandy sediments and modern muds. However, it is those sulphides in the muds which are more likely to be preserved geologically, since the relative impermeability of fine-grained sediments makes them less susceptible to subsequent penetration by oxygenated groundwaters.

The relative stability of the metastable iron sulphides, with respect towards dissolution and oxidation, further limits the environment of iron sulphide formation. Fig. 6 is a three dimensional diagram showing the relative stability of mackinawite and griegite in terms of $p\varepsilon$, pH and pS, at a total dissolved iron activity of 10^{-7}. The $p\varepsilon$ limiting factors are the lower stability limit of water and the oxidation of sulphide to sulphate. Both these boundaries are, of course, approximate. The presence of elemental sulphur (S^o) further limits the upper $p\varepsilon$ stability of griegite, since it dissociates to $Fe^{2+} + S^o$ at a lower $p\varepsilon$ value than to $Fe^{2+} + H_2S$. The solubility of these phases is highly pS dependent. At a total dissolved sulphide activity of 10^{-1} (pS = 1), griegite and mackinawite dissolve at pH less than about 5.5, producing $Fe^{2+} = 10^{-7}$ in solution. The griegite stability field is limited to pS values greater than 4, and is particularly well developed between pH 6-7. As pS increases, the solubility of mackinawite increases for any given pH. At pH 7, $Fe^{2+} = 10^{-7}$ is in equilibrium with mackinawite at about pS = 3.7, and at higher pS values, this boundary moves into alkaline pH range, until it reaches pH 9 at pS = 5.7.

The reducing zone normally occurs at some depth within the sediment. Dissolved oxygen at the sediment-water interface is removed by aerobic microorganisms. The intensity of their activity depends on the flux of utilizable organic matter and the temperature. If the organic matter flux is low, as for example in turbulent waters where sands are deposited, then the oxygen has a chance to diffuse to some depth within the sediment. The depth of diffusion depends on the rate of diffusion, and this is increased in coarser sediments with high porosity and low tortuosity factors. Oxygen in excess of that removed by aerobic organisms reacts with reduced substances such as sulphide diffusing up to the sediment surface and is removed. The top of the reduced zone in many sediments is thus marked with a more macroscopically sharp boundary by the disappearance of black-staining ferrous sulphides.

The thickness of the sediment's oxidized zone is very small, usually less than a millimetre. In the coarse sands of the Wash in England, bands of ferrous sulphide occur at depths of over 10 cm. Although a good indicator for the presence of sulphate-reduction, the absence of black staining in a sediment does not necessarily indicate the absence of sulphate-reducing bacteria. The reduced microenvironment may take the form of the decomposing interior of a foraminifera, for example, with the sulphide being rapidly oxidized at the shell surface. A sandy sediment was recently collected from the Skagerrak as a core of macroscopically homogeneous yellow sand in a perspex tube. The tube was sealed for storage. After three months, small (c. 2 cm diameter) circular spots of black iron sulphides were observed dispersed throughout the sand. The sealing of the tube had limited oxygen ingress into the sediment, and sulphide, produced by sulphate-reducers apparently within certain localised organic matter concentrations, was able to diffuse into the surrounding iron-stained sand without being oxidized.

The author is at present involved in attempting to calculate mass balances for bacteriogenic sulphide and metal fluxes at the boundary of the oxidized and reduced zones within a sediment. Observed sulphide fluxes may be very high. Berner (7) computed a value of about 10^{-12} g $S.cm^{-2}.sec^{-1}$ from observations of modern sediments, and Sorokin (70) has noted values as high as 10^{-10} g $S.cm^{-2}.sec^{-1}$ in lakes. Sorokin's values apparently include midwater as well as sedimentary sulphate-reduction. This seems to be exceptional since normally relatively little sulphide production occurs in the free water.

In normal sediments the flux of reactive iron is very low and is controlled by the sedimentation rate. Since sulphate-reducers develop to a greater extent in fine-grained sediments, where the sedimentation rate is low, sulphide is normally in excess of available iron.

The kinetics and mechanism of the sulphidation of goethite in low temperature aqueous solutions have been studied (58). The goethite used was a uniform product, prepared by the addition of dilute NaOH to $FeCl_3.6\ H_2O$ at pH = 9, followed by autoclaving at $120^{o}C$ for 72 hours. The surface area of the goethite used was estimated to be $7.5 \times 10^{5} cm^{2}.g^{-1}$, and was thought to approximate the aged goethite sulphidized in the natural environment. The rate of sulphidation was followed electrometrically and was shown to be first order with respect to the surface area of goethite. The increase in rate is therefore directly proportional to the increase in surface area. In other words, the more goethite a sediment contains the faster will be the fixation of sulphide.

Therefore, although the presence or absence of significant sulphide in a sediment is ultimately dependent on biological factors such as organic matter supply, sulphate diffusion, and oxygen concentration, the concentration of metal sulphide received may be directly dependent on the concentration of available reactant iron minerals. The relative infrequency of often catastrophic sulphide escapes from sediment interstitial waters is due to the rate of oxidation of sulphide in the uppermost sediment layer, rather than sulphide fixation as iron sulphides.

The bacterial production of sulphide after sediment burial is of interest to geologists. Ancient limestones, for example, commonly produce a fetid smell of hydrogen sulphide after being struck with a hammer. This post-depositional sulphide production further causes problems in the oil and natural gas industries, since hydrogen sulphide is commonly produced by bacteria using the oil or gas as nutrient and reducing sulphate concentrated in the associated waters. The hydrogen sulphide concentrations may reach commercial quantities. Like natural gas or oil, this hydrogen sulphide is a highly mobile constituent in the upper parts of the earth's crust, and metal sulphide concentrations may occur in any permeable metal-bearing rock through which the sulphide passes. The importance of this process in the formation of metal sulphides in ancient sediments in particular, and in ore genesis in general, is at present unknown. It seems probable that this process is of some importance with regard to permeable, oxidized rocks such as sandstones and limestones, rather than shales.
Sedimentary pyrite formation, through bacterial sulphate-reduction, occurs throughout the geologic record. Sulphur isotope analyses of pyrite from the earliest Precambrian sediments demonstrate considerable concentrations of the lighter ^{32}S isotope (18). Furthermore, there is considerable indirect evidence that sulphate-reducing bacteria were among the earliest organisms to appear,

perhaps 3 billion years ago (45). Present theories about the nature of the early superficial environment of the earth, particularly the probable presence of an anoxic atmosphere, indicate that sulphate-reducing bacteria could have been wide-spread. Indeed, it has been proposed that sulphate-reducing bacteria were members of the earliest stable ecosystem (55).

Summarising, the tolerances of sulphate-reducing bacteria provide only limited boundary conditions to the iron sulphide producing environment because of the possibility of their development in chronologically and spatially limited microenvironments. In contrast, the primary metastable iron sulphides are sensitive to oxidation and dissolution and thus will only form and be preserved in reduced, neutral to alkaline systems at moderate dissolved sulphide concentrations. Iron sulphide formation thus normally occurs at some depth within the sediment, up to a few centimetres depending on the efficacity of the removal of oxygen by aerobic microorganisms. The concentration of iron sulphides is normally ultimately limited by the concentration of reactive iron minerals in the sediments. Permeable oxidized deposits may become sulphidized after diagenesis by the movement of post-depositional hydrogen sulphide.

Discussion

The reaction of FeS with sulphur has been widely accepted as the mechanism of sedimentary pyrite formation (51, 77, 13, 58). There is little or no evidence of pyrite formation from low temperature aqueous solutions at neutral pH values in the absence of sulphur or sulphur-forming conditions.

The pyrite formed in sediments, however, commonly demonstrates a striking texture, called famboidal, consisting of spherical aggregates of pyrite microcrystallites (Fig.7). This pyrite texture is also often found in sediments intimately associated with certain stratiform sulphide ore deposits, and thus its genesis has been the subject of much discussion (44, 61). The pyrite formed in the laboratory commonly consists of small microcrysts, but they are usually not as aggregated as natural framboids. Framboid-like aggregates of microcrystalline pyrite have been synthetised (13, 24), and the writer has often observed crudely spherical loose aggregates of pyrite microcrystallites from synthetic experiments. However, a significant percentage of the natural framboids show a marked ordering of the constituent microcrysts (Fig.8), which has certainly not been reproduced as yet in the laboratory. Various theories have been proposed for the origin of framboids, but to date none has been entirely satisfactory.

In some sediments black ferrous sulphide is not converted to pyrite with depth. Griegite, for example, was first isolated from a Tertiary lacustrine sequence (67). The older buried sediments of the Black Sea include interbedded ferrous sulphide-rich clays with grey pyrite clays with no ferrous sulphide (23, 77). Berner (13) has shown that the black clays are much lower in both total reduced sulphur and pyrite sulphur than the grey pyritic clays. This indicates that the black clays, which contain similar total reactive iron contents to the grey clays, represent an arrested stage of diagenesis (77).

Most of the pyrite formed in sediments is normally produced in the uppermost few centimetres of the sediment. It has been shown that as the pyrite content increases the concentration of ferrous sulphide decreases, though not in stoichiometric proportions because of re-solution and re-precipitation of the ferrous sulphide (7).

Pyrite formation thus seems to be fast compared with the sedimentation rate. The reluctance of pyrite to nucleate at all temperatures and pressures is well known to laboratory workers. This is particularly noticeable at low temperatures. However, recent unpublished kinetic work by the writer shows a logarithmic dependence on time for pyrite formation in the reaction between < FeS >, sulphur and dissolved sulphide at pH = 7 and 40°C. Over 50% pyrite may be formed within the first hour of reaction at high sulphide concentrations and large sulphur areas. The fast formation rate is believed to be caused by the maintenance of a high rate of agitation throughout the experiments as well as the higher (40°C) temperatures. It is further possible that the rate of pyrite nucleation is affected by the state of the sulphur.

Berner (12) shows pyrite distributions with depth for Connecticut tidal flat sediments. In these sediments over 80% of the pyrite is formed in the uppermost 2 cm of the sediment, assuming that the pyrite concentration determined at depth represents 100% pyrite. The maximum pyrite concentration coincides (at 7-9 cm depth) with a ferrous sulphide concentration of only 10% of the initial value. Assuming a high sedimentation rate of 10^{-8} cm.sec^{-1}, this means that about 80% of the available iron was converted to pyrite in about 10 years. At a steady state sedimentation rate, it then takes several tens of years to pyritise the remaining 20% of the available iron. Assuming 90% porosity, the rate of pyrite formation in these sediments would average about 0.6 mg FeS -Fe.cm^{-2}.yr^{-1}. Berner (12) has attempted to estimate the annual loss of sulphate from the oceans to form pyrite. He arrived at the figure of about 7 x 10^{6} tons. S.yr^{-1}, considering only hemipelagic sediments and euxinic basins. This is probably a considerable under-estimate, since sulphur fixation as pyrite does not only occur in hemipelagic sediments, which make up a maximum 15% of the total ocean bottom area. Berner gives an estimate of the amount of sulphur delivered by rivers as 123×10^6 tons.yr^{-1}. This is almost exactly twice the estimate provided by Holser and Kaplan (19) of about 60×10^6 tons.yr^{-1} for sulphur from both river and volcanic sources. They also provide figures which suggest that about twice as much sulphur (5×10^{15} tons) is contained in ancient evaporites as in sediments (2.7×10^{15} tons). Thus although Berner (12) concluded that there is a considerable inbalance in the oceanic sulphur economy, other estimates suggest that the inbalance may not be as large as the suggested. At present no meaningful conclusion may be given because of the lack of adequate quantitative data.

Conclusions

Pyrite formation in sediments occurs through the sulphur oxidation of metastable ferrous sulphides, mainly mackinawite and griegite. The mechanism apparently involves dissolution of sulphur in sulphide solutions to produce polysulphide anions, which are the immediate oxidants at neutral to alkaline pH values. At more acid pH values the solubility of the metastable ferrous sulphides increases, sulphur becomes stable with respect to sulphide, and marcasite tends to form.

The metastable ferrous sulphides are produced through the reaction between detrital iron minerals, particularly ferric oxyhydroxides, and bacteriogenic sulphide. The iron sulphide-precipitating environment is limited by the physio-chemical tolerances of the bacteria and the stability of the iron sulphides towards dissolution and oxidation. Although dissimilatory sulphate-reducing bacteria of the genera Desulfovibrio and Desulfotomaculum are sensitive to oxygen, extremes of pH and temperature, their size and reproduction rate mean that they may exist in reduced microenvironments with different physico-chemical characters to the sediment as a whole. The stability limits of the metastable iron sulphides towards dissolution and oxidation coincide to a large extent with pH and pε tolerances of the bacteria. It is however necessary to have total dissolved sulphide activities of more than 10^{-6}, in order to precipitate these metastable ferrous sulphides from solutions containing a total dissolved ferrous iron activity of 10^{-7} or less at pH 9.

Generally, utilizable organic matter, dissolved sulphate and reactive iron are normally available in microenvironments within most sediments, and thus there seems to be few sedimentary environments where iron sulphide precipitation would be completely absent. This is further demonstrated by the apparent ubiquity of sulphide formation in modern sediments.

The concentration of pyrite is limited by the availability of utilizable organic matter, sulphate, iron, and oxygen. In areas with high rates of organic matter sedimentation, aerobic microorganisms rapidly remove the bulk of the dissolved oxygen, at or near the sediment-water interface. The rate of biologic oxygen uptake in sediments is also temperature dependent. The most reducing environments are therefore those containing fine-grained, organic-rich sediments associated with warmer waters. Sulphate-reducing bacteria are heterotrophic and the amount of sulphate-reduction is approximately quantitatively proportional to the concentration of organic matter. Organic-rich sediments therefore not only remove oxygen most rapidly, but also produce the greatest quantities of sulphide.

The relationship between organic matter and sulphide is not linear over the whole range of organic matter concentrations. The rate of bacterial metabolism decreases proportionally at extremely low organic nutrient concentrations, and sulphate becomes limiting in sediments containing very high organic matter concentrations. The rate of sulphate diffusion into the sediment from the effectively infinite marine and brackish water reservoirs is normally greater than the rate of sulphate-reduction. Dissolved sulphate is usually obtained at depth within the sediment, well below the major pyrite formation depths. In such organic-rich sediments as oil shales and coals, and in some modern polluted sediments, sulphate becomes limiting because of its slow diffusion rate into these exceptionally fine-grained materials. The pyrite content of oil shales and coals is thus commonly less than would be quantitatively expected.

The sulphidation rate has been shown to be directly dependent on the surface area of fine-grained goethite. The present methods of analyzing total reactive iron in sediments are not accurate, since not all HCl-soluble iron is highly reactive towards dissolved sulphide. The first order surface area dependence for goethite demonstrates that it is the grain size of the available iron which determines its reactivity towards sulphidation. Thus only rarely is more than 50% of the HCl-soluble iron pyritised. The surface area of the detrital iron minerals is a limiting factor for high pyrite concentrations. This is probably ultimately proportional to the total iron concentration, but more directly dependent on the sediment grain size. Fine-grained sediments should contain proportionally greater reactive iron surface areas than coarse grained sediments.

Pyrite formation may be fast in the laboratory at low temperatures with vigorous agitation. In sediments it is virtually instantaneous compared to the sedimentation rate, and most pyrite is formed in the upper centimetre or two of the reduced zone. It has also been established that at least 7 x 10^6 tons of sulphur are fixed annually as pyrite in modern sediments.

TABLE 1. Summary of major characteristics of dissimilatory sulphate-reducing bacteria, using Campbell and Postgate's (16, 56) classification

Genus	Desulfotomaculum			Desulfovibrio				
Spores	+			-				
Cytochrome	$\underline{b}$			$\underline{c}_3$				
Desulfoviridin	-			+				
Species	**nigrificans**	**orientis**	**ruminis**	**desulfuricans**	**vulgaris**	**salexigans**	**africanus**	**gigas**
Form	rod	curved rod	rod	vibrio	vibrio	vibrio	sigmoid vibrio	spirillum
Flagella	peritrichous	peritrichous	peritrichous	single polar	single polar	single polar	lopho-trichous	lopho-trichous
NaCl requirement	-	-	-	-	-	+	-	-
Thermophily	+	-	-	-	-	-	-	-
SO_4 requirement	also pyruvate	+	also pyruvate	also pyruvate and choline	+	+	+	+
Synonymy	Vibrio thermo-desulfuricans (22) Sporovibrio desulfuricans (71) Clostridium nigrificans (78)	Desulfovibrio orientis (1)	Coleman's organism (21)	Spirillum (5) Microspira (47) Vibrio (4) Sporovibrio (71)		Microspira aestuarii (76)		
Notes	From soils and thermal springs	Orig. from Singapore soil	From sheep rumen	Wide distribution. Halo-tolerant and N_2-fixing strains		From marine and estuarine muds	From Walvis Bay, S.W.Afr. Size up to 10×0.5 μ	From marine mud. Size up to 10×1.5 μ

TABLE 2. Major characteristics of the iron sulphides

	PYRITE	MARCASITE	PYRRHOTITE	MACKINAWITE	GRIEGITE	SMYTHITE	CUBIC FeS
Composition	FeS_2	FeS_2	$Fe_{(1-x)}S$ $(x > 0.125)$	c.FeS	Fe_3S_4	$Fe_{3.25}S$	c.FeS
Structure	Cubic	Orthorhombic	Hexagonal or monoclinic	Tetragonal	Cubic	Hexagonal, poss.monoclinic	Cubic
Stability	< 743 °C	metastable below c. 400 °C	< 1083 °C	metastable below c. 130 °C	metastable below c. 200 °C	possibly stable < 75 °C	metastable
Apparent H_2O requirement for formation	-	+	-	+	+	?	+
Occurrence	Most abundant crustal metal sulphide	Tends to form at acid pH. Absent or rare in rocks older than Palaeozoic	Poss.most abundant universal metal sulphides. Includes troilite	In "black FeS" of sediments, and certain ores. Often contains high Co, Ni and Cr	In "black FeS" of sediments and young sediments	In ores, usually associated with pyrrhotites	Not found naturally. Synthesized through the wet sulphidation of iron plates at 60 °C
heat	→ $Fe_{(1-x)}S$	→ pyrite	-	→ pyrrhotite	→ pyrite+ pyrrhotite/mackinawite	→ pyrite+ pyrrhotite	→ mackinawite/ pyrrhotite
Reactions + S^o	-	-	→ pyrite	→marcasite/ pyrite	→marcasite pyrite	-	-
+ S_n^{2-}	-	-	-	→pyrite	→ pyrite	-	-

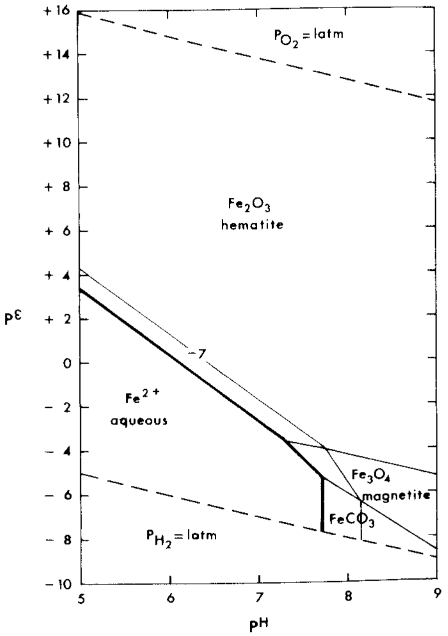


Fig.1. Relationships in the $Fe-H_2O-O_2-CO_2$ system as a function of pH and pε at a total dissolved iron activity of 10^{-6} and a total dissolved carbonate activity of 10^{-2}, 25 °C and 1 atm. total pressure. The boundaries at log $\Sigma Fe = -7$ are shown.

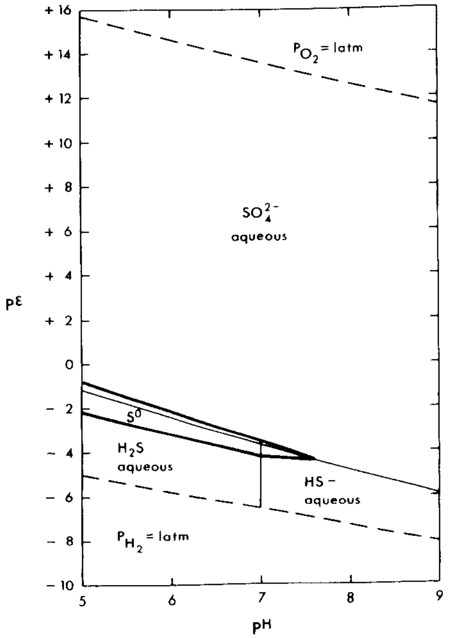


Fig.2. Relationships of sulphur species in water at 25 °C and 1 atm. total pressure, as a function of pH and pε. The stability field of elemental sulphur is limited by a total dissolved sulphur activity of 10^{-1}.

Fig.3. Electromicrograph of Desulfovibrio vulgaris, a typical sulphate-reducing bacterium. *Courtesy N.P.L.*

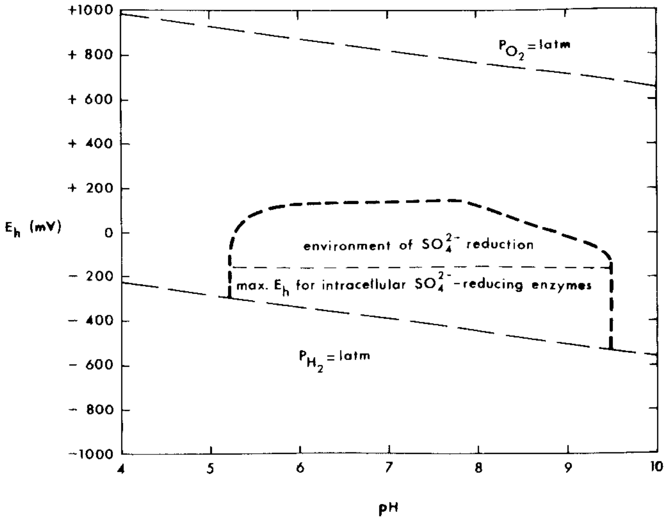


Fig.4. The sulphate-reducing environment in terms of pH and Eh from data collected by Baas Becking et al. *See (3)*

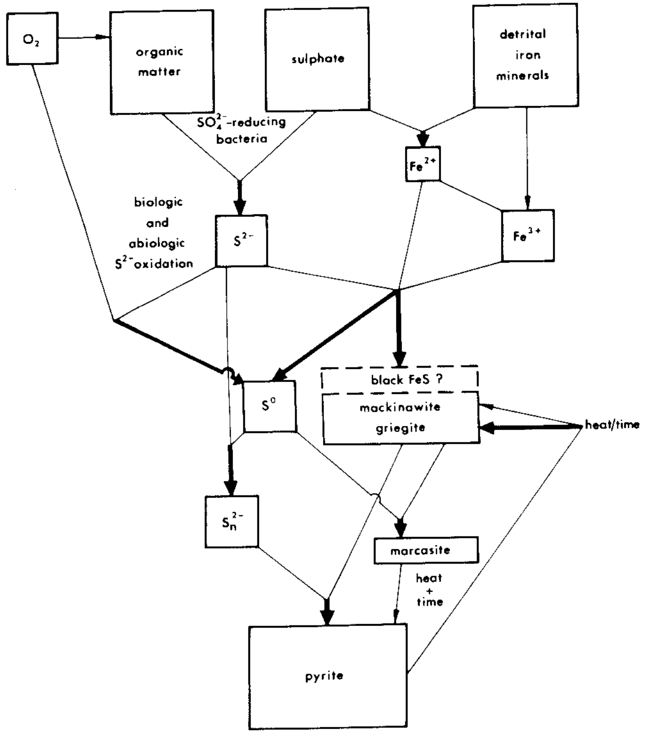


Fig.5. Schematic representation of the major processes leading to sedimentary pyrite formation

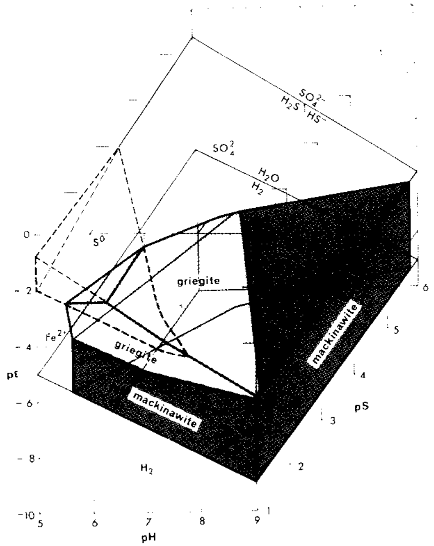


Fig.6. Relationships between griegite (Fe_3S_4), mackinawite (FeS), dissolved ferrous iron and sulphur species in terms of pH, pε and pS, at 25 °C and 1 atm. total pressure. Mackinawite and griegite solubilities are limited by log (Fe^{2+}) = -6

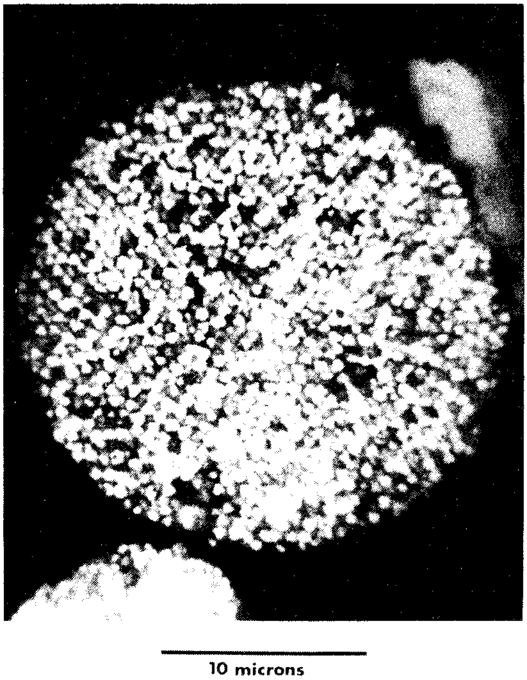


Fig.7. Photomicrograph of a polished section of a pyrite framboid from a Portuguese soil

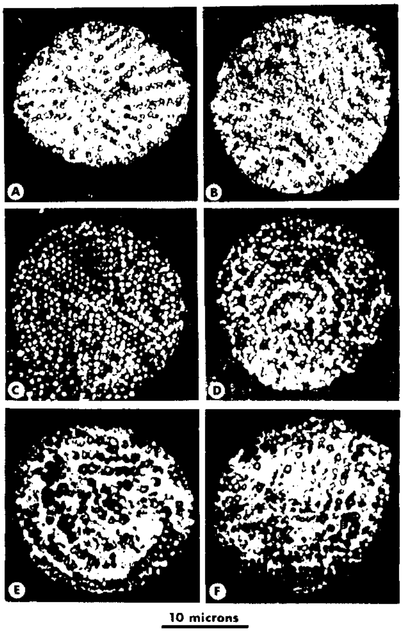


Fig.8. Photomicrographs of polished sections of ordered pyrite framboids from the Tynagh (Ireland) limestone residuum: A) Radial, B) Y-shaped, C) X-shaped, D) hexagonal (?), E) concentric, F) brachiate arrangements. *Courtesy A.P.Millman*

REFERENCES

(1) ADAMS, M.E. and POSTGATE, J.R. 1959. A new sulphate-reducing vibrio. J. Gen. Microbiol. 20: 252-257.

(2) ALLEN, E.T., CRENSHAW, J.S. and JOHNSON, J. 1912. The mineral sulphides of iron. Am. J. Sci. 33: 169-236.

(3) BAAS BECKING, L.D.M., KAPLAN, I.R. and MOORE, D. 1960. Limits of the natural environments in terms of pH and oxidation reduction potentials. J. Geol. 68: 243-284.

(4) BAARS, J.K. 1930. Over sulfaatreductie door Bacteriën. W.D. Meinema.

(5) BEIJERINCK, W.M. 1895. Über Spirillum desulfuricans als Ursache von Sulfat-reduktion. Centr.Bakteriol.Abt. L: 1-9, 49-59, 1o4-114.

(6) BERNER, R.A. 1962. Experimental studies of the formation of sedimentary iron sulfides. In (M.L.JENSEN, ed.) Biogeochemistry of sulfur isotopes. Yale Univ. Press.

(7) BERNER, R.A. 1964. An idealized model of dissolved sulfate distribution in recent sediments. Geochim. et Cosmochim. Acta, 28: 1497-1503.

(8) BERNER, R.A. 1964. Iron sulphides formed from aqueous solutions at low temperatures and pressures. J. Geol. 72: 3, 293-306.

(9) BERNER, R.A. 1967. Thermodynamic stability of sedimentary iron sulfides. Am. J. Sci. 265: 773-785.

(10) BERNER, R.A. 1969. Goethite stability and the origin of red beds. Geochim. et Cosmochim. Acta, 33: 267-273.

(11) BERNER, R.A. 1970. Low temperature geochemistry of iron. In Handbook of Geochemistry. II-1: 26. Springer-Verlag, Berlin.

(12) BERNER, R.A. 1970. Sedimentary pyrite formation. Am.J.Sci. 268:1-23.

(13) BERNER, R.A. 1971. Principles of chemical sedimentology. McGraw-Hill, Inc. USA.

(14) BERNER, R.A. 1972. Sulfate reduction, pyrite formation, and the oceanic sulfur budget. Nobel Symposium 20: 347-362.

(15) BOSTRÖM, K. 1967. Some pH-Controlling Redox Reactions in Natural Waters. Advances in Chemistry Series 67:286-311. Am.Chem.Soc.

(16) CAMPBELL, L.L. and POSTGATE, J.R. 1965. Classification of the spore-forming sulfate-reducing bacteria. Bacteriol. Rev. 29:359-363.

(17) CARROL, D. 1958. Role of clay minerals in the transportation of iron. Geochim. et Cosmochim. Acta. 14: 1-28.

(18) CHUKROV, F.V., VINOGRADOV, V.I. and ERMILOVA, L.P. 1970. On the Isotopic Sulfur Composition of some Precambrian Strata. Min.Dept.5; 3:209-222.

(19) CLINE, J.D. and RICHARDS, F.A. 1969. Oxygenation of hydrogen sulfide in seawater at constant salinity, temperature and pH. Environ.Sci.Technol. 3: 838-843.

(20) CLOUD, P.E. 1955. Physical limits of glauconite formation. Am. Assoc.Pet. Geol.Bull., 39: 484-492.

(21) COLEMAN, G.S. 1960. A sulphate-reducing bacterium from the sheep rumen. J. Gen. Microbiol. 22: 423-436.

(22) ELION, L. 1924. A thermophilic sulphate-reducing bacterium. Zentr.Bakter. Parasitenkde. 63: 58-67.

(23) EMEL'YANOV, E.M. and SHIMKUS, K.M. 1962. Contribution to the study of variability of the deep sea sediments of the Black Sea. Okeanologiya 2:1040-1049.

(24) FARRAND, M. 1970. Framboidal sulphides precipitated synthetically. Min. Dep. 5; 3: 237-247.

(25) FREKE, A.M. and TATE, D. 1961. Formation of magnetic iron sulphide by bacterial reduction of iron solutions. J.Biochem.Microbiol. Tech Eng. III: 29-39.

(26) GARRELS, R.M. 1959. Rates of geochemical reactions at low temperatures and pressures. In (ABELSON, P.H. ed.) Researches in geochemistry. Wiley, New York, 25-37.

(27) GARRELS, R.M. and CHRIST, C.L. 1965. Solutions, minerals and equilibria. Harper and Row.

(28) HALLBERG, R.O. 1968. Some factors of significance in the formation of sedimentary metal sulphides. Stockholm Cont. in Geol. XV, 4: 39-66.

(29) HALLBERG, R.O. 1972. Iron and zinc sulfides formed in a continuous culture of sulfate-reducing bacteria. (Manuscript)

(30) HARGRAVE, B.T. 1969. Similarity of oxygen uptake by benthic communities. Limnol. Oceanog. 14: 801-805.

(31) HARVEY, H.W. 1936. The supply of iron to diatoms. J. Mar.Biol.Assoc. 22: 423.

(32) HATA, Y. 1960. Influence of heavy metals upon the growth and the activity of the marine sulphate-reducing bacteria. J.Shimonoseki. Coll.Fish.9: 363-377.

(33) HATA, Y. 1960. Inorganic nutrition of marine sulphate-reducing bacteria. J. Shimonoseki. Coll. Fish. 9: 347-362.

(34) HOLSER, W.T. and KAPLAN, I.R. 1966. Isotope geochemistry of sedimentary sulfates. Chem. Geol. 1: 93-135.

(35) HUTCHINSON, G.E. 1957. A treatise on limnology. Vol.1. Geography, physics, chemistry. Wiley, New York.

(36) JEDWAB, J. 1967. Mineralisation en griegite de débris végétaux d'une vase récente (Grote Geul). Bull.Soc.Belge. Geol. Vol. 76.

(37) JENSEN, M.L. (ed.) 1962. Biochemistry of sulfur isotopes. Yale Univ.Press.

(38) JONES, G.E. and STARKEY, R.L. 1962. Some necessary conditions for the fractionation of stable isotopes of sulphur by Desulfovibrio desulfuricans. Symposium on the Biogeochemistry of Sulfur Isotopes. (M.L.JENSEN, ed.)Yale.

(39) KIMATA, M., KADOTA, H., HATA, Y. and TAJUMA, T. 1955. Studies of marine sulphate-reducing bacteria: I. Distribution of marine sulphate-reducing bacteria in the coastal waters receiving a considerable amount of pulpmill drainage. Bull.Jap.Soc.Sci.Fish. 21: 104-108.

(40) KIMATA, M., KADOTA, H., HATA, Y. and TAJUMA, T. 1955. Studies of marine sulphate-reducing bacteria: III. Influences of various environmental factors upon the sulphate-reducing activity of marine sulphate-reducing bacteria. Bull.Jap.Soc.Sci.Fish. 21: 113-116.

(41) KOROLEV, D.F. and KOZERENKO, S.V. 1965. Experimental study of the formation of iron sulfides from solution. Doklady Akad.Nauk.SSSR. 165: 194-196.

(42) KULLERUD, G. 1969. Hexagonal cubic inversions in some M_3S_4-type sulfides. Carnegie Institution Year Book. 67: 179-182.

(43) LANGMUIR, D. 1970. The effect of particle size of the reaction: hematite + water = goethite. Geol.Soc.Amer.Abstr.of Ann.Meetings. 601-602.

(44) LOVE, L.G. and AMSTUTZ, G.C. 1966. Review of microscopic pyrite from the Devonian Chattanooga Shale and Rammelsberg Banderz. Fortschr.Miner. 43: 273-309.

(45) MARGULIS, L. 1969. New Phylogenies of the lower organisms: possible relation to organic deposits in Precambrian sediment. J.Geol.77: 606-617.

(46) MENON, K.K. 1967. Origin of diagenetic pyrite in the Quilon Lst. Kerala, India. Nature 213; 5082: 1219-1220.

(47) MIGULA, W. 1900. System der Bakterien. Jena.

(48) MILLER, L.P. 1950. Formation of metal sulfides through the activities of sulfate-reducing bacteria. Contrib. Boyce Thompson Inst.16: 85-89.

(49) MORRIS, J.C. and STUMM, W. 1967. Redox equilibrium and measurements of potentials in the aquatic environment. Advances in Chemistry Series 67: 270-285. Am.Chem.Soc.

(50) ÖSTLUND, H.G. and ALEXANDER, J. 1963. Oxidation rate of dissolved sulfide in seawater - a preliminary study. J.Geophys.Res.68: 3995-3997.

(51) OSTROUMOV, E.A. 1953. Different forms of combined sulfur compounds in the bottom sediments of the Black Sea. Akad. Nauk. SSSR Inst.Okeanologii. Trudy 7: 70-90.

(52) POLUSHKINA, A.P. and SIDORENKO, G.A. 1963. Melnikovite as a mineral species. Zapiski Vses. Mineralogy. Obshch. 92: 547-554.

(53) POSTGATE, J.R. 1956. Iron and the synthesis of cytochrome c_3. J. Gen.Microbiol 15: 186-193.

(54) POSTGATE, J.R. 1965. Recent advances in the study of sulfate-reducing bacteria. Bacteriol. Rev. 29: 425-441.

(55) POSTGATE, J.R. 1967. Fringe biochemistry among microbes. Royal Society Lecture. London. 2 November 1967.

(56) POSTGATE, J.R. and CAMPBELL, L.L. 1966. Classification of Desulfovibrio species, the non-sporulating sulfate-reducing bacteria. Bacteriol.Rev.30: 732-738.

(57) POURBAIX, M., VAN MUYLDER, J. and DE ZHOUBOV, N. 1963. Atlas d'équilibres électrochimiques à 25 °C. Gauthier-Villars.

(58) RICKARD, D.T. 1968. The geological and microbiological formation of iron sulphides. Ph.D. Thesis. London University.

(59) RICKARD, D.T. 1969. The microbiological formation of iron sulphides. Stockholm Contr. in Geol. 20: 49-66.

(60) RICKARD, D.T. 1969. The chemistry of iron sulphide formation at low temperatures. Stockholm Contr. in Geol. 20: 67-95.

(61) RICKARD, D.T. 1970. The origin of framboids. Lithos 3: 269-293.

(62) ROBERTS, W.M.B., WALKER, A.L. and BUCHANAN, A.S. 1969. The chemistry of pyrite formation in aqueous solution and its relation to the depositional environment. Min.Dep. 4: 18-29.

(63) ROSENQUIST, I.TH. 1970. Formation of vivianite in holocene clay sediments. Lithos 3: 327-334.

(64) SCHIPPEL, F., HALLBERG, R. and ODEN, S. 1972. Phosphate dynamics of a Baltic sediment. (Manuscript)

(65) SCHMALZ, R.F. 1959. A note on the system Fe_2O_3 - H_2O. J.Geophys.Research. 64: 575-579.

(66) SIMINDU, K. and AISO, K. 1962. Occurrence and distribution of heterotrophic bacteria in sea water from Karogara Bay. Bull. Jap. Sci. Fish. 28:1133-1141.

(67) SKINNER, B.S., ERD, R.C. and GRIMALDI, F.S. 1964. Griegite, the thiospinel of iron: a new mineral. Am.Mineral. 49: 543-555.

(68) SKOPINTSEV, B.A. 1961. Recent work on the hydrochemistry of the Black Sea. Okeanologiya 1: 243-250.

(69) SMITH, F.G. and KIDD, D.J. 1949. Hematite-goethite relations in neutral and alkaline solutions under pressure. Am. Mineral. 34: 403-412.

(70) SOROKIN, Y.I. 1970. Interrelations between sulphur and carbon turnover in leromictic (sic) lakes. Arch. Hydrobiol. 66; 4: 391-446.

(71) STARKEY, R.L. 1938. A study of spore formation and other morphological characteristics of Vibrio desulfuricans. Arch.Microbiol. 9: 368-404.

(72) STUMM, W. and LEE, G.F. 1960. The chemistry of aqueous iron. Schweiz.Z. Hydrol. 22: 295-319.

(73) STUMM, W. and MORGAN, J.J. 1971. Aquatic Chemistry. Wiley-Interscience.

(74) TAKENO, S., ZOKA, H. and NIIHARA, T. 1970. Metastable cubic iron sulfide - with special reference to mackinawite. Am. Mineral. 55: 1639-1649.

(75) TEMPLE, K.L. and LEROUX, N.W. 1964. Syngenesis of sulfide ores: sulfate-reducing bacteria and copper toxicity. Econ.Geol. 59: 271-272.

(76) VAN DELDEN, A. 1903. Beiträge zur Kenntnis der Sulfatreduktion durch Bakterien. Centr. Bakteriol. Abt. II 11: 81-94.

(77) VOLKOV, I.I. Iron sulfides, their interdependence and transformation in the Black Sea bottom sediments. Akad. Nauk. SSSR Inst. Okeanologii. Trudy 50: 68-92.

(78) WERKMAN, C.H. and WEAVER, H.J. 1927. Studies in the bacteriology of sulphur stinker spoilage of canned sweet corn. Iowa State Coll. J.Sci. 2: 57-67.

(79) YAMAGUCHI, S. and WADA, H. 1970. Surface conversion of cubical tri-iron tetrasulfide (Fe_3S_4) into tetragonal ferrous sulfide (FeS). Kolloid. Z. Polym. 236 (2): 176-177.

(80) ZOBELL, C.E. 1946. Marine microbiology. Chronica Botanica Co. Waltham, Mass. USA. 240 pp.

(81) ZOBELL, C.E. 1958. Ecology of sulfate-reducing bacteria. Producers Monthly 22: 12.

Summary

After a review of the sources of sulphur and iron in the sedimentary environment, sedimentary iron sulphide formation is described as a sequence of: 1. biological sulphate reduction, 2. the formation of metastable ferrous sulphides (mainly mackinawite and griegite) and, 3. the formation of iron polysulphides (mainly pyrite). The chemistry and the environmental limitations of each of these processes are discussed. Some remarks are made on the origin of framboidal aggregates of pyrite microcrysts and on the sulphur balance of the world's oceans.

Résumé

Un aperçu des origines du soufre et du fer dans l'ambiance sédimentaire est suivi par une description de la formation des sulfures de fer comme une suite de: (1) la réduction biologique des sulfates, (2) la formation des sulfures ferreuses métastabiles (surtout mackinawite et griegite), et (3) la formation des polysulfures de fer (surtout pyrite). La chimie et les limitations ambientales de chacun de ces processus sont discutés. Enfin quelques remarques sont fait sur l'origine des agrégats de micro-cristallins de pyrite en forme de framboise, et sur la balance du soufre dans les océans.

Resumen

Después de una reseña de los origines del azufre y del hierro en el ambiente sedimentario, se da una descripción de la formación del sulfuro de hierro como una serie consecutiva de: (1) la reducción biologica del sulfato, (2) la formación del sulfuro ferroso meta-estable (sobre todo mackinawita y griegita), y (3) la formación de los poli-sulfuros de hierro (sobre todo pirita). Se discute la química et las limitaciones ambientales de cada uno de esos procesos. Al fin se hace unas observaciones sobre el origen de los cristalos compuestos de pirita en forma de frambuesa y sobre la balance del azufre en los océanos mundiales.

Zusammenfassung

Zuerst wird der Ursprung des Schwefels und des Eisens in den Ablagerungen besprochen. Dementsprechend erfolgt die Bildung der Eisensulfiden in drei Stufen: (1) biologische Sulfatreduktion, (2) Bildung meta-stabiler Eisensulfiden (meistens Mackinawit und Griegit), und (3) Bildung der Eisenpolysulfiden (meistens Pyrit). Für jeden dieser Prozesse werden Chemie und Umweltsbedingungen behandelt. Schliesslich werden einige Bemerkungen gemacht über die Herkunft framboider Aggregaten von Pyritmikrokristallen und über die Schwefelbilanz der Weltmeere.

DISCUSSION

HARDAN: To what level of organic matter does the direct relationship between organic matter content and sulphide production hold?

RICKARD: Berner (Am.J.Sci.268:1-23) has observed an approximate direct relation up to 6% C in modern Connecticut sediments.

VAN VEEN: Are the fibrous FeS compounds on the Desulfovibrio cell of which a micrograph was shown, related to excretions of proteins or enzymes by the bacteria?

RICKARD: The compound produced is not fibrous, it has a sheet structure. Its possible relation with proteins is not known. It has not been produced inorganically or abiologically.

VIEILLEFON: To which extent is the iron content of sediments a limiting factor in sedimentary pyrite formation?

RICKARD: Only part of the iron present reacts to form pyrite. The rate of sulphidation of the iron compounds depends on the source and nature of their origin. Under high organic matter conditions reactive iron may become limiting.

PONNAMPERUMA: After flooding soils undergo reduction roughly according to a thermodynamic sequence. Subsequently are disappearing: oxigen, nitrate, manganese oxides, iron oxides and sulphates. In flooded soils appreciable sulphate reduction only occurs when pE is down to -2. How then could FeS be formed by the action of S^{2-} on goethite?

RICKARD: A similar sequence is observed in sedimentary environments. However the non-sulphide producing stages are extremely compressed and virtually absent. The sulphide bearing reduced zone within the sediment has a sharp contact with the upper oxidized zone and thus goethite may be directly sulphidized.

PONS: How varies the rate of metabolizable organic mattter in the total of sedimentary organic matter?

RICKARD: Comparison of organic matter contents in sediments at depth e.g. 50 or 100 cm and at the surface suggests that 30-70% of the original organic matter is normally lost during diagenesis.

PONS: What happens when oligotrophic peats (e.g.Sphagnum spec.) are inundated with seawater?

RICKARD: At pH values below about 5, sulphate-reducing bacteria will not operate. Sulphides produced in those conditions will be formed from decomposition of organic matter.

BLOOMFIELD: When soils are incubated anaerobically with plant matter, considerable amounts of Fe^{2+} are dissolved, the lower the pH the greater the amount. When SO_4^{2+}-reduction is imposed on the same system, the FeS : H_2S ratio is greater at lower pH's than at higher - i.e. more FeS is formed under conditions in which more Fe^{2+} would be expected if H_2S were not being formed. Also for soils of about equal total Fe_2O_3 content, the FeS : H_2S ratio is greater with poorly drained than with well drained soils - i.e. with soils containing the greater amount of more readily mobilized (as Fe^{2+}) ions.

RICKARD: The rate of reaction between dissolved sulphide and dissolved Fe^{2+} is much faster than between dissolved sulphide and α-FeOOH. Therefore with experiments of short duration the percentage FeS - S formed will indeed be dependent on the initial content of dissolved Fe in the soil samples. However, the rate of sulphidation of α-FeOOH is faster than its reduction by organic compounds. Thus in a steady state diagenetic system, in the presence of SO_4^{2-} - reduction, the percentage FeS - S formed should be the same in samples containing equal quantities of total reactive Fe and total available sulphide. Dr Bloomfield's observations give rise to an interesting implication for the formation of acid sulphate soils. The formation of pyrite requires the presence of sulphur. The subsequent sulphidation of organic-rich-non-sulphide-bearing soil layers, with high Fe^{2+}/Fe^{3+} ratios, should result in the formation of the metastable and difficultly preservable <FeS> rather than pyrite.

VAN BREEMEN: According to Van Bemmelen (Natuurk.Verk.der Koninkl.Akademie, Deel XXV B p.90. Amsterdam 1887) the mechanism of pyrite formation involving dissolved polysulphide was postulated already in 1847 by Bunsen (Ann.Ch.u.Pharm. B, 61, p.265. 1847).

SOIL FORMING PROCESSES IN ACID SULPHATE SOILS

N. van Breemen
Department of Soil Science and Geology, Agricultural University
Wageningen

Introduction

Sulphuric acid, which is responsible for the peculiar characteristics of acid sulphate soils, is produced mainly by the oxidation of reduced sulphur compounds (esp. pyrite) present in reduced soils. In some cases acidity is caused by SO_2 or SO_3 originating from volcanic emanations or from industrial pollution, but sedimentary iron sulphides are by far the most important sources.

This review deals with the sulphur compounds present in soils and with the oxidation of sulphides. Also discussed are the formation of various iron- and sulphur compounds in acid sulphate soils, interactions of sulphuric acid with soil minerals, and the accompanying acid buffering of the soils. The last chapter deals with horizon differentiation in acid sulphate soils.

1. Sulphur compounds in potential and developed acid sulphate soils

Potentially acid muds may contain up to 5% pyrite-S, but values between 1 and 4% are most common (15,122). Generally ferrous monosulphide comprises less than 0.01% S (16) and rarely exceeds 0.6%, even in highly blackened reduced muds (14). No monosulphide could be detected in 15 potentially acid subsoils from Thailand (20). Under special conditions elemental S can be produced in large quantities by chemical and microbiological oxidation of H_2S (77, 102). In reduced marine muds elemental S generally occurs in small (usually less than 2% of total S) quantities (13, 66, 112). Elemental S may be produced during oxidation of FeS and FeS_2, but it is generally kept at low concentrations (15).

Organic S is generally the most abundant form of S in "normal" soils, but it is quantitatively insignificant in pyritic sediments and in acid sulphate soils (cf.14, 66).

Published data on the sulphur fractions present in reduced or partly oxidized soils should be examined critically, because some fractions are very susceptible to oxidation during and after sampling. Moreover there is no generally satisfactory available method for the analysis of monosulphide (89). Elemental sulphur may be amorphous, in which case it is insoluble in various organic solvents used for elemental S extraction.

It is abundantly clear that pyrite is by far the most important sulphide mineral in potential acid sulphate soils. This conforms with its predicted thermodynamic stability over other Fe-sulphides in most reduced sediments (95). FeS seems to be responsible for acid production in some Gyttya soils in Sweden and Finland (90, 130, 131), but here total S contents are considerably lower than in typical FeS_2-rich potentially acid soils.

A large number of sulphate minerals can be found in association with oxidizing pyritic material (6, 83), but most of these compounds are very soluble and are formed only in the absence of leaching. During dry periods, gyttya soils sometimes have crusts of watersoluble sulfates of Al, Fe^{III}, Ca, Mg, K, and Na (1, 71, 130). Chemical and X-ray analyses have shown the presence of Na- alum ($NaAl(SO_4)_2 . 12\ H_2O$) and tamarugite ($NaAl(SO_4)_2 . 6\ H_2O$) together with gypsum and halite (NaCl) in efflorescences on the surface of young, saline acid sulphate soils in Thailand (20). Pickeringite ($MgAl_2(SO_4)_4.22H_2O$) is reported from efflorescences in acid materials associated with the oxidation of sulphur compounds of volcanic origin (37, 77). This mineral was found together with rozenite ($FeSO_4.4H_2O$) in efflorescences on pyritic subsoil material exposed to the atmosphere (20).

Even in dry periods these efflorescences of easily soluble salts are rare in acid sulphate soils. Under non-arid conditions, most of the SO_4^{2-} from the oxidation of pyrite in low pH environments at normal temperatures is tied up in the minerals of the alunite-jarosite group which are only slightly soluble (74, 87). Van Bemmelen (11) analysed the Fe_2O_3- and SO_3 contents of the yellow mottles from acid sulphate soils. He found a molar SO_3/Fe_2O_3 ratio of about 1.30 and postulated the presence of carphosiderite, $Fe_3(SO_4)_2(OH)_5.2H_2O$ ($SO_3/Fe_2O_3 = 1.33$), which is now considered identical to hydronium jarosite, $(H_3O)Fe_3(SO_4)_2(OH)_6$ (114). Van Bemmelen did not analyse the alkali content and undoubtedly the yellow material contained appreciable amounts of K_2O and perhaps Na_2O. Numerous X-ray diffraction studies on the yellow mottles typical for acid sulphate soils invariably+) yielded

---

+) Fleming and Alexander (38) report the very soluble coquimbite ($Fe_2(SO_4)_3.9H_2O$) together with jarosite in yellow efflorescences scraped from peds in South Carolina acid sulphate soils. The simultaneous occurrence of these two minerals is very unlikely on theoretic grounds. The identification of coquimbite was probably based on an ASTM pattern belonging to a mineral of the jarosite family erroneously labelled as coquimbite (cf.128).

patterns very similar to those of jarosite ($KFe_3(SO_4)_2(OH)_6$ and natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) (3, 4, 15, 20, 30, 32, 38, 60, 99).

The presence of alunite ($KAl_3(SO_4)_2(OH)_6$) in acid sulphate has been postulated (57, 85), but chemical and mineralogical evidence is lacking. Apart from the jarosite minerals, the only sulphate commonly reported in acid sulphate soils is gypsum (11, 20, 38, 68, 85). Moreover soil solution studies indicated the probable existence of an (amorphous?) basic aluminium sulphate with the stochiometric formula $AlOHSO_4$ in acid sulphate soils in Thailand and Sarawak (19).

Under acid conditions the oxidation products of pyrite can be incorporated into jarosite, but if the pH does not drop below 3 or 4, hydrated ferric oxides or poorly crystallized ("limonitic") goethite, lepidocrocite or hematite are formed along with (dissolved) sulphate (27, 46, 73, 74, 103).

Because of the relatively large number of possible oxidation states of sulphur, many dissolved sulphur species may exist, but only sulphide and sulphate are present in appreciable quantities at equilibrium (118). Dissolved compounds of intermediate oxidation state, such as thiosulphate (63, 90, 127), polythionates (46, 63, 90, 127) and sulphite (90), occur under natural conditions (127) or during laboratory experiments on the oxidation of sulphides or elemental S (46, 63, 90), but their concentrations relative to SO_4^{2-} are low and diminish with time.

The stability relationships among the most important Fe- and S compounds discussed so far can be described conveniently by means of a pe (or E_H)-pH diagram (Fig.1).

The standard free energy of formation (ΔG_f^o) for limonitic ferric oxide was taken as -169.2 kcal/mole Fe_2O_3, which is typical for limonitic Fe_2O_3 in jarosite-rich horizons in acid sulphate soils in Thailand. $\Delta G^o_{f\ jarosite}$ (26) was taken as -788.5 kcal/F.M. (calculated from data on a jarosite dissolution experiment provided by Brown (26) using a computer programme as described by van Breemen (19); thermodynamic data for the other compounds were taken from Robie and Waldbaum (96). The diagram is valid for dissolved sulphur (H_2S, HS^-, HSO_4^- or SO_4^{2-}) and K^+ activities of 5×10^{-3} and 5×10^{-4} respectively. The solid-solution contours are for activities of (uncomplexed) Fe^{2+} or Fe^{3+} equal to 10^{-5} and 10^{-2}. The symbols refer to measured Eh-pH data and will be discussed later.

The diagram indicates that (a) pyrite is dominant under reduced conditions over a wide pH range (b) at low pH, elemental S can coexist with pyrite in a narrow pe-pH zone (c) jarosite is stable only under acid, oxidized conditions whereas

(d) ferric oxide occurs at higher pH and over a much wider pe- range. Other phases such as szomolnokite and melanterite (hydrous ferrous sulphates), butlerite, and other ferric sulphates with a lower Fe/OH ratio than jarosite, for which ΔG_f^o data are available (see Table 1) have no stability fields under the conditions specified for Fig.1.

TABLE 1. ΔG_f^o VALUES FOR SEVERAL Fe- AND Al SULPHATES (25 °C, 1 atm)

CHEMICAL FORMULA	MINERAL	ΔG_f^o(kcal/F.W.)	REFERENCES
$FeSO_4.H_2O$	szomolnokite	-257.5	(2)
$FeSO_4.7H_2O$	melanterite	-599.4	(2)
$Fe_2(SO_4)_3$	-	-535.8	estimated+)
$Fe_3(OH)_4SO_4$	(basic Fe^{II} sulphate)	-435.8	(72)
$Fe_4(OH)_2(SO_4)_5$	-	-1033.3	(72)
$Fe_3(OH_3(SO_4)_3$	butlerite?	-725.4	(72)
$Al_2(SO_4)_3.6H_2O$	-	-1105.14	(75)
$(H_3O)Fe_3(SO_4)_2(OH)_6$	hydronium jarosite	-773	(18)x)
$KFe_3(SO_4)_2(OH)_6$	jarosite	-788.5	see text
$KAl(SO_4)_2.12H_2O$	K-alum	-1227.8	(75)
$KAl_3(SO_4)_2(OH)_6$	alunite	-1112.95	(54)
$Al_4(OH)_{10}SO_4$	basaluminite	-1104.13	(105)++)
$AlOHSO_4$	amorphous?	-355.06	(20)++)

+) calculated from enthalpy (7) and estimated entropy (cf. 75)

++) calculated from the solubility product, using ΔG_f^o data by Robie and Waldbaum (96)

x) estimated from data by Posnjak and Merwin (86) on the composition of a solution in equilibrium with goethite "$Fe_3(SO_4)_2(OH)_5.2H_2O$"

The predicted relationships of the diagram are in good agreement with the natural occurrences of the Fe-S minerals in acid sulphate soils. The boundaries of the stability fields are valid only for equilibrium conditions. Because mineral transformations take place under non-equilibrium conditions and because metastable intermediates may be formed, the diagram gives no explicit information on the mineral sequences and physico chemical conditions characteristics of the mineral transformations that occur in nature.

Details on the oxidation of sulphur compounds and on the formation of sulphate minerals are discussed in the following chapters.

2. Oxidation of sulphides and elemental S

The oxidation of sulphur compounds, and especially of pyrite, has been studied extensively in relation to acid sulphate soil formation (15, 16, 50, 51, 52, 53, 81, 90, 92, 120, 131) and the evolution of acid mine water (31, 33, 76, 98, 106, 116). Many references to earlier physico chemical studies are given by Sato (98). Lorenz (78) gives a comprehensive list of the publications on the role of microorganisms in the formation of acid mine water. Fletcher (39) has reviewed various aspects of these organisms in relation to metal winning from low grade ores. Silverman and Ehrlich (102) surveyed the literature on interactions between microorganisms and minerals, and paid particular attention to the microbiological aspects of sulphur oxidation.

Some oxidation reactions involving sulphur compounds (notably the oxidation of H_2S to elemental S) occur rapidly in vitro at normal temperature and pressure. But the reduction of SO_4^{2-} and the oxidation of more reduced compounds proceed only if they are mediated by certain microorganisms. Most of these microorganisms belong to the Thiobacilli, a group of chemoautotrophic organisms, capable of utilizing the energy obtained from the oxidation of H_2S, S^o, $S_2O_3^{2-}$, $S_4O_6^{2-}$ and SO_3^{2-} to SO_4^{2-} for the assimilation of CO_2 (cf. 110). In general they are aerobic, but Thiobacillus denitrificans and perhaps T. thioparus can grow anaerobically if nitrate is present as an electron acceptor. T. thiooxidans and T. ferooxidans are remarkable for their tolerance to extreme metal ion concentrations and very acid conditions.

T. ferrooxidans and Ferrobacillus ferrooxidans are able to mediate oxidation of Fe^{2+} to Fe^{3+}. Members of the Beggiatoaceae, photoautotrophic bacteria of the Rhodobacteriaceae, and Sphaerotilus can also catalize the oxidation of sulphur compounds, but Thiobacilli are by far the most important group.

a) Oxidation of FeS

The oxidation of amorphous or tetragonal FeS (=mackinawite) by atmospheric O_2 proceeds quickly over a wide pH range. The products of oxidation in vitro are elemental S and ferric oxide (12, 120). From near neutral to slightly alkaline pH (5-9.5) lepidocrocite (γFeOOH) is formed (12, 77), at still higher pH goethite and hematite are produced (77).

Bloomfield (15) 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. Because elemental S is oxidized almost exclusively through microbial action, these results indicate that the initial (purely chemical) oxidation of FeS yields ferric oxide and elemental S. The latter appears to be oxidized rapidly to SO_4^{2-} if conditions for microbial growth are favourable. This sequence of reactions can be written as follows:

$$\begin{array}{lll}
2FeS + 3/2_2O + n\ H_2O & Fe_2O_3.nH_2O + 2S^o & \ldots\ldots\ 1 \\
2S^o + 3/2\ O_2 + H_2O & 2H^+ + SO_4^{2-} & \ldots\ldots\ 2 \\
\hline
2FeS + 3\ O_2 + (n+1)H_2O & Fe_2O_3.nH_2O + 2H^+ + SO_4^{2-} & \ldots\ 3
\end{array}$$

b) Pyrite oxidation

Based on the measurements of pyrite electrode potentials in aqueous ferrous sulphate solutions of different pH, Sato (98) concluded tentatively that the initial processes accompanying pyrite oxidation can be represented by:

$$FeS_2 = Fe^{2+} + S_2^o + 2e \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 4$$

in agreement with potentials according to:

$$E_H = 0.751 + 0.0295 \log \left[Fe^{2+}\right]^{+)} \text{ (at pH <2)} \quad \ldots\ldots\ldots \quad 4a$$

and by:

$$FeS_2 + 3H_2O = Fe(OH)_3 + S_2^o + 3H^+ + 3e \quad \ldots\ldots\ldots\ldots \quad 5$$

in agreement with:

$$E_H = 0.857 - 0.059\ pH \text{ (at pH >3)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 5a$$

The standard potentials of 0.751 and 0.857 V were calculated from free energy data for Fe^{2+}, amorphous ferric hydroxide, pyrite, liquid water and solid diatomic molecular sulphur, assumed to be present in equilibrium with gaseous S_2^o at P_{S_2} = 1 atm. Observed E_H values agreed within 10 to 100 mv with those calculated from equations 4a and 5a over the whole pH trajectory (pH 0-12) considered.

Attempts by the present author to reproduce Sato's findings gave similar results. The potential of pyrite was constant from pH 0.7 to 2.7, and decreased 60 mV per 1 unit pH increase at lower acidities. However, at pH values below 2.7 $E_{H\ (pyrite)}$ did not change with increasing concentration of dissolved Fe^{2+} in the range of 10^{-4} to 2×10^{-2}M, whereas according to Equation 4a it should have increased by

---

+) Square brackets denote activities

about 70 mV.

Potentiometric titration curves of ferrous sulphate with $KMnO_4$ were identical over much of the titration range, whether recorded by an inert (Pt-) electrode or by a pyrite electrode (see Fig.2). Only after all Fe^{2+} was oxidized, did $E_{H(pyrite)}$ not increase with further addition of $KMnO_4$, but levelled off at 950 ± 3 mV. The results indicate that the pyrite electrode is inert at E_H values lower than about 900 mV. A similar inert character of pyrite is pointed out by others (44, 88, 106).

So the data by Sato (98) cannot be explained by specific electrode reactions. Probably $E_{H(pyrite)}$ is determined by the Fe^{3+}/Fe^{2+} activity ratio at low pH, and is equal to the so called "irreversible oxygen potential" +) at higher pH, similar to the E_H as measured by a Pt-electrode.

Although the experiments with pyrite electrodes do not give information on the mechanism of pyrite oxidation, they illustrate that pyrite is very inert (at least on the time scale of the experiments) over a considerable E_H range, and that the mineral can be oxidized at a measurable rate only in an environment characterized by much higher E_H values than indicated by upper limits of the FeS_2 field shown in Fig.1.

Barnes et al. (8) postulated that pyrite is oxidized by H_2O in the absence of free O_2, with coal acting as a H_2-sink:

$$FeS_2 + 8H_2O = Fe^{2+} + 2\ SO_4^{2-} + 2H^+ + 7H_{2(g)} \quad \ldots\ldots\ldots\ldots\ 6$$

This is extremely unlikely, because reaction 6 could take place only just above the stability field of pyrite. Only two oxidants need to be considered for the weathering of pyrite under natural conditions at the surface of the earth: dissolved Fe^{3+} and O_2.

With either oxidant, elemental sulphur seems to be the initial product (52, 91, 101, 111), although the results by various authors indicate that during pyrite oxidation by Fe^{3+} at low pH (<2) SO_4^{2-} is released essentially instantaneously, whereas elemental S is produced at higher pH (15, 44, 101) ++). Elemental S con-

---

+) The upper limits of E_H values measured in aerated aqueous media, characterized by $E_H = 0.85 - 0.06$ pH (cf. 5, 80, 97).

++) Silverman (101) reported that the recovery of Fe^{2+} and Fe^{3+} was in complete agreement with $2Fe^{3+} + FeS_2 \rightarrow 3Fe^{2+} + 2S^o$, but that CCl_4-extractable sulphur was negligable. This may indicate that most of the elemental S was amorphous (μ)S which is practically insoluble in CCl_4.

centrations generally remain low because the sulphur is further oxidized to SO_4^{2-}, either chemically by Fe^{3+} or microbiologically by Thiobacilli.

If O_2 and Fe^{3+} are the oxidants, and S^o is the initial oxidation product, the following reactions characterize the processes accompanying pyrite oxidation:

$FeS_2 + 1/2O_2 + 2H^+ \rightarrow Fe^{2+} + 2S^o + H_2O$ 7
$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O$ 8
$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$ 9
$FeS_2 + 2Fe^{3+} \rightarrow 3Fe^{2+} + 2S^o$ 10
$2S^o + 12Fe^{3+} + 8H_2O \rightarrow 12Fe^{2+} + 2SO_4^{2-} + 16H^+$ 11
$2S^o + 3O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+$ 12

Reaction 7 represents the purely chemical oxidation of pyrite by O_2. This is a slow process as follows from the behaviour of FeS_2 electrodes and from the sluggishness of pyrite decomposition in moist, aerated (sterile) media where Fe^{3+} is absent (81, 106, 116).

If the pH is below 3.5, the chemical oxidation of Fe^{2+} to Fe^{3+} (reaction 8) is very slow. The rate is independent of the pH:

$$\frac{-d(Fe^{2+})}{dt} = k\ (Fe^{2+})(O_2) \qquad 13$$

with $k = 1.0 \times 10^{-7}\ atm^{-1}\ min^{-1}$ (106)

At atmospheric O_2, only 5% of the ferrous iron i a solution originally containing 9×10^{-4} M Fe^{2+} /l was oxidized in 150 days, but under the same conditions iron oxidizing microorganisms (probably T. ferrooxidans or Ferrobacillus ferrooxidans) accelerated the reaction by a factor larger than 10^6 (106).

Fe^{3+} can remain in solution in appreciable amounts only at pH values below 3 to 3.5. At higher pH almost all Fe^{3+} hydrolyses and precipitates as ferric hydroxide (reaction 9) a process that proceeds at much higher rates than the (chemical) oxidation of Fe^{2+}

So if the pH is low, dissolved ferric iron can oxidize pyrite or elemental sulphur according to the reactions 10 and 11.

The combined process of reactions 10 + 11:

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

takes place rapidly at room temperature (44, 53, 106). The rates are pH-independent at pH between 0 and 2 but they may differ considerably (4 to 8 fold) for pure pyrite samples from different localities (44).

It was postulated that the instantaneous rate is controlled by differential absorption of Fe^{3+} and Fe^{2+} ions on the pyrite surface, and is proportional to the fraction of the pyrite surface occupied with Fe^{3+}. The general equation that fits the observed rates is:

$$\frac{-d(Fe^{3+})}{dt} = k\,\frac{(Fe^{3+})}{(Fe^{3+})^{o}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 15$$

where $(Fe^{3+})^{o}$ is the initial Fe^{3+} concentration (44).

The data given by Hart (53) for soil pyrite can be interpreted in the same way. As pointed out before, the oxidation of elemental S by atmospheric O_2 (reaction 12) is a very slow process, unless it is catalized by microorganisms. A review on various aspects of elemental S oxidation is reported by Freney (40).

The information presented above can be summarized by a model useful for discussing a number of relevant factors of pyrite oxidation (Fig.3). The essential features of the model are similar to that suggested by Temple and Delchamps (116) and Stumm and Morgan (113).

The pathways involving elemental sulphur and jarosite were not considered in the earlier model. According to the present model (Fig.3), the first step (reaction a) in the decomposition of pyrite is the release of Fe^{2+} and the oxidation of pyrite-sulphur to elemental S. Microbial oxidation of the S^{o} produces SO_4^{2-} and H^{+} (reaction b).

If the pH drops sufficiently, considerable amounts of ferric iron may appear in solution as a result of oxidation of Fe^{2+} by iron oxidizing Thiobacilli (reaction c). In the presence of pyrite and of (amorphous?) elemental S, Fe^{3+} is reduced rapidly to Fe^{2+}, thereby oxidizing pyrite and/or elemental S. The newly formed Fe^{2+} can be utilized again by the Thiobacilli. Once the cycle involving formation and reduction of Fe^{3+} (c → (d+e) ↠ c → (d+e) etc.) is well established, pyrite can be oxidized quickly with dissolved iron acting as a catalyst.

If sufficient buffering substances are available to prevent a quick decrease in pH below about 4, the Fe^{2+} produced will oxidize relatively fast and precipitate as $Fe(OH)_3$ (h). At lower pH jarosite may become the dominant solid Fe^{III} phase. Upon further acidification these compounds may dissolve partly or wholly, and thus act as a source of Fe^{3+} for pyrite oxidation (j, k, g). A number of factors of particular importance for pyrite oxidation will be discussed at length below.

Microbiological activity

Numerous investigations (cf. the review by Lorentz (78)) show that pyrite oxidation proceeds much faster in the presence of Thiobacilli than in their absence. If the pH remains high, their effect lies mainly in the oxidation of elemental S (reaction b). The acid produced by this reaction may ultimately lead to the low pH values favourable for the growth of T. and Ferrobacillus ferrooxidans (cf. 15, 102) and necessary for the presence of dissolved Fe^{3+}. In contrast to T. ferrooxidans, T. thiooxidans has little effect on the oxidation of pure, well crystallized pyrite, whereas it increases the acid formation from marcasite and "sulphurballs" (porous pyritic concentrations from coal deposits) (15, 116). Quispel et al. (91) found that the addition of elemental S significantly enhanced pyrite oxidation, presumably as a result of acid formation (leading to conditions favourable for T. ferrooxidans) from elemental S by non-acidophilic organisms, and later by T. thiooxidans.

The acid tolerant Thiobacillus species seem to be ubiquitous in habitats where metal sulphides and O_2 occur under acid conditions. In addition to mine waters (cf. 78), they have been found repeatedly in acid sulphate soils (15, 52, 91). T. thioparus and T. thiooxidans were even isolated from reduced pyritic seabottom muds off Ivory coast (35). Their widespread occurrence is somewhat surprising, considering their seemingly obligate autotrophic character. Provided the conditions are favourable, microbial activity does not appear to be a limiting factor in pyrite oxidation in natural environments.

Environmental conditions for microbial growth

Microbial oxidation is strongly inhibited at temperatures below 10 °C. Optimum growth occurs between 20 and 40 °C (40, 102).

For moist aerated soil with 5% pyrite-S, incubated at different temperatures, Rasmussen (92) found that oxidation rates at 3 °C and at 13 °C were about 20% and 60% of the rate at 23 °C.

Several authors point out that sufficient moisture is extremely important (15, 40, 81, 92). Optimum conditions seem to be present at or just below field capacity; in air-dry soils pyrite oxidation essentially ceases. The moisture effect probably reflects both the requirements for microbial growth and the fact that water is a reactant in the process.

The iron oxidizing Thiobacilli are very resistant to high concentrations of metal ions (concentrations up to 15 000 ppm Cu and 40 000 ppm Fe and Zn can be tolerated (102). However, relatively low concentrations (2.3×10^{-3}M) of chloride are slightly inhibitory while 5×10^{-3}M is completely inhibitory (101).

This effect probably explains the observation (20) that in pyritic soils treated with seawater, the (Fe^{3+})/(Fe^{2+}) ratio in the soil solution did not exceed 0.25 (at pH 2) even after 6 months of aeration, whereas the ratio became much higher (between 1 and 2) if the same soils were treated with distilled water before aeration. Pyrite oxidation, as indicated by direct pyrite analyses was only slightly inhibited.

pH and dissolved Fe^{3+}

Numerous experiments show that pyrite oxidation is promoted strongly by acid (pH 1-4) conditions (15, 51, 73, 81, 92, 116). The oxidation rate decreases if the pH is brought down below 1 by addition of H_2SO_4, probably because the Thiobacilli are affected by such extreme acidity (92).

In order to explain the sometimes rapid pyrite oxidation upon aeration of near-neutral mangrove muds, Hart (32) postulated that the oxidation of FeS was necessary as a first step to make the soil acid enough for pyrite oxidation. Elemental S (cf. 91) might also be important in this respect. However, as pointed out by Bloomfield (16) the amounts of FeS and S^0 normally present in potentially acid soil are far too small to have much effect on the pH. The presence of a certain fraction of very small, probably poorly crystallized FeS_2 that is relatively susceptible to oxidation by O_2, may explain the initial pH drop. The effects of particle size and crystallinity will be discussed in more detail under a separate heading.

Probably the single most important reason that pH affects the oxidation rate is the role of Fe^{3+} as an oxidant under acid conditions. If the upper limit of the Fe^{3+} concentration is regulated by jarosite, the pH dependence of (Fe^{3+}) can be expressed as follows:

$$KFe_3(SO_4)_2(OH)_6 + 6H^+ = K^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \quad 16$$

for which the equilibrium condition reads (for 25 °C and 1 atm):

$$\log K = -12.5 = \log \left[K^+\right] + 3 \log \left[Fe^{3+}\right] + 2 \log \left[SO_4^{2-}\right] + 6pH \quad . \; . \quad 16a$$

At SO_4^{2-} and K^+ activities as used in Fig.1, the activity of Fe^{3+} is simply a a function of the pH:

$$\log \left[Fe^{3+}\right] = -1.53 - 2pH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad 16b$$

If, in addition to free Fe^{3+}, the complexes $FeSO_4^+$ and $Fe(SO_4)_2^-$ are considered, and if the ionic strength is known, the total Fe^{III} concentration

$$(Fe_T^{III}) = (Fe^{3+}) + (FeSO_4^+) + (Fe(SO_4)_2^-)$$

can be calculated. Using values for the dissociation constants for the complexes summarized by Sillén and Martell (100), and individual ion activity coefficients according to the Davies equation (cf.29) at an ionic strength of 0.1 gives:

$$\log (Fe_T^{III}) = 0.52 - 2pH \quad \ldots\ldots\ldots\ldots\ldots \quad 16c$$

At pH > 3.7 "limonitic" Fe_2O_3 replaces jarosite, and the relationship becomes:

$$\log (Fe_T^{III}) = 4.2 - 3\ pH \quad \ldots\ldots\ldots\ldots\ldots \quad 17$$

Fig. 4 depicts the pH-(Fe_T^{III}) relationships given by the Equations 16c and 17 (broken line). The amount of pyrite oxidized in one hour by ferric iron at an initial concentration of (Fe_T^{III}), is shown by the solid line. The oxidation rate was calculated from Equation 15 (assuming $(Fe^{3+}) = (Fe_T^{III})$) using a rate constant of 10^{-4} mole.h^{-1}, computed from data by Hart (53) for the oxidation of partly weathered soil pyrite by $FeCl_3$ at pH 1.2.

With increasing acidity, the rate increases rapidly until $(Fe_T^{III}) = 10^{-4}$. A further increase in the ferric iron concentration has little effect, because, in accordance with the theory of Garrels and Thompson (44), the pyrite surface is saturated with adsorbed ferric iron.

According to Fig.4, complete oxidation of a given quantity of pyrite will take 10^3, 10^5, and 10^7 hours at pH 2, 3, and 4 respectively. Theoretically the rate is independent of the amount of pyrite present. However, at high pyrite contents the microbial oxidation of Fe^{2+} to Fe^{3+} may lag behind the reduction of Fe^{3+} by pyrite. This would result in lower rates. The rate of precipitation or dissolution of jarosite and ferric oxide perhaps influences the actual value of (Fe_T^{III}) and may thus affect the rate of pyrite oxidation. Values for (average) oxidation rates observed in different laboratory experiments on pyrite oxidation under well aerated conditions are indicated by symbols. In spite of considerable differences in materials and techniques applied by the various investigators, all observed values but one are roughly in the order of magnitude as predicted by the rate curve. In a neutral to slightly acid environment, direct oxidation by O_2 (path a in Fig.3), followed by microbial oxidation of S^o may be more important than oxidation by Fe^{3+}. At high pH the formation of a protective coating of ferric oxide may also help to slow down oxidation. The strongly depressing effect of high levels of dissolved phosphate on the decomposition of pyrite at pH values above 4 (50, 81, 91) has been ascribed to a decrease in the solubility of Fe^{3+} by the formation of ferric phosphate.

Particle size and crystallinity

Several investigators demonstrated the strong positive influence of small particle size on the oxidation rate (52, 91, 116). To a large extent, this effect must be ascribed to the increase in surface area with decreasing particle size.

For typical porous sulphur ball material the specific surface area is 10^5 cm^2/g at an average particle size of 30 µm, and about 10^3 cm^2/g for particles of 1000 µm (31).

Hart (53) explained the observed decrease in oxidation rate of pyrite in mangrove mud with time on the basis of the expected decrease of the total exposed surface area, accompanying the weathering of the pyrite.

The susceptibility to oxidation of very small pyrite particles need not be the result of a larger specific surface area per sé, but may also reflect the increase in standard free energy (=equivalent to a decrease in stability) accompanying an increase in specific surface (113). Lattice defects could have a similar effect. Both phenomena can be important for sedimentary pyrite which generally consists of aggregates of minute particles with diameters in the 0.1 to 1 µm range (92).
The rapid oxidation of a small (about 5%) fraction of soil pyrite observed by Hart (53) can be explained in this way.

Some non-acid soils that had been well drained for many decades were found to contain appreciable quantities of pyrite (50, 65). Harmsen et al.(50) postulated the existence of different polysulphide fractions to explain the presence of seemingly very stable pyrite. Chemical and mineralogical evidence to support their postulation is completely lacking. Preservation of the pyrite in question is probably the result of a relatively large particle size (Kanno et al. (65) found well-crystalline particles between 10 and 100 µm in diameter) combined with a relatively high pH.

O_2 partial pressure

In typical reduced pyritic soils, ferric oxide is usually absent, so all dissolved ferric iron for pyrite oxidation must come from ferrous iron, which in turn comes mainly from the pyrite itself, by oxidation with O_2. Thus the ultimate oxidant for pyrite is atmospheric oxygen. During an experiment on pyrite oxidation at fixed O_2 partial pressures in closed containers, the average oxidation rate was found to depend on the O_2 concentration according to:

$$\frac{d(SO_4^{2-})}{dt} = a \times (O_2)^b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 18$$

For a particular experimental set-up (pH about 1, presumably under sterile conditions) a and b were 0.023 and 2/3, respectively, for (O_2) expressed in mg/l and the rate expressed in terms of SO_4^{2-} production ($mg. l^{-1}.h^{-1}.(g\ pyrite)^{-1}$) (31).

Under conditions favourable for pyrite oxidation (ready access to O_2, low pH, and intensive microbial activity), the O_2 consumption during pyrite oxidation is in the order of 3×10^{-3} g $O_2.h^{-1}$. $(g\ pyrite)^{-1}$ for moist, aerated, pyritic mangrove soil (52) to 7×10^{-3} g O_2. h^{-1}. $(g\ pyrite)^{-1}$ for finely ground coal pyrite after inocculation by Ferrobacillus ferrooxidans (101).

O_2 fluxes from the atmosphere (20% O_2) into reduced soil are generally in the order of 2 to 7×10^{-6} g $O_2.cm^{-2}.h^{-1}$. Such fluxes may maintain thin (0.5 to 2 mm) oxidized layer on top of reduced soil (61).

For pyrite oxidation in a 2 mm thick layer of soil that has a bulk density of 0.7 $g.cm^{-3}$ and that contains 5% pyrite, the O_2-flux necessary to maintain the optimum O_2 consumptions cited above is between 2 and 5×10^{-5} g O_2. $cm^2.h^{-1}$. Assuming that the observed fluxes are also valid for pyritic soil, it appears that about 1/10th of the O_2 necessary for optimal pyrite oxidation is actually available.

Moreover, the O_2 concentrations near to the reduced soil horizon will generally be much lower than 20%. This will further decrease the availability of O_2. Oxygen fluxes at the reduced soil-water interface are approximately proportional to the square root of the O_2 concentration (61). These calculations indicate that O_2 diffusion is probably a rate limiting factor in pyrite oxidation under field conditions as suggested by Rasmussen (92). Further evidence for the low rates of pyrite oxidation under field conditions compared to those for the well-aerated laboratory conditions, will be discussed later.

3. The formation of solid sulphates

As discussed in Chapter 1, the basic iron sulphates of the jarosite group and gypsum may be present in acid sulphate soils. The Al-analog of jarosite, alunite, has not been identified in acid sulphate soils, but there is strong evidence that another basic aluminum sulphate, $AlOHSO_4$, occurs.

Typically, jarosite occurs as conspicuous, pale yellow, earthy material as fillings of biopores or as efflorescences on ped faces and pore walls. Individual particles are often smaller than 1 µm and their diameter rarely exceeds 5 µm (4, 30, 128).

The most important members of the jarosite group are jarosite ($KFe_3(SO_4)_2(OH)_6$), natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) and hydronium jarosite ($(H_3O)Fe_3(SO_4)_2(OH)_6$). A continuous solid solution exists as a result of K-Na-H_3O substitution but there is a strong preference for K^+ over Na^+ and H_3O^+ in the structure (25, 74).

Fig. 5 shows how jarosite formation (indicated by the increase in the apparent $\Delta G^o_{f\ jarosite}$ to values around -788.5 kcal/F.W.) affects the concentrations of dissolved K^+ and Na^+ during oxidation and acidification of pyritic soil material. The appearance of jarosite coincides with an abrupt decrease in the K^+ concentration whereas a significant decrease in dissolved Na^+ occurs only after the K^+ concentration has reached very low levels. Uptake of appreciable amounts of Na^+ starts after the activity ratio of dissolved K^+ and Na^+ ($[K^+]$ / $[Na^+]$) has dropped below about $10^{-3.8}$ (20). If no acidification takes place (sample Mc) the concentrations of K^+ and Na^+ remain essentially constant.

The factors governing the degree of substitution among the three monovalent ions can be evaluated as follows:

For the reaction

$$\text{jarosite} + H_3O^+ = \text{hydronium jarosite} + K^+ \quad \ldots\ldots\ldots\ldots \quad 19$$

the equilibrium constant can be calculated (cf.42) from the free energy data of Table 1 and $\Delta G^o_{fK^+}$ and $\Delta G^o_{fH_2O}$ (= $\Delta G^o_{fH_3O^+}$) as given by Robie and Waldbaum (96):

$$\log K = \log [K^+] + pH = -3.45 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 19a$$

Data on the standard free energy of formation of natrojarosite is not available but if the K^+ - Na^+ activity ratio mentioned before can be considered valid for equilibrium between jarosite and natrojarosite, we can write:

$$\text{jarosite} + Na^+ = \text{natrojarosite} + K^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 20$$

and

$$\log K = \log [K^+] - \log [Na^+] = -3.8 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 20a$$

Assuming ideal solid solution among the three minerals, the relationships between the molefractions of jarosite, natrojarosite and hydronium jarosite (written as X_K, X_{Na}, and X_H) can be expressed as follows (cf. 113):

$$\frac{X_K}{X_{Na}} = 10^{3 \cdot 8} \frac{[K^+] \; / \; [H^+]}{[Na^+] / \; [H^+]} \quad \ldots\ldots\ldots\ldots\ldots \quad 21$$

and

$$\frac{X_K}{X_H} = 10^{3 \cdot 5} \; [K^+] \; / \; [H^+] \quad \ldots\ldots\ldots\ldots\ldots \quad 22$$

Moreover, if the molefractions are expressed as percent:

$$X_K \; + \; X_{Na} \; + \; X_H \; = \; 100 \ldots\ldots\ldots\ldots\ldots \quad 23$$

For given values of K^+, Na^+ and H^+ (or pH), the molefractions can be calculated from the equations 21, 22 and 23.

Fig.6 gives the result of such calculations by means of contours showing solution compositions in terms of log $[K^+]$ + pH and log Na^+ + pH in equilibrium with jarosite minerals of a certain composition. The plotted activity data+) on actual water compositions show that, according to the graph, in acid sulphate soils in Thailand and Sarawak, even at Na concentrations higher than in seawater (0.48 M Na^+), some 99% of the univalent positions in the jarosite structure is filled by K^+. Only after depletion of essentially all available K^+ (realised by allowing jarosite to form in pyritic mud in pots in the laboratory) considerable amounts of Na^+ are built into the mineral. The pH values obtained in the laboratory experiments (as low as pH 1.8) could, according to the graph, result in H_3O^+ occupying 10% of the monovalent ion positions.

The uptake of appreciable quantities of Na in jarosite during the experiment in question was confirmed qualitatively by X-ray diffraction of jarositic soil samples taken before and after depletion of dissolved K^+. The pattern for the second sample showed a larger separation of the strong 021 and 113 reflections than the one for the first sample.

The respective d-values are reported as 3.11 and 3.08 Å for jarosite and 3.12 and 3.06 Å for natrojarosite (Index to the Powder Diffraction File 1970, No. 10-443 and No. 11-302 (64)).

+) Activities of dissolved species referred to here and in the following were calculated by means of a computer programme (19).

Table 2 gives the results of chemical analyses+) of jarosite samples from acid sulphate soils in Thailand, typical for each of the three salinity classes distinguished in Fig. 6.

TABLE 2. VALUES FOR X_K, X_{Na} AND X_H OF THREE DIFFERENT JAROSITE SAMPLES FROM ACID SULPHATE SOILS AS FOUND BY CHEMICAL ANALYSES AND AS CALCULATED FROM THE CORRESPONDING SOIL SOLUTION DATA (20)

SAMPLE	DEPTH	pH	$[K^+]$	$[Na^+]$	X_K		X_{Na}		X_H	
					found	calc.	found.	calc.	found.	calc.
Ra-1-43	125	3.5	4.5×10^{-4}	2×10^{-2}	88	99.3	12	0.7	0.0	0.0
BP-5-34	15	4.0	3.8×10^{-3}	2.3×10^{-1}	62	99.0	8	1.0	30x)	0.0
Ca-1-8	60	3.25	7.4×10^{-3}	5.6×10^{-1}	90	98.5	10	1.5	0.0	0.0

The hydronium content of Bp-5-34 is surprisingly high, especially when it is realised that the corresponding pH is the highest in the series. The soil in question was reclaimed from a mangrove swamp a few years before, and the jarosite is of recent date compared to the other two samples. Perhaps high hydronium jarosite can be formed as a metastable product upon rapid pyrite oxidation even in the presence of much alkali (cf. 25).

The hydronium contents of the two other jarosite samples are essentially zero as predicted. The Na contents are roughly ten times higher than the calculated figures. No clear relationship is found between the K-Na activity ratio in solution and the degree of Na substitution, but in all samples K^+ is predominant in qualitative agreement with Fig. 6.

The X-ray patterns of jarosite and natrojarosite are only slightly different and minerals synthetized or formed at various temperatures may show slightly divergent patterns that may obscure correlations between lattice parameters and che-

---

+) After repeated washing with distilled water, the earthy yellow material was dissolved in hot 4 N HCl and the residue (50-60%) discarded. The HCl extracts were analysed for Al, Fe, Na, K, and SO_4. Except for BP-5-34 which was alkali-deficient, the sum of Na and K was 10 to 20% higher than expected from the amount of dissolved sulphate and the theoretical alkali/SO_3 ratio for jarosite, possibly due to the contribution of other minerals. The X_K and X_{Na} values reported are proportional to the molar K- and Na concentrations found in the extract.

x) Calculated from $100-X_K-X_{Na}$, for a 1:2 monovalent ion-sulphate ratio, assuming that all extracted SO_4 came from jarosite.

mical composition such as reported by Brophy and Sheridan (25) (cf. 26). In view of the strong preference for K^+, reported occurrences of natrojarosite or Na-rich jarosite based on X-ray data are questionable unless accompanied by chemical analyses (cf. Clark et al. (32)).

Jarosite can be prepared at room temperature within a few weeks or months, by bubbling air or oxygen through solutions of ferrous (or ferric-) sulphate and potassium sulphate. The characteristic efflorescence-like occurrences of jarosite both in soil profiles and on pyritic mud after a few weeks exposure to the atmosphere indicate that in nature it can also be formed from solutions containing ferrous sulphate by oxidation and precipitation.

However, oxidizing pyrite muds often develop a reddish brown surface coating before the typical yellow jarosite efflorescences appear. Thus ferric hydroxide may form initially, possibly as an intermediate in jarosite formation. It is unlikely that less basic ferric sulphates are formed as intermediate compounds (cf.109) because such compounds are generally too soluble, except possibly in the most arid soils. Direct alteration of pyrite to jarosite has frequently been reported (41). The potassium in jarosite may come from the soil solution, from K^+ adsorbed on the soil exchange complex and from K-bearing minerals (mainly mica's, feldspars, and locally glauconite (23, 30)). Data on the bulk density, the jarosite contents and the levels of dissolved and adsorbed K^+ in typical mangrove soils and acid sulphate soils in Thailand (20, 108, 125) indicate that for a representative acid sulphate soil (containing 23 g jarosite-K in a 100 cm^2 x 140 cm vertical column) 65% of the jarosite-K can be accounted for by the observed drop in exchangeable K since the mangrove stage and 15% by the decrease in dissolved K. Thus about 20% of the K^+ must have come from minerals. The actual contribution of K-bearing minerals is probably higher because (a) jarosite is continuously being destroyed in one part of the profile while being formed in another part and the present amount of jarosite constitutes a fraction ($\pm$ 50%) of all jarosite ever produced (20) and (b) there is probably a net outward flux of K^+ from the profile, brought about by diffusion into the flood water during the wet season and, to a lesser extent, by leaching.

Jarosite is stable only under relatively oxidized and acid conditions. The occurrence of jarosite in acid sulphate soils in Thailand is in good agreement with the theoretically predicted E_H-pH conditions (see Fig. 1).

Both a decrease in pe or E_H and an increase in pH may lead to the disappearance of jarosite by solution-reduction (yielding Fe^{2+}, SO_4^{2-}, and K^+) and by hydrolysis (yielding ferric oxide, K^+ and SO_4^{2-}) respectively. The presence of jarosite in environments with pH values well above 4 could be explained by arid conditions and/or by the sluggishness of the hydrolysis to ferric oxide (27). The latter factor is illustrated convincingly by the occurrence of yellow mottles in "fossil" acid sulphate soils in a Dutch polder even 40 years after reclamation and regular liming to maintain pH values between 5 and 7 (119).

It should be emphasized that the limonitic Fe_2O_3 used in Fig.1 is unstable with respect to goethite or hematite. If either of these more stable Fe_2O_3 minerals were considered in the diagram, the jarosite-Fe_2O_3 boundary would move to a pH of about 0.6. Thus jarosite cannot exist if overall equilibrium (characterized by the presence of the most stable polymorph of Fe_2O_3) prevails under acid sulphate soil conditions, and, given enough time it is bound to hydrolyse even under strongly acid conditions. Aluminum can substitute for Fe^{III} in the jarosite structure, and a complete jarosite-alunite solid solution exists (24). Van Bemmelen (11) found Al-contents in yellow mottles from acid sulphate soils in Holland equivalent to between 1.4 and 8% of the trivalent ion positions in jarosite. The jarosite samples from Thailand, referred to in Table 2, show 5 to 12% Al substitution for Fe^{III} if it is assumed that all Al dissolved by the hot 4 N HCl came from jarosite. However, these figures represent maximum values because no correction was made for Al dissolved from other minerals.

The reaction

$$\text{2 jarosite} + \text{3 kaolinite} = \text{2 alunite} + \text{3 limonitic } Fe_2O_3 + 6\ SiO_{2\,(amorph)} + 6\ H_2O \quad \ldots\ldots \quad 24$$

which involves, apart from alunite, compounds typical for acid sulphate soils, has a positive standard free energy change (viz. + 4.7 kcal). This implies that the assemblage jarosite + kaolinite is stable over alunite + limonitic Fe_2O_3 + amorphous silica, in accordance with field and laboratory observations.

Experiment on the formation of alunite-jarosite in sulphuric acid solutions either containing dissolved K, Fe^{III} and/or Al (24) or in contact with ground K-, Al- and Fe-bearing minerals and rocks (58) at high temperatures (80 to 180 °C) showed a strong preference for uptake of Fe. This preference decreases with increasing temperature and with decreasing acidity. The experimental results are in agreement with the frequent concurrence of alunite as hydrothermal alteration product of alkali rich rocks in the presence of sulphuric acid from volcanic emanations (24, 54, 93) and its rarity in low temperature, oxidized environments, associated with pyritic material.

For 37 watersamples from an oxidation experiment on pyritic mud (19, 20) with pH values between 4 and 1.8, Al concentrations between 0.1 and 58 mmoles/l, SO_4 concentrations between 12 and 260 mmoles/l and ionic strengths between 0.03 and 1.0, the values of $\log\left[Al^{3+}\right] + 3\ pH$ and $\log\left[SO_4^{2-}\right] - 2\ pH$ showed a nearly perfect linear relationship. Regression analysis yielded a slope of -1.002 and a correlation coefficient of 0.994 (see open rhombs and circles in Fig.7). Assuming a slope of -1, the data correspond to $\log\left[Al^{3+}\right] + \log\left[SO_4^{2-}\right] + pH = -3.23 \pm 0.16$ (mean and standard deviation resp.). This relationship can be explained by equilibrium between the solution and a basic aluminum sulphate with the stochiometric formula $AlOHSO_4$:

$$AlOHSO_4 + H^+ = Al^{3+} + E_2O \quad \ldots\ldots\ldots\ldots \quad 25$$

with

$$\log K = \log\left[Al^{3+}\right] + \log\left[SO_4^{2-}\right] + pH \quad \ldots\ldots\ldots\ldots \quad 25a$$

For 46 groundwater samples from acid sulphate soils in Thailand, with pH values between 2.8 and 5.5 and Al concentrations between 2.12 and 0.023 mmoles/l, log K (eq. 25a) was obeyed within ± 0.2, and the data on the 120 watersamples in the same pH range considered in this study (20) indicate that precipitation of this compound dictates the upper limit of dissolved Al in the waters in question (Fig.7).

The same is true for acid sulphate waters draining from a strip mining area in Kentucky, U.S., as follows from the data by Musser and Whetstone (82). The only sulphate of such stoichiometry is mentioned in Dana's system of mineralogy (83), is $Al_2(OH)_2.(SO_4)_2.9H_2O$ (lapparentite), which, however, is very soluble and easily hydrolyses to more basic sulphates.

So far no systematic attempts were made to separate and identify or to synthesize the sulphate in question. No patterns attributable to unknown minerals were detected during X-ray diffraction studies on soil material presumably containing $AlOHSO_4$. The material may be amorphous and/or occur in small quantities. The last possibility is suggested by the relatively small amounts of Al (compared to Fe^{III} from jarosite) extracted by HCl from acid sulphate soil material.

The presence of clay minerals is perhaps important in the formation of $AlOHSO_4$ through sulphate absorption (cf. 45) as an intermediate step. Oxidation experiments with pyritic muds in the laboratory have shown that this compound can be formed within a few weeks. During the experiments equilibration with the soil solution (approached from undersaturation, viz. by adding distilled water to the soil) took place within three days.

Fig. 8 displays the range of observed ionic activities in relation to the solubility curves for various Al minerals in typical acid sulphate soil water. It appears that alunite can control dissolved Al at the lowest levels. The actual levels are much higher so the soil solution is in fact oversaturated with alunite and $AlOHSO_4$ is metastable under the specified conditions. log $[Al^{3+}]$ + 3 pH values occur most frequently near to the solubility curve of kaolinite, indicating that this mineral plays a role in the ultimate control of the aluminum hydroxide potential.

Gibbsite, nor basaluminite (= $Al_4(OH)_{10}SO_4$), which can be prepared by partial neutralization of a suspension of Al-saturated montmorillonite in a $Al_2(SO_4)_3$ solution by a saturated solution of $Ca(OH)_2$ (cf.Singh and Brydon (104)), appear to influence dissolve Al. Theoretically, these minerals cannot persist in acid sulphate soils at log $[SO_4^{2-}]$ - 2 pH values above -11.

This corresponds roughly to pH values below 4.5; because of the fairly constant SO_4^{2-} activity in the order of 5 x 10^{-3} for most waters in question, approximate pH values can be indicated on the log $[SO_4^{2-}]$ - 2 pH axis of Fig.8.

Gypsum precipitates rapidly from saturated solutions, and the formation of gypsum crystals of several cms in length was found to take place within a few months in Tertiary pyritic clays in the Netherlands (P. Buurman, pers.com.).

As shown by Fig.9 the Ca^{2+} and SO_4^{2-} activities in groundwater from gypsic soils correspond well to those predicted theoretically. Fig.7 discloses also that gypsum occurs over a wide pH range. At pH values between 6.5 and 8 gypsum is often associated with calcite, at a pH below 4 with jarosite.

Theoretically, jarosite replaces gypsum at low pH, low $[Ca^{2+}]$ or high $[K^+]$ according to:

$$4 \text{ gypsum} + 3 \text{ limonitic } Fe_2O_3 + 2K^+ + 6H^+ = 2 \text{ jarosite} + 4\ Ca^{2+} + 5\ H_2O \quad ..26$$

with

$$\log K = 2 \log [Ca^{2+}] - \log [K^+] + 3 \text{ pH} = 9.85 \quad ....26a$$

However, partly due to very low $[K^+]$ values, jarosite and gypsum were found to occur simultaneously at pH values as low as 2 in pyritic soils oxidized in the laboratory (20).

The Ca^{2+} in gypsum comes either from Ca-carbonate or other Ca-bearing minerals (silicates such as plagioclaze feldspars) or from dissolved and adsorbed Ca^{2+}. $CaCO_3$ as a Ca^{2+}-source for gypsum, formed upon pyrite oxidation, is well-known from Dutch polder soils. In the soils used for the laboratory experiment mentioned before, $CaCO_3$ was absent, and Ca^{2+} for the formation of gypsum came mainly from the exchange complex. The gypsum in the acid sulphate soils in the western part of the Central Plain of Thailand, which may contain up to 18% (by weight) of $CaSO_4.2H_2O$ in some horizon (20), is the result of high concentrations of dissolved Ca^{2+} in the annual floodwater (68).

Due to its comparatively high solubility, gypsum can only persist in soils under relatively dry climatic conditions or in the absence of appreciable leaching. In most soils under humid conditions, its existence is temporary and often seasonal.

4. Acid production, mineral weathering, and the pH of acid sulphate soils

The acid production accompanying pyrite oxidation depends on the fate of the iron. If all iron is oxidized and remains in solution as Fe^{3+}, every "mole" of pyrite produces one equivalent of H^+.

$$FeS_2 + 15/4O_2 + 1/2\ H_2O \rightarrow Fe^{3+} + 2\ SO_4^{2-} + H^+ \quad . . . . \quad 27$$

When dissolved Fe^{2+} is formed instead, the H^+ yield is twice as high:

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \quad . . . . \quad 28$$

Maximum acid production takes place when all iron is oxidized and hydrolysed to solid ferric oxide:

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 4\ H^+ \quad . . . . \quad 29$$

Formation of jarosite in fact represents an incomplete hydrolysis of ferric iron, and less H^+ is generated:

$$FeS_2 + 15/4\ O_2 + 5/2\ H_2O + 1/3\ K^+ \rightarrow 1/3\ \text{jarosite} + 4/3\ SO_4^{2-} + 3\ H^+ \quad 30$$

The strong tendency of ferric iron to hydrolyse and precipitate strongly favours the last two processes and makes pyrite oxidation one of the most acidic of all weathering reactions (113).

The stoichiometry of these reactions is incorporated graphically in Fig.10, which shows the quantitative relationships between pyrite oxidation, acid production, and amounts of $CaCO_3$ necessary for complete neutralization.

Normally negligible amounts of dissolved iron escape precipitation as jarosite or ferric oxide, so Curves a and b have little practical significance. In most acid sulphate soils a large fraction of the iron is incorporated in jarosite (Curve c). With time, jarosite is hydrolysed to ferric oxide and an additional amount of acid (equivalent to d-c) is released. This difference is rather small and H^+ and SO_4^{2-} are produced in nearly equivalent quantities.

The pH depends both on the amount of sulphuric acid produced and on the pH buffering characteristics of the soil material. The frequency distribution of pH values for groundwater samples from the coastal plain in Thailand (Fig.11) shows several prevalent pH ranges. For mangrove soils, reduced subsoils, and non-acid marine soils the pH is generally between 6.5 and 7. In acid sulphate soils (including partly oxidized pyritic subsoils) the pH is between 2.9 and 6, with distinct peaks at pH 3.3 to 4 (jarositic horizons) and 4.2 to 4.5 (top soils).

Much lower values (pH 1.8 to 2.5) are obtained when the parent materials of the acid sulphate soils in question are subjected to aeration under moist conditions in the laboratory. On the other hand a similar treatment of pyritic soil with excess of $CaCO_3$ for neutralization yields distinctly higher pH values (7.2 to 7.8) than the corresponding soils in the field.

The samples referred to in Fig.11 were not taken at random so the frequencies given have little significance, but the predominant pH ranges are representative.

pH values between 1.3 and 2.5 in pyritic soil upon aeration under moist conditions in the laboratory or upon slow air-drying are frequently reported (36, 92, 132). Simple air-drying of potentially acid soil generally produces a slightly higher pH, viz. between 1.5 and 4 (3, 47, 60, 115, 121), probably because oxidation is hampered under dry conditions.

The ready acidification of potentially acid pyritic mud, even when stored for a few weeks in thin polythene bags (16), illustrates that "fresh" pH values reported for potentially acid pyritic subsoils are questionable, unless pH readings were taken within a few days after sampling. The pH values of hundreds of partly oxidized pyritic soil samples from Thailand, Sarawak, The Netherlands, and Germany, measured within 2 days after sampling by simple electrode insertion, were generally well above 3 and only rarely as low as 2.8 to 3.0 (20).

A pH between 3 and 4 is typical for samples of acid sulphate soil horizons from which the pyrite has been removed by oxidation under field conditions (cf. 4, 17, 21, 32, 38, 79). Thus it appears that the pH values for the acid sulphate soils shown in Fig.11 are fairly representative. This indicates that the pH is buffered in certain ranges, which are different for samples oxidized in the field (pH 2.8 to 4) and oxidized in the laboratory (pH 1.3 to 2.5)+).

The effect of these buffering processes can be appreciated by considering the changes in the composition of the soil solution accompanying pyrite oxidation. During a particular experiment (20, 22) involving a non-calcareous (BP) and a calcareous (Mc) pyritic mud (Tab.3) the increase in dissolved SO_4^{2-} as a result of oxidation of a part of the pyrite is balanced for 98% (BP) and for 92% in (Mc) by an equivalent increase in the concentrations of cations.

A decrease in carbonate alkalinity (HCO_3^-) accounts for the remaining 2% (BP) and 8% (Mc). In the acid soil (BP) only 0.3% of the increase in cations can be attributed to H^+, so 99.7% of the sulphuric acid is inactivated by buffering processes.

Three questions arise: (a) where do the cations come from, (b) what mechanisms are responsible for the specific pH ranges encountered, and (c) why are these pH ranges different for oxidation in the field and in the laboratory?

Two sources are available for the cations released into solution: the exchange complex and the soil minerals.

Data on the exchangeable cations of the soil samples corresponding to the water samples in Table 3 are given in Table 4 (determined by Vlek (126)). Except for exchangeable Ca^{2+} in Mc, the exchangeable bases decrease dramatically upon aeration. The decrease is adsorbed Na^+, Mg^{2+}, and Ca^{2+} (in BP only) is roughly proportional to the corresponding increase in the ionic concentrations in the interstitial water. In Mc, both adsorbed and dissolved Ca^{2+} have increased by dissolution of $CaCO_3$ and partial replacement of adsorbed Na^+ and Mg^{2+} by Ca^{2+}. In BP the decrease in adsorbed bases is balanced in part by an increase in exchangeable Al^{3+}, and partly by a decrease in the effective CEC (=the CEC measured at soil pH). The appearance of adsorbed and dissolved Al and the increase in dissolved silica indicate that part of the sulphuric acid has been inactivated by silicate minerals (the soils in question contain no free Al oxides).

More refined calculations (22) have shown that in BP after 47 days of aeration

---

+) Many soil characteristics related to or influenced by pH (CEC data, watersoluble salts (notably Fe and Al), titration curves etc.) are also affected by air-drying. Consequently a tremendous amount of published data on acid sulphate soils has limited value, because it is not representative for actual or future field conditions. Freeze-drying immediately after sampling (123) is advantageous over conventional drying techniques, to prevent or minimize such unwanted effects.

TABLE 3. COMPOSITION OF THE INTERSTITIAL SOLUTION (me/l) OF TWO PYRITIC SOILS UNDER REDUCED CONDITIONS (a) AND AFTER AERATION UNDER MOIST CONDITIONS IN THE LABORATORY FOR 47 DAYS (b). IN ORDER TO FACILITATE COMPARISON, THE Cl^- CONCENTRATIONS WERE SET AT 100 AND THE CONCENTRATIONS OF THE OTHER CONSTITUENTS WERE CHANGED PROPORTIONALLY (20).

	NON-CALCAREOUS PYRITIC SOIL (BP)					CALCAREOUS PYRITIC SOIL (Mc)				
	a	b	b-a	b-a % of SO_4 increase	b-a % of Σ cations	a	b	b-a	b-a % of SO_4 increase	b-a % of Σ cations
pH	6.90	3.34				7.57	7.47			
Cl^-	100	100	0	0		100	100	0	0	
HCO_3^-	2.0	0	- 2.0	- 2.2		8.3	3.4	- 4.9	- 8.3	
SO_4^{2-}	15.1	104.0	88.9	100.0		50.4	109.8	59.4	100.0	
Σ anions	117.1	204.0	86.9	97.8		158.7	213.2	54.5	91.7	
K^+	2.7	2.7	0	0	0	3.7	5.1	1.4	2.4	2.6
Na^+	88.8	103.0	14.2	16.0	16.5	112.0	124.0	12.0	20.2	21.9
Ca^{2+}	4.1	14.9	10.8	12.2	12.5	9.8	25.6	15.8	25.6	28.8
Mg^{2+}	21.4	64.6	43.2	48.6	50.1	32.8	58.2	25.4	42.7	46.3
Fe^{2+}	0.0	10.1	10.1	11.4	11.7	0.0	0.0	0.0	0.0	0.0
Al	$0.0^{+)}$	4.7	4.7	5.3	5.5	$0.0^{+)}$	$0.0^{+)}$	0.0	0.0	0.0
Mn^{2+}	0.1	3.0	2.9	3.3	3.4	0.0	0.2	0.2	0.3	0.4
H^+	0.0	0.3	0.3	0.3	0.3	0.0	0.0	0.0	0.0	0.0
Σ cations	117.1	203.3	86.2	97.2	100.0	158.3	213.1	54.8	92.1	100.0
$H_4SiO_4^0$	0.42	2.74	2.3			0.57	0.28	-0.29		
$Cl^{-++)}$	191	185				74.1	70.9			
moist$^{x)}$	190	190				179	179			

+) not determined

++) analysed Cl^- concentrations

x) The soils were brought to this moisture content by addition of distilled water, 3 days before collecting the solutions by means of centrifuging.

TABLE 4. EXCHANGE CHARACTERISTICS (me/100 g soil) OF THE BP AND Mc SOILS (cf. TABLE 3), AS DETERMINED BY THE BASCOMB (9) METHOD SLIGHTLY MODIFIED BY VLEK (126)

	NON-CALCAREOUS PYRITIC SOIL (BP)				CALCAREOUS PYRITIC SOIL (Mc)			
	a	b	b-a	b-a as % of Σ(b-a) bases	a	b	b-a	b-a as % of Σ(b-a) bases
K^+	2.7	0.8	- 1.9	10.5	2.1	2.1	0	0
Na^+	4.1	1.6	- 2.5	13.9	2.5	2.1	- 0.4	- 50
Ca^{2+}	4.7	1.2	- 3.5	19.4	13.5+)	15.8+)	+ 2.3	+260
Mg^{2+}	16.1	6.0	-10.1	55.1	11.3	10.3	- 1.0	-110
Al^{3+}	0.0	7.2	7.2		0.0	0.0		
Σ cations	27.6	16.8	-10.8		29.4	30.3	0.9	
Σ bases	27.6	9.6	-18.0	100	29.4	30.3	0.9	100
effective CEC	25.2	18.6			23.2	25.0		
CEC at pH 8.2	28.6	29.3			n.d.++)	n.d.++)		

+) adsorbed Ca^{2+} is overestimated due to dissolution of $CaCO_3$ during the extraction of adsorbed cations (compare Σ cations and effective CEC)

++) not determined

TABLE 5. pH IN EQUILIBRIUM WITH AMORPHOUS SILICA, KAOLINITE, AND DIFFERENT MONTMORILLONITES AT $[Ca^{2+}] = [Mg^{2+}] = 10^{-3}$, 25 °C AND 1 atm TOTAL PRESSURE, CALCULATED FROM PUBLISHED STABILITY CONSTANTS OR STANDARD FREE ENERGY DATA

NAME	FORMULA	REFERENCE	EQUILIBRIUM pH
"Mg-montm"	$Mg_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	(55)	3.90
Colony Wyom.	$Mg_{0.229}Al_{1.71}Si_{3.81}O_{10}(OH)_2$	(129)	4.46
Belle Fourche	$Mg_{0.29}Fe^{III}_{0.225}Al_{1.58}Si_{3.935}O_{10}(OH)_2^{0.265-}$	(69)	4.14+)
Aberdeen	$Mg_{0.445}Fe^{III}_{0.335}Al_{1.46}Si_{3.82}O_{10}(OH)_2^{0.415-}$	(70)	3.45+)
Cheto	$Mg_{0.40}Ca_{0.19}Al_{1.71}Si_{3.93}O_{10}(OH)_2$	(94)	6.30

+) Dissolved Fe^{III} assumed to be in equilibrium with hematite about 65% of the increase in dissolved Mg^{2+} and the total increase in dissolved Ca^{2+} and Na^+ come from the exchange complex. The remaining 35% of dissolved Mg^{2+} must come from Mg-bearing minerals.

Three different fractions capable of inactivating sulphuric acid have been identified: (a) (carbonate) alkalinity in solution, (b) exchangeable bases, and (c) weatherable minerals.

a) Alkalinity

The alkalinity of interstitial waters in non-alkaline soils rarely exceeds 10 me/l. So, at moisture contents up to 100%, dissolved alkalinity can contribute to the neutralization of 1 me of acid per 100 g of soil at the most. Sea-water has an even lower alkalinity (2 to 2.5 me/l) than most near-neutral ground waters, and cannot be considered an effective buffering agent, even if copious leaching is applied.

However, in the eastern part of the Central Plain of Thailand, centuries of seasonal flooding with moderately alkaline water (2 to 5 me HCO_3^-/l (20)) have probably increased the pH of the upper horizons of acid sulphate soils to near-neutrality.

b) Exchangeable bases

Except perhaps at extremely low pH, with time, essentially all H^+ adsorbed by the clay complex is taken up by the clay minerals and replaced by Al^{3+}. Exchangeable Al^{3+} appears in appreciable amounts only if the pH (in 0.01 N $CaCl_2$) drops below 5 or 4 (3,34) but a considerable amount of non-exchangeable acidity+) is formed already at higher pH. The pH-dependent CEC is influenced by the nature and the quantities of clay and organic matter present in the soil. For 15 surface soils with widely different clay- and organic C contents the contribution of the organic C and the clay to the pH-dependent CEC of the soil (taken as CEC at pH 8.2 minus CEC at pH 3) was 370 ± 105x) and 15.6 ± 3.4x) me per 100 g of the respective materials (87). In the soils in question between 70 to 80% of the decrease in CEC with decreasing pH took place in the pH range 8.2 to 5.0. Thus, especially for soils high in organic matter and/or clay, the uptake of H^+ associated with the formation of non-exchangeable acidity can contribute significantly to the neutralisation of strong acid under neutral to slightly acid conditions. Between

---

+) For the following discussion, the nature of the "non-exchangeable acidity" or the "pH-dependent CEC" is irrelevant.

x) mean and standard deviation

5 and 10 me of acid per 100 g of soil is taken up by the exchange complex of typical acid sulphate soils in Thailand when the pH drops from 7.5 or 7 to about 5 (see Fig.12).

At a lower pH more H^+ can be consumed because exchangeable Al^{3+} enters the complex. The total amount of acid taken up by the exchange complex of an acid soil is approximately equivalent to the difference between the CEC at pH 7 and the amount of exchangeable bases at soil pH. Data by Sombatpanit (108) for acid sulphate soils (pH 3.5 to 4) from Thailand indicate that this amounts to 10 to 30 me/100 g of soil.

c) Weatherable minerals

The spontaneous transformation of H-clays to Al-clays illustrates that there is no sharp boundary between ion exchange reactions and mineral transformations. Whereas the study of ion exchange equilibria is rather complicated, the equilibria between one or more solid phases at unit activity and the dissolved constituents can be tackled in a relatively simple and straightforward manner. Incongruent or congruent dissolution of minerals by acid involve ion exchange processes, but the actual pathways and mechanisms need not be known for thermodynamic equilibrium studies, and hence the ion exchange reactions can be ignored for our purpose.

The dissolution of divalent metal carbonates by strong acid can be represented by:

$$MCO_3 + 2H^+ \rightarrow M^{2+} + CO_2 + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 31$$

The complete (congruent) dissolution of a metal-aluminum silicate can be written schematically as follows:

$$\text{M-Al-silicate} + (3+a)\ H^+ + b\ H_2O \rightarrow M^{a+} + Al^{3+} + c\ H_4SiO_4^o \quad \ldots\ldots \quad 32$$

Incongruent dissolution can be represented by:

$$\text{M-Al-silicate} + aH^+ + b\ H_2O \rightarrow M^{a+} + c\ H_4SiO_4^o + \text{Al(silicate) residue} \quad \ldots \quad 33$$

$CaCO_3$ (calcite or aragonite) is the most common carbonate in soils. Essentially all metal aluminum silicates are attacked by acid, releasing metal ions and monomeric silica into solution. Generally the silicate minerals are concentrated in the clay fraction and because of their large specific surface area, clay minerals can be important H^+ consumers. The best choice for the Al-silicate residue (Eq.33) is kaolinite. It is the end product of most weathering processes under acid conditions, and occurs widely in acid sulphate soils.

For equilibrium between calcite and solution:

$CaCO_3 + 2H^+ = Ca^{2+} + CO_{2\,(g)} + H_2O$ 34

we can write (square brackets denote activities; equilibrium constants (for 25 °C and 1 atm pressure) according to Stumm and Morgan (113):

$\log [Ca^{2+}] + \log P_{CO_2} + 2pH = 9.78$ 34a

If C_A equivalents of a strong acid (H_2SO_4) are added to 1 liter of pure water brought in contact with calcite, the only ions important quantitatively at near neutral pH are Ca^{2+}, HCO_3^- and SO_4^{2-}. Thus electroneutrality requires (brackets denote molar concentrations):

$C_A + (HCO_3^-) = 2\,(Ca^{2+})$ 35

Moreover, P_{CO_2} and the activities of HCO_3^- and H^+ are related by (113):

$[HCO_3^-]\;[H^+] = 1.48 \times 10^{-8} \times P_{CO_2}$ 36

Neglecting activity corrections, substituting a representative value for P_{CO_2} (10^{-2} atm), and combining Equations 34a, 35, and 36 gives:

$1.2 \times 10^{12}\;[H^+]^3 - C_A\,[H^+] - 1.48 \times 10^{-10} = 0$ 37

Equation 37 enables us to calculate the pH of the system $CaCO_3$ -H_2O at $P_{CO_2} = 10^{-2}$ atm as a function of the amount H_2SO_4 added.

Fig.7 (Curve 2) shows that the pH remains close to 7 even after the addition of considerable amounts of strong acid.

As an example of the incongruent dissolution of a silicate mineral, the transformation of Mg-montmorillonite ($Mg_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2$) to kaolinite ($Al_2Si_2O_5(OH)_4$) is considered:

6 Mg-mont. $+ 2H^+ + 23\,H_2O = Mg^{2+} + 7$ kaolinite $+ 8\,H_4SiO_4^0$ . . . 38

At equilibrium, the following relationship holds (log K from data by Helgeson (55)):

$\log K = \log [Mg^{2+}] + 2pH + 8 \log [H_4SiO_4^0] = -16.8$ 38a

The addition of one equivalent of strong acid (H_2SO_4) releases 4 moles of silica, so:

$(H_4SiO_4^0) = 4\,C_A$ 39

Electroneutrality of the solution requires:

$$2(Mg^{2+}) + (H^{+}) = C_A \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 40$$

If activity corrections are neglected, Equations 38a, 39, and 40 can be combined to give

$$10^{(-21.3-8\log C_A)} \times \left[H^{+}\right]^2 + \left[H^{+}\right] - C_A = 0 \quad \ldots\ldots\ldots\ldots \quad 41$$

The pH of the system montmorillonite-kaolinite-H_2O as a function of the amount of strong acid added can be calculated from Equation 41 (Curve 3 in Fig.13). Once, the concentration of $H_4SiO_4^0$ will become high enough to permit precipitation of amorphous SiO_2. Amorphous silica will then hold the activity of dissolved $H_4SiO_4^0$ at a constant level of $10^{-2.7}$. Now, according to Equation 38a, log $\left[Mg^{2+}\right]$ + 2pH is fixed at 4.8 and Equation 41 reduces to:

$$10^{5.1}\left[H^{+}\right]^2 + \left[H^{+}\right] - C_A = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 42$$

which is represented by Curve 3a in Fig. 13.

Similar curves are given for the congruent dissolution of kaolinite before and after precipitation of amorphous SiO_2 (Curves 4 and 4a), and for the incongruent dissolution of Mg-chlorite ($Mg_5Al_2Si_3O_{10}(OH)_8$) to yield kaolinite (Curve 1). All necessary equilibrium constants were calculated from data by Helgeson (55).

The buffer intensity (=the amount of strong acid necessary to cause a drop in pH of one unit, or .$-dC_A$/pH, cf. (113)) is very high for calcite (Curve 2)moderately high for Mg-chlorite (Curve 1), for montmorillonite + amorphous SiO_2 (Curve 3a) and for kaolinite + amorphous SiO_2 (Curve 4a) and very low for Mg-montmorilllonite in the absence of amorphous silica (Curve 3). Buffering takes place at high pH levels in the presence of calcite or Mg-chlorite, and under acid conditions (pH 2.5 to 4) if montmorillonite or kaolinite and amorphous silica are present.

Whether the pH is actually kept at the levels predicted by Fig.13 depends on the rates of the weathering processes. Data on acid sulphate soils rich in Mg-chlorite (79) indicate that this mineral is not very effective in maintaining high pH values. Calcite dissolves rapidly under acid and slightly acid conditions and near-equilibrium with $CaCO_3$ in partly oxidized pyritic soil has been demonstrated (19).

Relatively low CO_2 pressures in samples exposed to the atmosphere are responsible for high pH values in air-dried calcareous soil compared with the same material oxidized in the field (see Fig.11).

Buffering according to Curves 3a and 4a can take place only if dissolved silica is regulated by amorphous silica. Fig. 14 shows a stability diagram of Mg-montmorillonite, Mg-chlorite, kaolinite, and gibbsite together with data on some 360 samples of surface-and ground waters from the coastal plain in Thailand. It appears that amorphous silica saturation does provide an upper limit of $[H_4SiO_4^o]$. Many acid sulphate waters with log $[H_4SiO_4^o]$ close to - 2.7 have a composition in the vicinity of the Mg-montmorillonite - kaolinite boundary. This suggests that the relevant soil solution parameters are indeed governed by reaction 3a in Fig. 13.

Fig.15 shows a part of the same diagram with data on water samples from two different acid sulphate soils. The water samples were taken from the field and in the laboratory upon oxidation of the corresponding pyritic muds by aeration after treatment with distilled water and with seawater, both in a "closed" system and after repeated washing with fresh distilled water and seawater. In the laboratory, the pH drops to around 2 and log $[Mg^{2+}]$ + 2pH reaches extremely low figures compared with field conditions. The waters become supersaturated with amorphous silica but their composition remains close to the Mg-montmorillonite-kaolinite boundary. This suggests that equilibrium between the two minerals is established rapidly, while precipitation of amorphous silica lags behind the release of $H_4SiO_4^o$ from silicate minerals.

Fig.13 illustrates that the failure of amorphous silica to maintain log $[H_4SiO_4^o]$ at - 2.7 gives rise to very low pH values according to the broken extension of Curve 3. The presence of $H_4SiO_4^o$ in equilibrium with amorphous silica (Curve 3a) would have kept the pH at about 3.6, a value typical for field conditions.

Considerable variation in the composition and stability of montmorillonites occurs. However, as shown by Table 5 the pH at equilibrium between different montmorillonites, kaolinite, and amorphous silica is generally close to the values observed in typical acid sulphate soils.

The different levels of log $[Mg^{2+}]$ + 2pH for the BP samples and the Ra samples (Fig.15) are well within the range typical for the montmorillonites given in Table 5.

The effectiveness of the congruent dissolution of kaolinite as a buffering process (Curves 4 and 4a in Fig.13) can be checked by considering the value of log $[Al^{3+}]$ + 3pH + log $[H_4SiO_4^o]$. This is 3.815 at equilibrium at 25 °C and 1 atm (55).

In two representative acid sulphate soils from Thailand, 8 water samples taken from the field at depths between 50 and 140 cm had lowest values for log $[Al^{3+}]$ + 3pH + log $[H_4SiO_4^o]$ at two months after the start of flooding in the rainy season, viz 3.0 ± 0.15 (mean and standard deviation for 8 samples).

The values increased steadily with time and reached 3.81 ± 0.16 four months later. Apparently near-equilibrium with kaolinite had been established. However, during the oxidation experiment referred to in Fig 15, log $[Al^{3+}]$ + 3pH + log $[H_4SiO_4^o]$ reached values as low as 0 to 0.3 suggesting that the dissolution of kaolinite did not keep up with the decrease in pH. The same was true for congruent dissolution of montmorillonite.

The high frequency of pH values between 1.5 and 2.5 in artificially aerated pyritic muds can be attributed mainly to the buffering by water: the amount of acid necessary to decrease the pH from 2 to 1 is roughly 9 times the amount required to decrease the pH from neutrality to 2. Moreover, under acid conditions H^+ ions can be consumed by SO_4^{2-} :

$$SO_4^{2-} + H^+ = HSO_4^- \quad \ldots\ldots \quad 43$$

$$\log K = \log [HSO_4^-] - \log [SO_4^{2-}] + pH = 1.99 \quad \ldots\ldots \quad 43a$$

Owing to the large amount of dissolved sulphate generally present (0.1 to 0.3 M SO_4^{2-}) at such low pH values, the formation of bisulphate can contribute significantly to the stabilisation of the pH at about 2.

Summarizing, it appears that the incongruent dissolution of montmorillonite takes place rapidly. This process is capable of maintaining an equilibrium solution even at high rates of acid formation. If sufficient time is available for dissolved silica to polymerize and precipitate as amorphous silica (which appears to be the case under field conditions) the montmorillonite-kaolinite equilibrium can buffer the pH between 3.5 and 4.5.

A much lower equilibrium pH is established if dissolved silica increases beyond the solubility of amorphous SiO_2. This happens upon rapid oxidation associated with high rates of silica release.

In the course of months, equilibrium between kaolinite (as well as montmorillonite) and its dissolved constituents is established and can help to maintain pH values between 3.5 and 4 under field conditions.

It should be pointed out that other processes may be involved in maintaining the typical field pH values of 3 to 4. The assemblage jarosite-limonitic goethite will tend to keep the pH at about 3.7 (see Fig.1). The same holds for kaolinite + $AlOHSO_4$ + amorphous silica:

$$\text{kaolinite} + 4H^+ + 2SO_4^{2-} = 2AlOHSO_4 + 2SiO_{2\,(amorph.)} + 3H_2O \quad \ldots\ldots \quad 44$$

with

$$\log K = 2pH - \log \left[SO_4^{2-}\right] = 9.75 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 44a$$

which gives pH = 3.73 at $\log \left[SO_4^{2-}\right] = -2.3$.

The dark shaded area near to the intersection of the solubility curves of kaolinite and $AlOHSO_4$ in Fig.8 shows that this relationship is obeyed reasonably well in many acid sulphate soils.

Of course numerous other weathering processes may contribute to acid consumption and pH buffering. Mica's and feldspars are particularly important because they probably provide much of the K^+ in jarosite.

So far the emphasis has been on the regulation of the pH, which is an intensity factor. A very important capacity factor is the amount of acid that can be inactivated by a given quantity of soil. If ion exchange processes and incongruent dissolution of silicates (with Al conserved in the solid phase) take place only, the acid neutralizing capacity of the soil is equal to the total amount of bases ($MgO+CaO+Na_2O+K_2O$, expressed in equivalents) present in the soil. Most non-calcareous marine clay soils contain 75 to 200 me bases/100 g of soil. Each percent of $CaCO_3$ present increases these figures by 20 me/100 g soil. The carbonate-Ca^{2+} is readily available for exchange with H^+, but the release of cations by silicate minerals is often slow.

Soils consisting mainly of kaolinite are poor in bases, but here acid can be inactivated by congruent dissolution, whereby H^+ in fact displaces Al^{3+}. This process takes place at low pH only and cannot prevent serious acidification. No buffering can be provided by free silica minerals as quartz.

The extent of mineral weathering in actual acid sulphate soils can best be evaluated by studying the mineralogy. Unfortunately little research has been done on the (clay-) mineralogy of acid sulphate soils.

Kaolinite was found as the dominant clay mineral in acid sulphate soils from Guinea (59), Senegal (124), Vietnam (57), and Malaysia (3). This reflects mainly the kaolinitic nature of many sediments in tropical areas, but formation of kaolinite at the expense of 2:1 clay minerals in acid sulphate soils is frequently evident (3, 30, 67, 107). On the other hand no changes in clay mineralogy could be observed in acid sulphate soils in Sarawak (4). In California, acid sulphate soil formation was accompanied by a distinct decrease in chlorite content and an accompanying increase in montmorillonite (79). This was attributed to selective removal of the "brucite layer" of Mg-chlorite under acid conditions.

Both in Malaysian and Californian acid sulphate soils a decrease in the amount of crystalline material was observed (3, 79). Amorphous silica ("opal") was reported from acid sulphate soils in Australia and Senegal (115, 124).

The formation of montmorillonite from chlorite and the formation of kaolinite from 2:1 clay minerals in acid sulphate soils is in accordance with the theoretical stability relationships depicted in Fig.14.

Dissolution of quartz and subsequent silification of low-silica clays as postulated for acid sulphate soils in Senegal (124) is very unlikely on theoretical grounds.

A subject of great practical importance is the problem of increasing the pH of acid sulphate soils to near neutral values by applying soil amendmends. The pH is kept low by "H^+-dissociating groups" including (1) the exchangeable and non-exchangeable acidity, (2) basic sulphates such as jarosite and $AlOHSO_4$, and (3) dissolved acidity, including H^+ ions and hydrolysable ions (mainly Al- and Fe^{III} species). Theoretically the weathering of silicates is reversible. "Reverse weathering" (cf. 43), e.g. the formation of montmorillonite from kaolinite, would contribute to the amount of base that must be added to obtain a certain increase in pH above pH 3.5 to 4. Fortunately kaolinite is very inert in this respect, and "reverse weathering" takes place to a significant extent only under near-neutral to alkaline conditions (10).

Dissolved acidity is quantitatively unimportant in acid sulphate soils in the field, because normally the pH does not drop below 3 and because much of the dissolved acidity is removed (or can be removed easily) by leaching and diffusion. However, dissolved acidity can be responsible for more than 75% of the base-neutralizing capacity of pyritic material oxidized in laboratory experiments or by air-drying (cf.data by Rasmussen (92) and by Sombatpanit (108)).

In practice the base neutralizing capacity (in me/100 g soil), or the amount of base (e.g. $CaCO_3$) necessary to obtain near-neutral pH values, is equal to the CEC at pH 7 minus the sum of the exchangeable bases at soil pH plus the amount of SO_4^{2-} in basic sulphates, expressed in me/100 g soil. The best way to determine the base neutralizing capacity is to prepare a "slow" titration curve of the soil in question (28).

It is interesting to realize that sulphate reduction (and hence pyrite formation) involves a production of alkalinity that is equivalent to the acidity released during pyrite oxidation.

The decrease in the concentration of SO_4^{2-} in the interstitial water during sulphate reduction and formation of iron sulphides is balanced by an equivalent increase in dissolved HCO_3^- (4, 14). The overall process can be schematized as follows (CH_2O represents organic matter):

$$3\ SO_4^{2-} + 6\ CH_2O \rightarrow 6\ HCO_3^- + 3\ H_2S$$

$$3\ H_2S + Fe_2O_3 \rightarrow FeS_2 + FeS + 3\ H_2O$$

$$3\ SO_4^{2-} + 6\ CH_2O + Fe_2O_3 \rightarrow FeS_2 + FeS + 6\ HCO_3^- + 3\ H_2O \quad \ldots\ldots \quad 45$$

The (carbonate) alkalinity formed by this process is either removed by diffusion and/or leaching or retained by precipitation as $CaCO_3$ (cf. 49). The interstitial water of marine muds associated with sulphate reduction is often highly supersaturated with calcite, possibly because dissolved organic compounds inhibit crystallization (14). The alkalinity is carried away, leading to a separation between a potentially acid material (pyritic mud) and actual alkalinity (HCO_3^-), which is mainly absorbed by the vast mass of the oceans. This process is the crucial step that is ultimately responsible for the formation of acid sulphate soils.

5. Profile development of acid sulphate soils

Hitherto the emphasis was placed on properties and processes in relation to soil material. Soils, however, are characterized by a vertical sequence of horizons with different properties. Knowledge of the nature of the horizon differentiation is important for understanding and evaluating the acid sulphate soil problem.

Due to the character of their parent material and as a result of their physiographic position, acid sulphate soils generally have a permanently water-saturated, reduced horizon at some depth. Depending on the drainage condition, the upper part of the soil is aerated and oxidized permanently, or, in case of seasonally flooded soils, during a part of the year.

Fig. 16 shows diagrams of the pH (fresh and after aeration in the laboratory), and of the contents of jarosite-S and pyrite-S as a function of depth for ten acid sulphate soils and one non-acid marine soil from Thailand and from The Netherlands (20).

The profiles BP-5, KD-1, Ca-1, Ra-2, Ra-1, and Na-2 can be regarded as a chronosequence, with BP-5 as the youngest soil, and Na-2 as the oldest. In BP-5, the distribution of pyrite with depth still reflects the situation in the original mangrove mud, where the pyrite content generally increases with depth in the upper 100 to 150 cm (3, 4, 21).

Reclamation and shallow drainage has resulted in acidification of the surface soil, but as yet no jarosite is present in the BP-5 samples (the soil profile showed a few yellow mottles locally between 20 and 30 cm). In the next stage (KD-1) the pyritic horizon starts at greater depth and a distinct jarositic horizon appears. As the soils become older and better drained, the jarositic and pyritic horizons are found at progressively greater depths. These two horizons are distinctly separated, in accordance with the difference in stability areas (in terms of E_H and pH) of jarosite and pyrite (see Fig.1). Where the horizons overlap (KD-1 and Mij-1), jarosite occurs in pyrite-free, vertical zones along cracks and root channels, which penetrate locally into the reduced subsoil.

With time, the jarositic horizon moves downwards as a result of hydrolysis to ferric oxide in the upper part (leaving a distinct accumulation of ferric oxide above the jarositic horizon) and formation of new jarosite in the lower part (20).

The diagrams indicate clearly that only a part of the pyrite-S is conserved after oxidation; most of the sulphate is removed by leaching and/or diffusion (water soluble sulphate-S is generally negligible compared with pyrite-S and jarosite-S; only Na-2 shows a (distinct) accumulation of gypsum between 50 and 80 cm below the surface).

The occurrence of jarosite can be explained on the basis of the physico-chemical conditions in the horizons in question (see Fig.1), but the amount present seems to depend in part on the volume available for precipitation (root channels and cracks) (125).

Below the predominantly oxidized layer the pyrite content increases abruptly with depth, suggesting that pyrite oxidation takes place mainly in a very narrow zone. The non-acid soil T-1 is situated nearer to the coast than Ra-1 and Ra-2 and is undoubtedly younger than these acid sulphate soils, but yet the pyritic subsoil occurs at a greater depth. T-1 also shows a higher degree of physical ripening (as evidenced by bulk density figures and N-values) than the acid sulphate soils (125). Before reclamation (all three soils are presently under lowland rice) the non-acid soil was probably subjected to a relatively high level of evapotranspiration compared with the acid sulphate soils, where adverse soil conditions prevented the development of a luxuriant vegetation. This probably explains the greater depth of the reduced pyritic subsoil in the non-acid soil.

The pH increases distinctly with depth in the upper part of the pyritic subsoil, especially in the younger acid sulphate soils from Thailand (BP-5, KD-1, and Ca-1) and in the Dutch soils (former lake bottoms (marine sediments) reclaimed between 90 and 125 years ago). However, in some soils (BP-5, Ra-1, and Ra-2) pH values between 3.5 to 4 occur in the pyritic horizon. This probably reflects, at least in part, downward diffusion of acid from the oxidizing zone.

The relatively high pH-values in the surface soils of the older acid sulphate soils appear to result from a combination of factors: (1) the disappearance of jarosite, (2) the slow "back titration" of the soil acidity by weatherable minerals still present, (3)(in the acid sulphate soils in Thailand) the effect of fresh sediment and of dissolved alkalinity (especially in Na-2) in the flooding water, and (4) (in the Dutch soils) the application of lime as a soil amendment.

On the other hand, during the dry season in Thailand, the capillary rise of an acid soil solution (pH 3.5 to 4) has an opposite effect.

The various equilibria between soil minerals and the interstitial water reported in the previous chapters, may be valid for certain zones only (in this respect information is available only for soils from Thailand). The relationship expressed by Equation 25a, which suggests the presence of $AlOHSO_4$, was found to hold regardless of age of the soil or of depth. In the Ra-soils equilibrium between kaolinite and the soil solution was observed only between 50 and 140 cm at some time of the year, whereas above and below this zone supersaturation with kaolinite was observed always. Saturation with amorphous silica is typical for all acid sulphate soils, but only at intermediate depths. Surface soils and pyritic subsoils are generally undersaturated with amorphous SiO_2.

Except in the (near-neutral) top soil of Na-2, soil reduction upon flooding is strongly impeded in the older acid sulphate soils. This is especially true for the jarositic horizons and, to a lesser extent, for the surface soils.

Low contents of easily decomposable organic matter in combination with a low pH (which hampers microbial growth) and the presence of relatively stable ferric compounds (especially jarosite can be expected to counteract a decrease in E_H) are probably responsible.

Organic matter is generally higher in younger acid sulphate soils and in pyritic subsoils. This is probably the main reason for the relatively rapid development of reduced conditions when flooding young acid sulphate soils. Very high concentrations of dissolved iron and a relatively rapid rise in pH are typical for these soils upon submergence. Such relationships are probably important in understanding the differences in chemical and electrochemical kinetics exhibited by various acid sulphate soils used for lowland rice cultivation (cf. 84).

Conclusions

Sulphate reduction and pyrite formation in tidal swamps and seabottom sediments are invariably associated with the production of alkalinity (dissolved HCO_3^-).

The carbonate alkalinity is generally not conserved in the sediment (e.g. by precipitation as $CaCO_3$), but carried away to the sea. This separation between potential acidity (pyrite) and actual alkalinity is the crucial step in the formation of acid sulphate soils.

Potential acid sulphate soils usually contain between 1 and 5% pyrite-sulphur. After drainage and aeration, pyrite oxidizes and yields sulphuric acid.

The rate of pyrite oxidation is low at near-neutral pH but increases strongly with decreasing pH. At pH 1 to 4 certain microorganisms oxidize Fe^{2+} to Fe^{3+}, which is a far more efficient oxidant for pyrite than free oxygen. In the absence of these microorganisms, ferrous iron oxidation is very slow at low pH. The acidophilic character of the microorganisms and the fact that ferric iron is appreciably soluble only at low pH are the main reasons for the strong influence of pH on the oxidation of pyrite. Sufficient moisture and a favourable temperature are important for microbial activity and hence promote pyrite oxidation. The diffusion of O_2 (necessary for oxidation of Fe^{2+})seems to be a rate-limiting step in pyrite oxidation in field soils.

Under acid ($pH < 4$), oxidized conditions, jarosite ($KFe_3(SO_4)_2(OH)_6$) is the most important product of pyrite oxidation. Sodium and hydronium can substitute for K^+ in the jarosite structure but the preference for potassium (derived from the soil exchange complex, from the soil solution and from K-bearing minerals) is very high.

Another basic sulphate, $AlOHSO_4$, appears to be important in controlling the level of dissolved aluminium in acid sulphate soils. Gypsum is commonly associated with pyrite oxidation both in acid sulphate soils and in non-acid marine soils, if sufficient Ca^{2+} is available and strong leaching is absent.

In most acid sulphate soils more than 99% of the sulphuric acid is inactivated by dissolved (carbonate) alkalinity, by ion-exchange processes and by mineral weathering. In the absence of $CaCO_3$, the montmorillonite-kaolinite equilibrium in the presence of amorphous silica may play an important role in buffering the pH between 3 and 4, a range typical for acid sulphate soils. Other equilibria that contribute to maintaining such pH values involve kaolinite + $AlOHSO_4$, and jarosite + limonitic ferric oxide. At the high rates of pyrite oxidation observed under well-aerated conditions encountered during air-drying and oxidation experiments in the laboratory, these buffering reactions lag behind the release of sulphuric acid, and the pH drops to much lower values (1.5 to 2.5).

The buffer capacity of the soil during acidification is determined mainly by the pH-dependent CEC (especially important in the pH range 7 to 4) and by the exchangeable bases and the bases contained in easily weatherable minerals. The exchangeable and non-exchangeable acidity and the basic sulphates determine the amount of base (e.g. $CaCO_3$) necessary for increasing the pH of acid sulphate soil material.

Well developed acid sulphate soils are characterized by a jarositic horizon overlying the pyritic subsoil. With time, the jarositic horizon and the upper boundary of the pyritic subsoil move downward. In the upper part of the jarositic horizon jarosite hydrolyses, leaving a residue of ferric oxide.

The chemical characteristics of acid sulphate soil material differ depending on depth below the surface and stage of soil development.

Acknowledgements

Much of the material presented in this paper was collected by the author during his research on acid sulphate soils in Thailand. This work was supported by a grant from the Netherlands Foundation for the Advancement of Tropical Research (WOTRO). The cooperation of the Director General, Dr Bancherd Balankura, and staff of the Land Development Department, Government of the Kingdom of Thailand, is gratefully acknowledged. Thanks are due especially to Miss Suwatana Rangsikul, Mr. P.Vlek, Mr. L.Th.Begheijn, Mr. J.van Doesburg and Mr. R.Schoorl for help with water- and soil analyses.

The author wishes to thank Mr.W.L.Lindsay and Mr.J.van Schuylenborgh for their critical reading of parts of the manuscript.

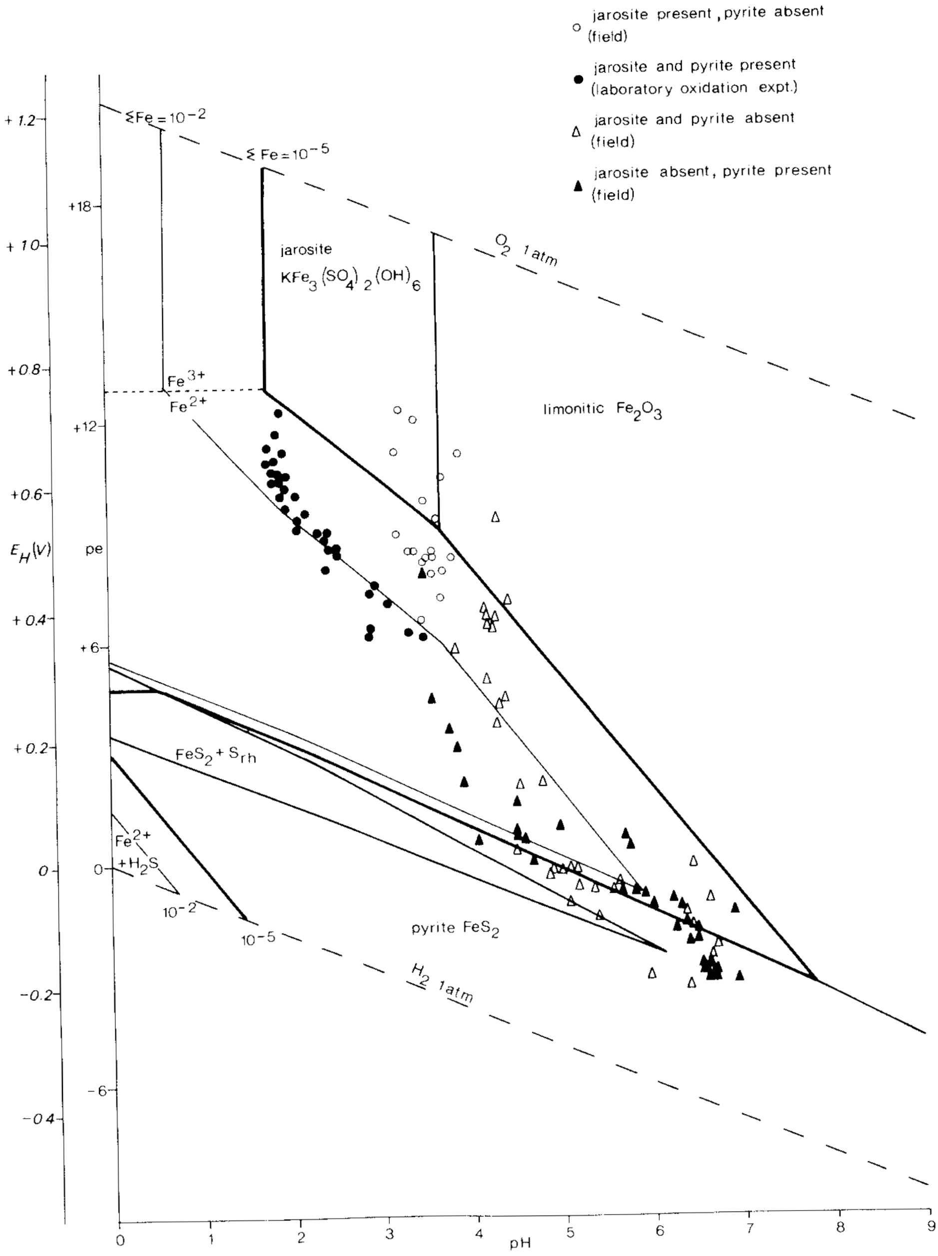


Fig.1: pe - pH diagram of pyrite, rhombic sulphur, limonitic Fe_2O_3, jarosite and dissolved K^+, SO_4^{2-}, Fe^{2+} and Fe^{3+} at $\log\left[SO_4^{2-}\right] = -2.3$ $\log\left[K^+\right] = -3.3$, 25 °C and 1 atm. total pressure. Symbols refer to E_H - pH data measured in coastal plain soils in Thailand.

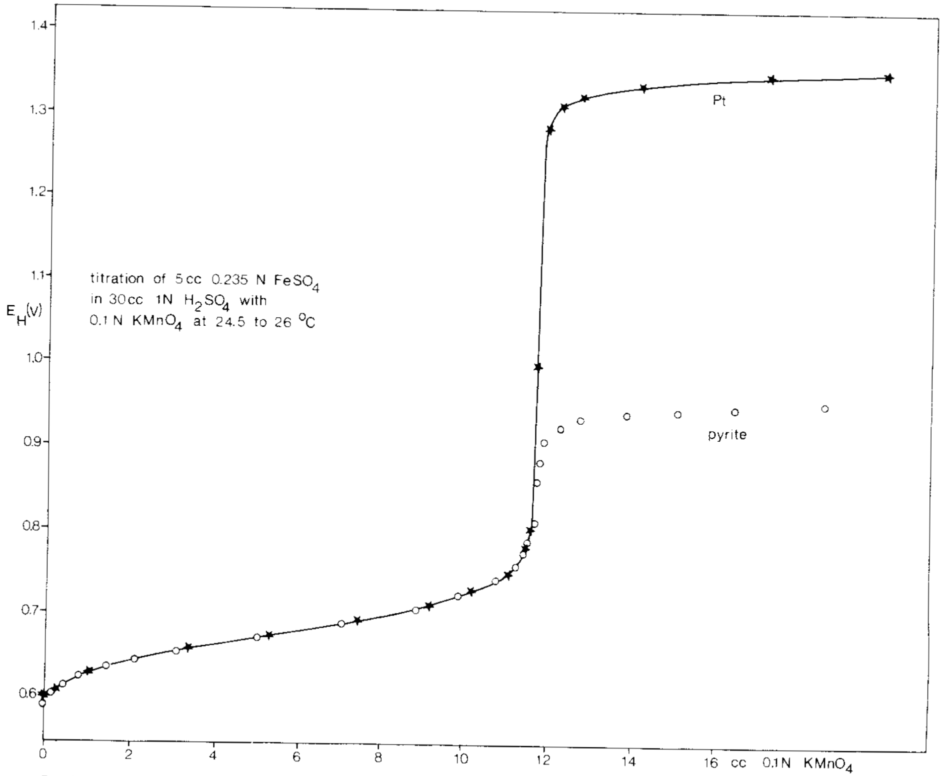


Fig. 2: Potentiometric titration of $FeSO_4$ by $KMnO_4$ recorded by a Pt-electrode and a pyrite electrode.

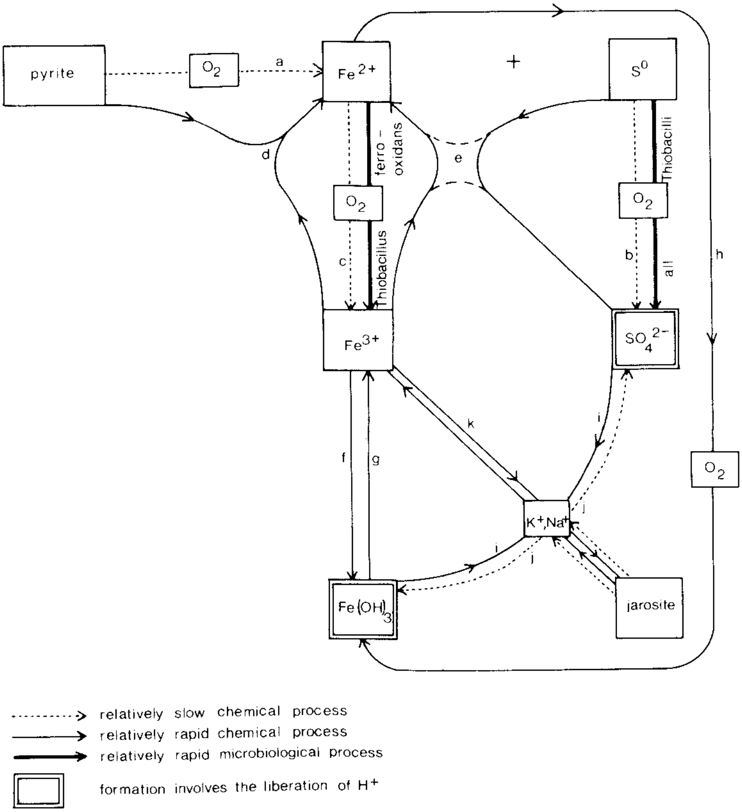
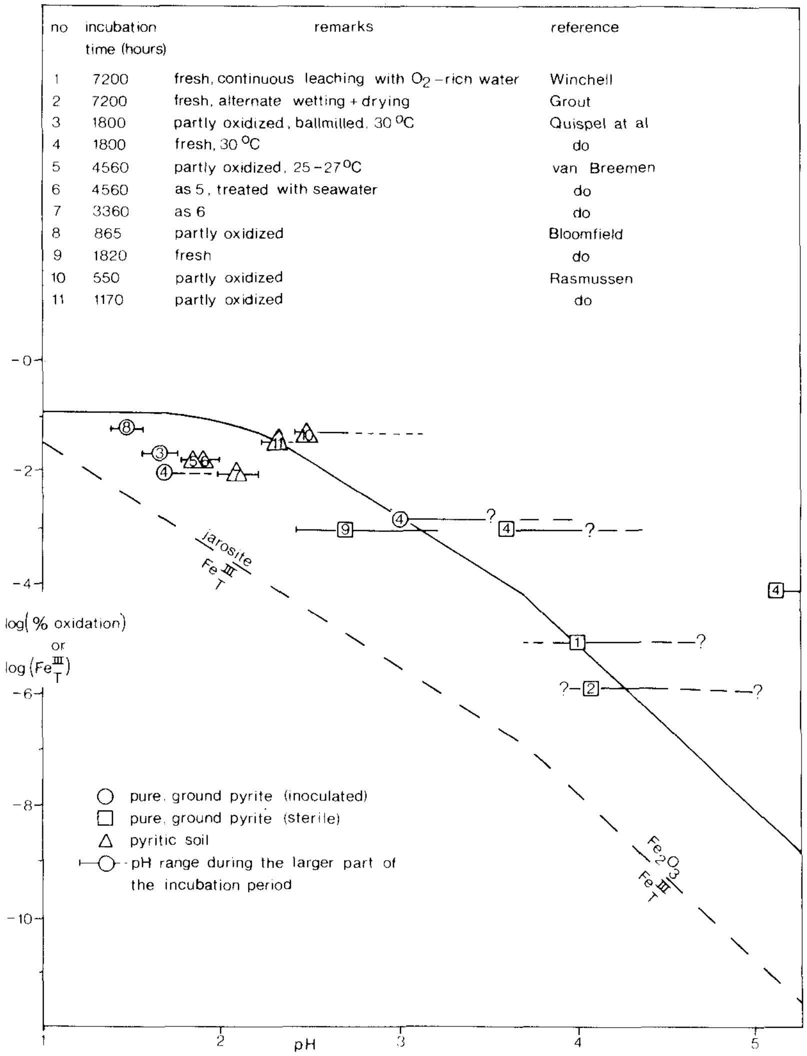


Fig. 3 Pathways in pyrite oxidation



no	incubation time (hours)	remarks	reference
1	7200	fresh, continuous leaching with O_2-rich water	Winchell
2	7200	fresh, alternate wetting + drying	Grout
3	1800	partly oxidized, ballmilled, 30 °C	Quispel at al
4	1800	fresh, 30 °C	do
5	4560	partly oxidized, 25-27°C	van Breemen
6	4560	as 5, treated with seawater	do
7	3360	as 6	do
8	865	partly oxidized	Bloomfield
9	1820	fresh	do
10	550	partly oxidized	Rasmussen
11	1170	partly oxidized	do

Fig.4 Amount of pyrite (expressed as % of the original quantity) oxidized per hour (solid line) by dissolved ferric iron in equilibrium with jarosite or 'limonitic' Fe_2O_3 (broken line) at $\log[SO_4^{2-}]=-2.3$, $\log[K^+]=-3.3$, ionic strength = 0.1, 25 °C and 1 atm. total pressure. The oxidation rate curve is valid for partly oxidized soil pyrite (see text). Symbols indicate observed (average) oxidation rates.

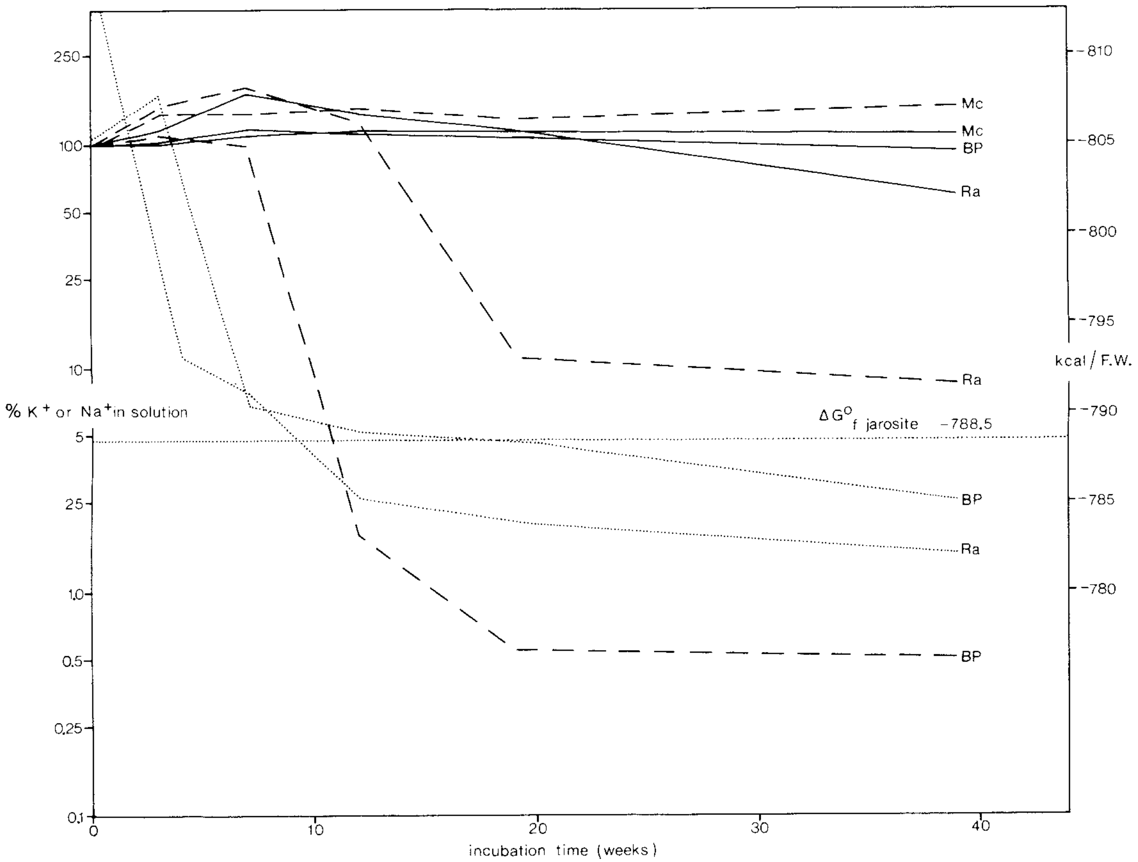


Fig. 5: Concentrations of Na^+ (solid line) and K^+ (broken line), expressed as % of the initial concentrations, in three pyritic soils (Ra, BP and Mc) upon aeration of originally reduced samples in the laboratory.
Ra and BP show strong acidification, accompanied by the formation of jarosite. Mc is calcareous and does not acidify. The dotted lines indicate the apparent $\Delta G^o_{f\ jarosite}$, calculated from soil solution data, E_H and pH for Ra and BP, and the actual $\Delta G^o_{f\ jarosite}$.

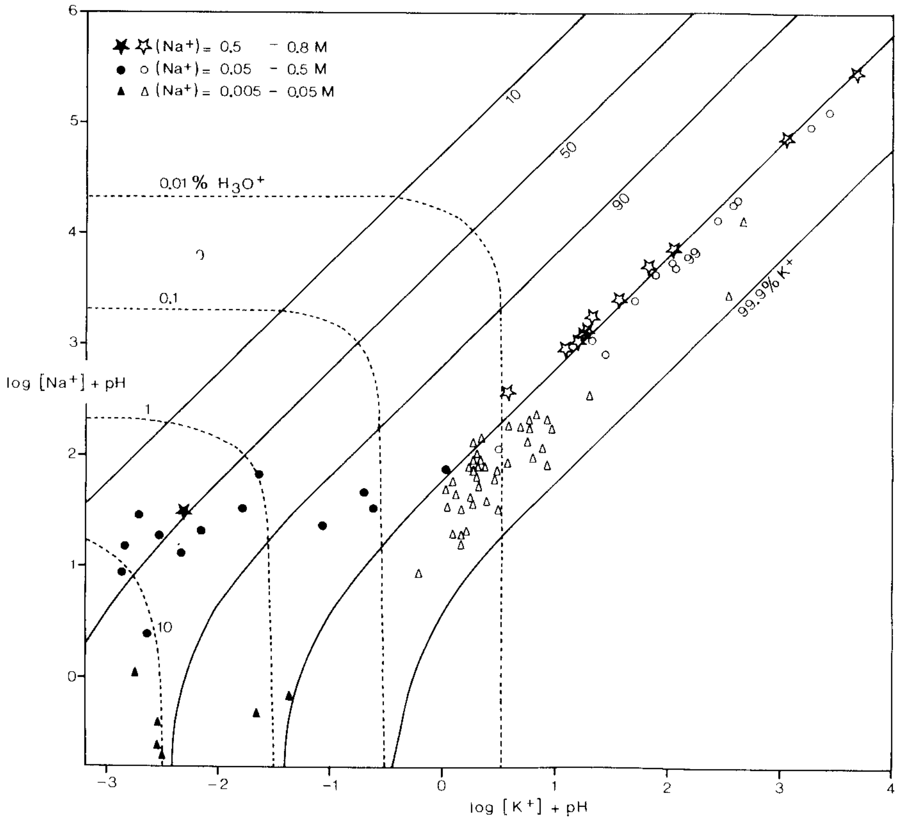


Fig.6: Compositional variation in jarosite resulting from $K^+ - Na^+ - H_3O^+$ substitution as a function of pH and the activities of K^+ and Na^+ in the equilibrium solution at 25 °C and 1 atm. total pressure. The symbols indicate the composition of the soil solution of acid sulphate soils in Thailand and Sarawak (open symbols) with pH 3 to 5, and of pyritic samples oxidized in the laboratory with pH values between 1.8 and 3 (solid symbols).

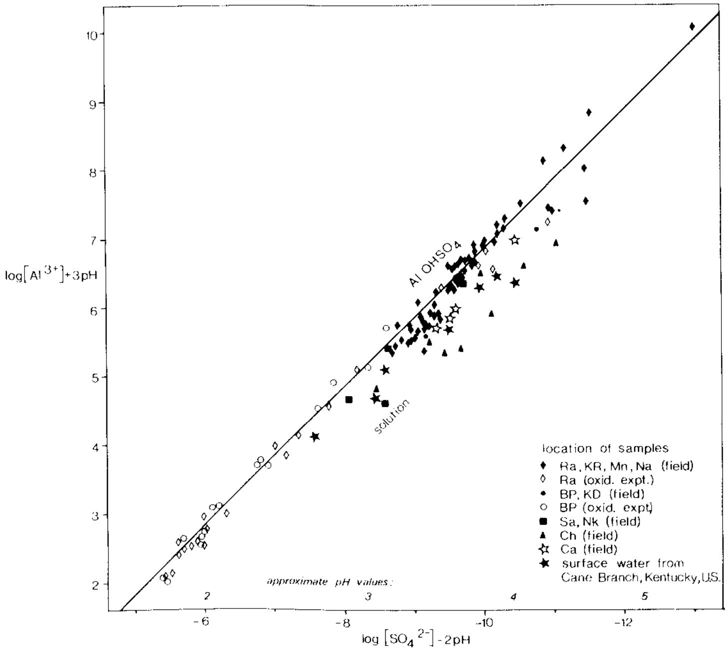


Fig. 7: Observed pH values and activities of dissolved Al^{3+} and SO_4^{2-} in different acid sulphate soils in Thailand in relation to the solubility curve of Al $OHSO_4$.

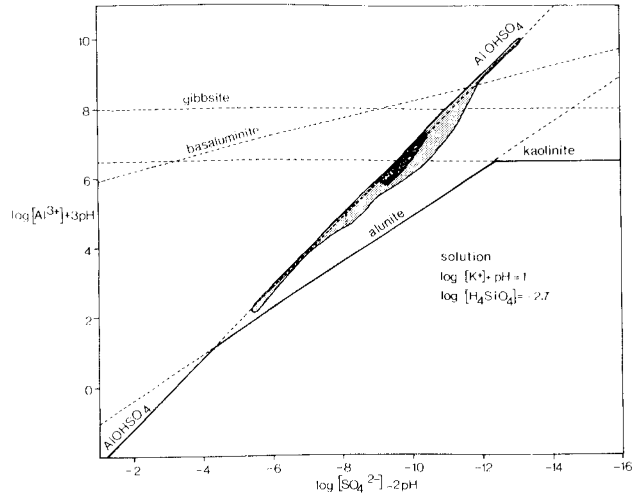


Fig. 8: The range of log $[Al^{3+}]$ +3pH and log$[SO_4^{2-}]$ - pH values in relation to the solubility curves of Al $OHSO_4$, alunite, kaolinite, basaluminite and gibbsite. Darker shaded area denotes the range of most frequent values.

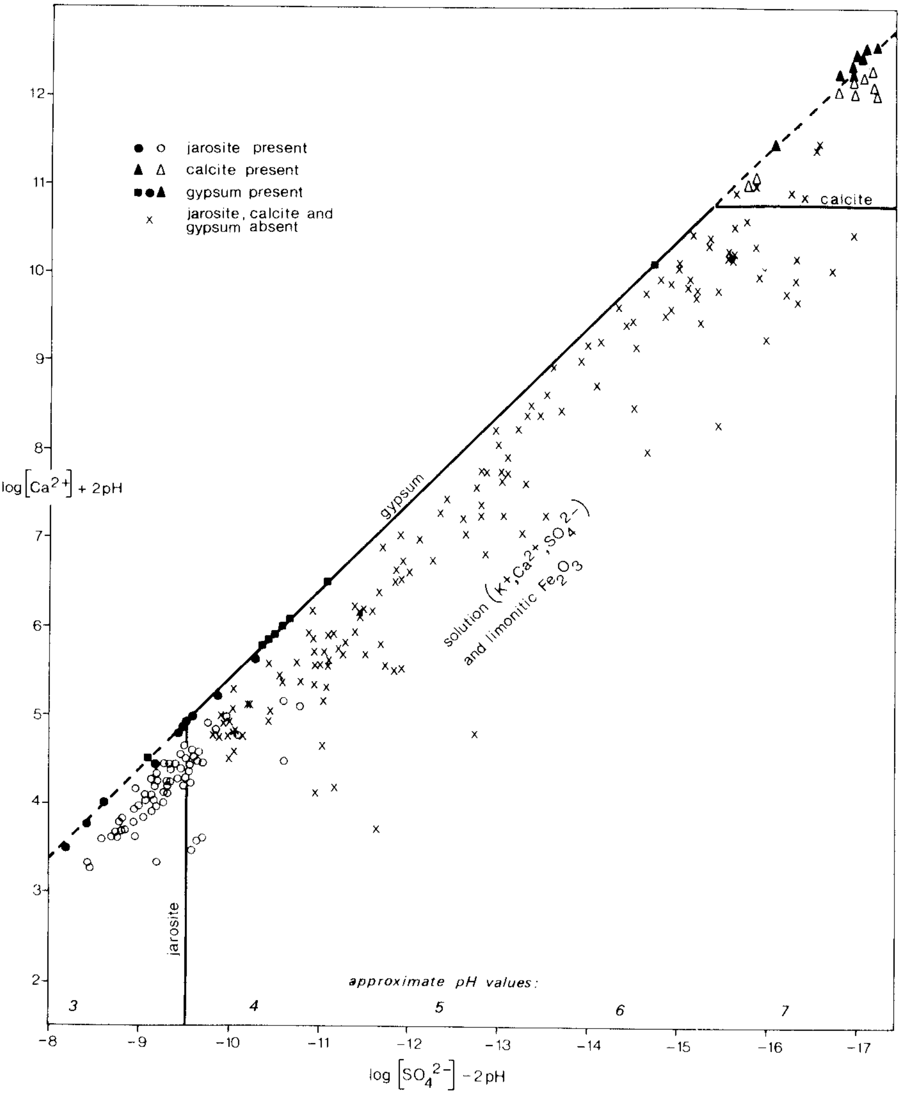


Fig.9 Solubility contours for jarosite, gypsum and calcite at 25 °C, 1 atm total pressure, log $[K^{+}]+pH=0$ ΔG^{o}_{f} limonitic Fe_2O_3 $= -169.2$ kcal/ F.W and $P_{CO_2}=0{,}1$ atm. Symbols represent waters from coastal plain soils in Thailand.

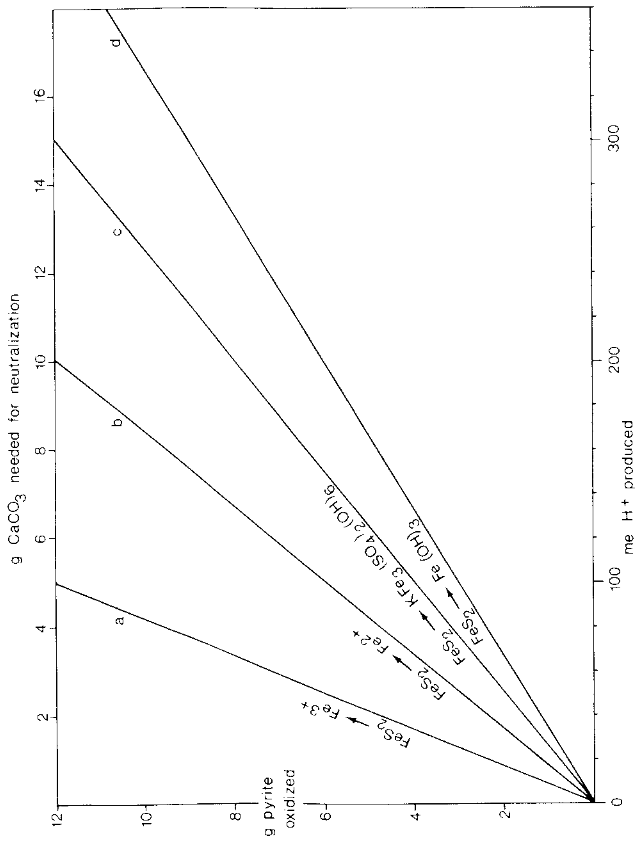


Fig. 10: Acid production during pyrite oxidation.

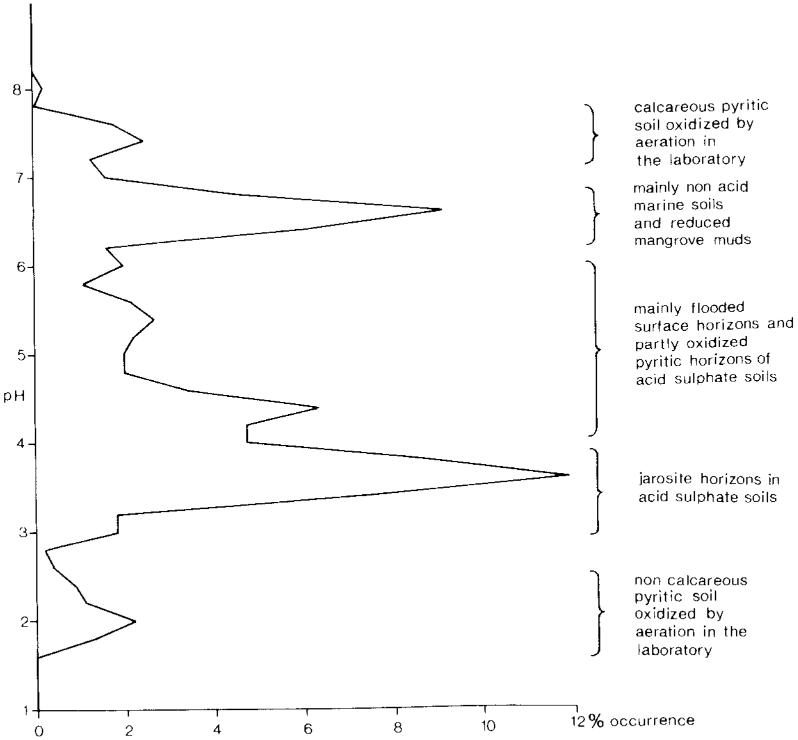


Fig.11: Frequency distribution of pH values of water samples from various coastal plain soils in Thailand (446 samples).

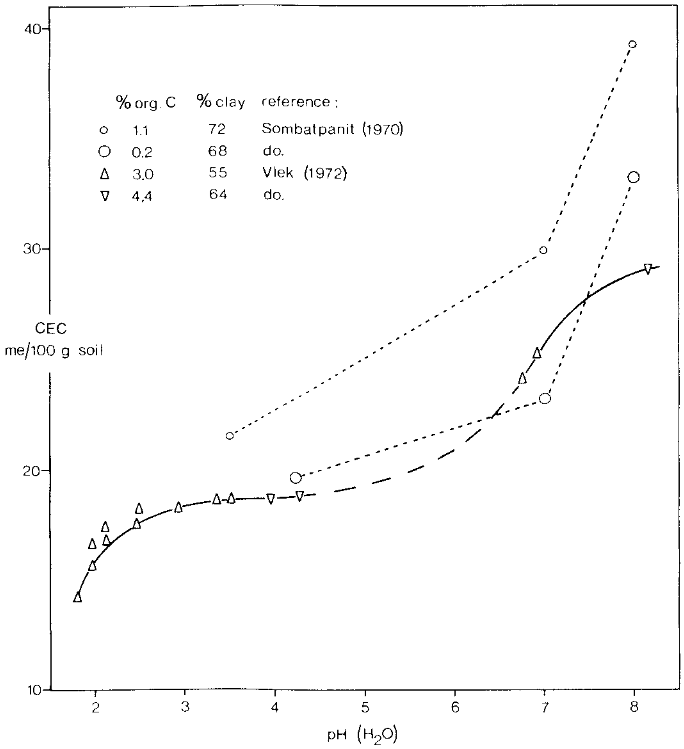


Fig. 12: CEC of samples of artificially dried potential and actual acid sulphate soils from Thailand. CEC 's at pH ≥7 were measured in buffered suspensions; other values are for soil pH.

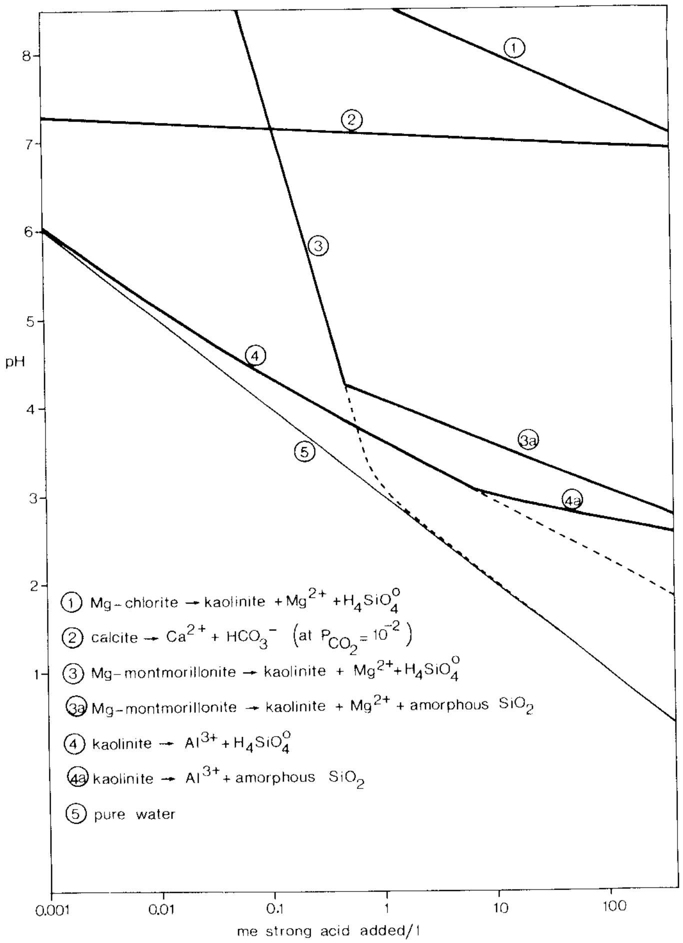


Fig.13: Equilibrium pH values during congruent or incongruent dissolution of various minerals upon addition of strong acid.

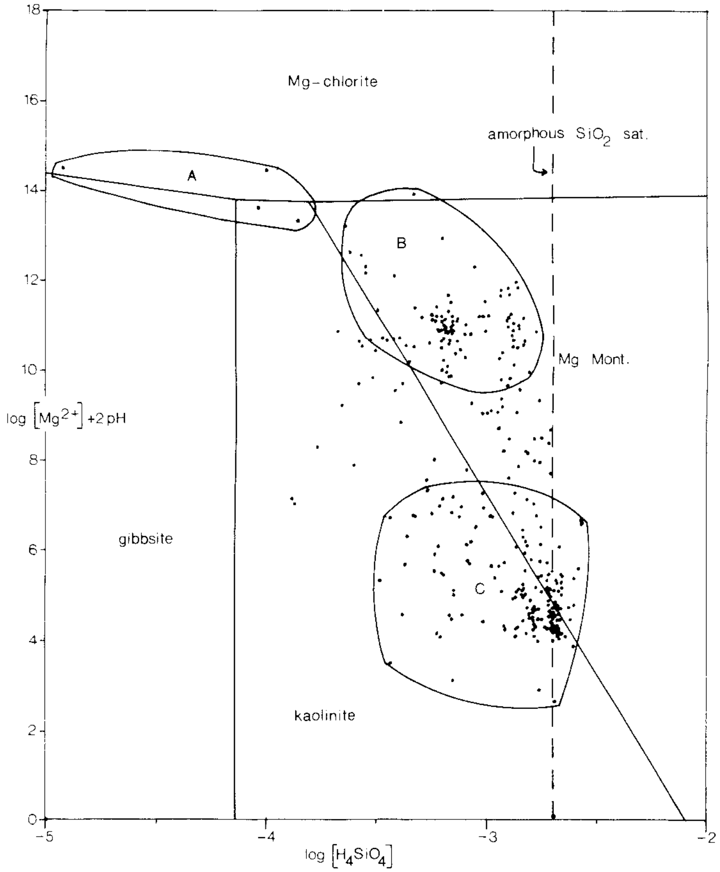


Fig 14 Stability diagram of Mg-chlorite, Mg-montmorillonite, kaolinite and gibbsite at 25 °C and 1 atm. total pressure (Helgeson et. al. 1969). Dots refer to seawater and surface waters from mangrove creeks (A), to interstitial waters from mangrove soils and non-acid marine soils (B) and to ground waters from acid sulphate soils (C) in Thailand.

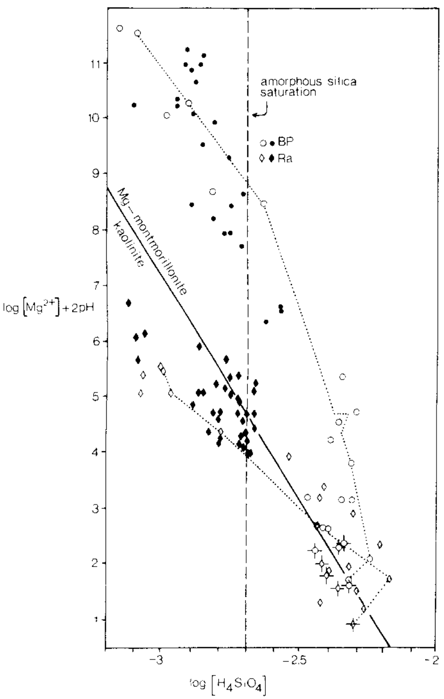


Fig. 15: Stability diagram of Mg–montmorillonite and kaolinite at 25°C and 1atm. total pressure. Symbols refer to interstitial water of two soils (BP and Ra) from the field (solid symbols) and after oxidation by aeration under laboratory conditions (open symbols). For two samples the change in water composition during oxidation is indicated by a dotted line. The oxidation experiment was terminated after 39 weeks of incubation (cross-marked symbols).

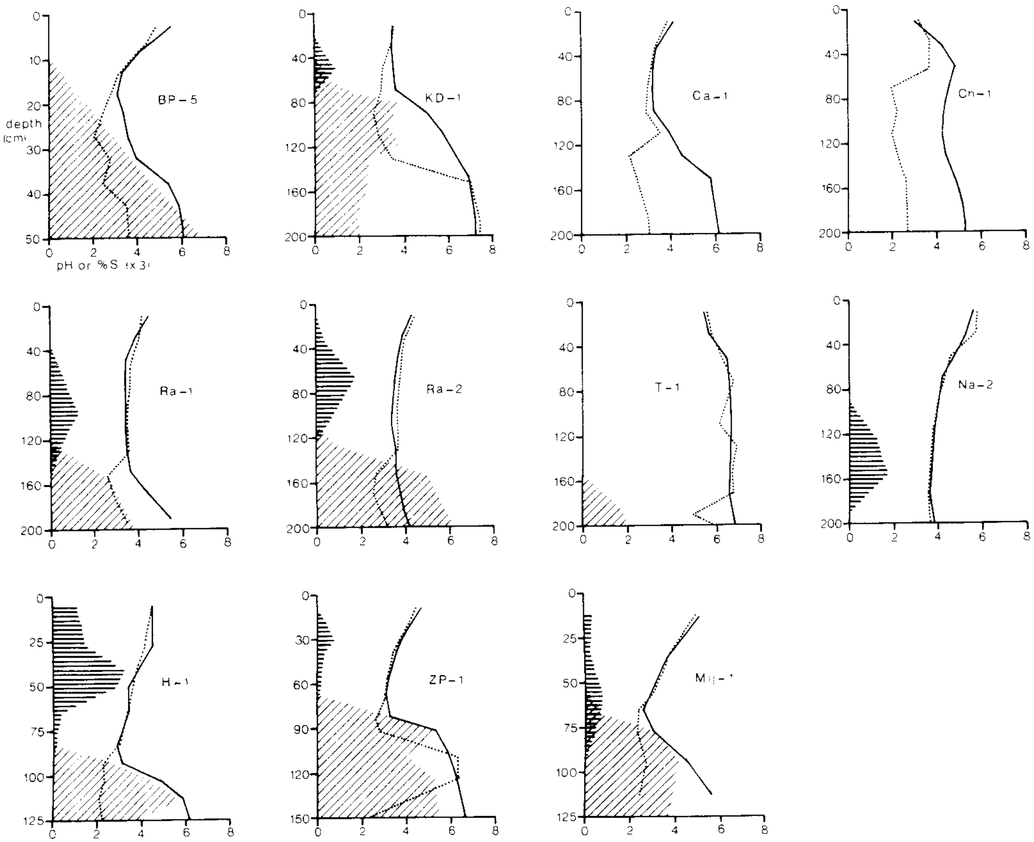


Fig. 16 Fresh pH (solid line), pH after oxidation under moist, aerobic conditions in the laboratory (broken line), jarosite-S content (horizontal hatching) and pyrite-S content (diagonal hatching) for a number of acid sulphate soils from Thailand and from the Netherlands (viz H-1, ZP-1 and Mij-1). No sulphur fractions were analysed for Ca-1 and Ch-1.

REFERENCES

(1) AARNIO, B. 1922. Über Salzböden (Alaunböden) des humiden Klimas in Finnland. Int. Mitt. f. Bodenk. XII: 180-185.

(2) ADAMI, L.H., KELLEY, K.K. 1963. Heats of formation of two crystalline hydrates of ferrous sulfate. U.S. Bur. Mines Rept. Invest. 6260. 7 pp.

(3) ALLBROOK, R.F. 1972. The identification of acid sulphate soils in North-West Malaysia. Proc. Int. Symp. Acid. Sulph. Soils, Wageningen.

(4) ANDRIESSE, J.P., van BREEMEN, BLOKHUIS, W.A. 1972. The influence of mudlobsters (Thalassina anomale) on the development of acid sulphate soils in mangrove swamps in Sarawak (East Malaysia). Proc. Int. Symp. Acid. Sulph. Soils, Wageningen.

(5) BAAS BECKING, L.G.M., KAPLAN, I.R, MOORE, D. 1960. Limits of the natural environment in terms of pH and oxidation-reduction potential. Journ.Geol. 68: 243-284.

(6) BANDY, M.C. 1938. Mineralogy of three sulfate deposits of Northern Chile. Amer. Min. 23: 669-760.

(7) BARANI, R., ADAMI, L.H. 1965. Heats of formation of anhydrous ferric sulfate and indium sulfate. U.S.Bur.Mines Rept.Invest. 6697. 8 pp.

(8) BARNES, I., STUART, W.T., FISHER, D.W. 1964. Field investigations of mine waters in the northern anthracite field, Pennsylvania. U.S.Geol.Surv. Prof.Paper 473-B. 8 pp.

(9) BASCOMB, C.L. 1964. Rapid method for the determination of cation exchange capacity of calcareous and non-calcareous soils. J.Sci.Food Agric. 12:821-823.

(10) BEEK, C.G.E.M.van, van BREEMEN, N. 1973. The alkalinity of alkali soils. J.Soil Sci. In press.

(11) BEMMELEN, J.M.van, 1886. Bijdragen tot de kennis van den alluvialen bodem in Nederland. Derde Verhandeling: De samenstelling en de vorming van de zure gronden in het Nederlandsche alluvium. Verh.Acad.Wetensch.Amsterdam. Vijfentwintigste Deel B: 33-105.

(12) BERNER, R.A. 1962. Tetragonal iron sulfide. Science 137:669.

(13) BERNER, R.A. 1963. Electrode studies of hydrogen sulfide in marine sediments. Geoch. et Cosmoch. Acta 27: 563-575.

(14) BERNER, R.A. 1971. Principles of chemical sedimentology. McGraw-Hill. 240 pp.

(15) BLOOMFIELD, C. 1972. The oxidation of iron sulphides in soils in relation to the formation of acid sulphate soils, and of ochre deposits in field drains. J.Soil Sci. 23:1-16.

(16) BLOOMFIELD, C. 1972. Acidification and ochre formation in pyritic soils. Proc.Int.Symp.Acid Sulph.Soils, Wageningen.

(17) BLOOMFIELD, C., COULTER, J.K., KANARIS-SOTIRIOU, R. 1968. Oil palms on acid sulphate soils in Malaya. Trop. Agric. (Trin.) 45: 289-300.

(18) BREEMEN, N. van, 1968. Vorming en omzettingen van sulfiden en sulfaten in zeebodem sedimenten en kattekleigronden. Unpubl.M.Sc.Thesis. Agric.Univ. Wageningen. 67 pp.

(19) BREEMEN, N. van, 1973. Calculation of ionic activities in natural waters. Geochim.et Cosmochim.Acta 37:101-107.

(20) BREEMEN, N. van, 1973. The genesis of acid sulphate soils. Ph.D.Thesis. Agric.Univ. Wageningen. In prep.

(21) BREEMEN, N. van, TANDATEMIYA, M., CHANCHAREONSOOK, S. 1972. A detailed survey on the actual and potential soil acidity at the Bang Pakong Land Development Centre, Thailand. Proc. Int. Symp. Acid Sulph. Soils, Wageningen.

(22) BREEMEN, N. van, VLEK, P. Pyrite oxidation and the inactivation of sulphuric acid in pyritic soil. In prep.

(23) BRIGGS, L.I. 1951. Jarosite from the California Tertiary. Amer. Min. 36: 902-906.

(24) BROPHY, G.P., SCOTT, E.S., SNELLGROVE, R.A. 1962. Sulfate studies. II. Solid solution between alunite and jarosite. Am.Min. 47: 112-126.

(25) BROPHY, G.P., SHERIDAN, M.F. 1965. Sulfate studies. IV. The jarosite-natrojarosite-hydronium jarosite solid solution series. Am.Min.50: 1595-1607.

(26) BROWN, J.B. 1970. A chemical study of some synthetic potassium-hydronium jarosites. Can.Min. 10: 696-703.

(27) BROWN, J.B. 1971. Jarosite-goethite stabilities at 25 °C, 1 atm. Min.Dep. (Berl.) 6:245-252.

(28) BRUGGENWERT, M.G.M. 1972. Adsorptie van Al-ionen aan het kleimineraal montmorilloniet. Versl. Landbk.Onderz. 768. Wageningen 120 pp.

(29) BUTLER, J.N. 1964. Ionic equilibrium. A mathematical approach. Addison-Wesley. 547 pp.

(30) BUURMAN, P., van BREEMEN, N. 1972. A fossil acid sulphate soil in ice-pushed Tertiary deposits near Uelsen, W. Germany. Proc.Int.Symp.Acid Sulph. Soils, Wageningen.

(31) CLARK, C.S. 1966. Oxidation of coal mine pyrite. J.San.Eng.Div., Proc.Amer. Soc.Civil Eng. 92:127-145.

(32) CLARK, J.S., GOBIN, C.A., SPROUT, P.N. 1961. Yellow mottles in some poorly drained soils of the lower Frase Vale, British Columbia. Can.J.Soil Sci. 41:218-227.

(33) COLMER, A.R., TEMPLE, K.L., HINKLE, M.E. 1950. An iron oxidizing bacterium from the acid drainage of some bituminous coal mines. J.Bacteriol. 59:317-328.

(34) COULTER, B.S. 1969. The chemistry of hydrogen and aluminum ions in soils, clay minerals and resins. Soils and Fert. 32:215-223.

(35) DEBYSER, J. 1961. Contribution à l'étude geochimique des vases marines. Inst.Franç.du Pétrole. Société des éditions technip. Paris VIIe. 249 pp.

(36) DOYNE, H.C. 1937. A note on the acidity of mangrove swamp soils. Trop. Agric. (Trin.) 14:286-287.

(37) EDELMAN, C.H., van BEERS, W.F. 1938. On mineralogical soil investigations with special reference to the Netherlands Indies. Soil Res.6:339-351.

(38) FLEMING, J.F., ALEXANDER, L.T. 1961. Sulfur acidity in South Carolina tidal marsh soils. Proc. Soil Sci. Soc. Amer. 25:94-95.

(39) FLETCHER, A.W. 1970. Metal winning from low grade ore by bacteriological leaching. Trans.Inst.Mining Metall. Sect.C. 79:247-252.

(40) FRENEY, J.R. 1967. Oxidation of sulphur in soils. Min.Dep.(Berl.) 2:181-187.

(41) FURBISH, W.J. 1963. Geological implications of jarosite, pseudomorphic after pyrite. Am.Min. 48:703-706.

(42) GARRELS, R.M., CHRIST, L.CH. 1965. Solutions, minerals and equilibria. Harper and Row, Weatherhill. 450 pp.

(43) GARRELS, R.M., MACKENZIE, F.T. 1971. Evolution of sedimentary rocks. Norton. 397 pp.

(44) GARRELS, R.M., THOMPSON, M.E. 1960. Oxidation of pyrite by iron sulfate solutions. Am.J.Sci. 258 A:56-67.

(45) GEBHARDT, W. 1972. Cation exchange and anion adsorption properties of some acid soils in the Central German Mountain range. Proc.Int.Symp.Acid Sulph. Soils, Wageningen.

(46) GINZBURG, I.I., OL'SHANSKY, Y.I., BELYATSKII, V.V. 1961. (Oxidation of sulfides, experimental studies.) Trud.Inst.Geol.Rudnykh Mestorozhden. Petr.Min.i Geokh. 59:1-131. (C.A. 56: 181 c)

(47) GRANT, C.J. 1972. Acid sulphate soils in Hong Kong. Proc.Int.Symp. Acid Sulph.Soils, Wageningen.

(48) GROUT, F.F. 1908. The oxidation of pyrite. Discussion of a paper by A.N. Winchell. Econ.Geol. 3:532-534.

(49) HARDAN, A. 1972. Rate of calcium carbonate accumulation by biological sulphate reduction. Proc.Int.Symp.Acid Sulph.Soils, Wageningen.

(50) HARMSEN, G.W., QUISPEL, A., OTZEN, D. 1954. Observations on the formation and oxidation of pyrite in the soil. Plant and Soil 5:324-347.

(51) HART, M.G.R. 1959. Sulphur oxidation in tidal mangrove soils of Sierra Leone. Plant and Soil 11:215-235.

(52) HART, M.G.R. 1962. Observations on the source of acid in empoldered mangrove soils. I. Formation on elemental sulphur. Plant and Soil 17:87-98.

(53) HART, M.G.R. 1963. Observations on the source of acid in empoldered mangrove soils. II. Oxidation of soil polysulphide. Plant and Soil 19:106-114.

(54) HARVEY, R.D., VITALIANO, C.J. 1964. Wall-rock alteration in the Goldfield district, Nevada. J.Geol. 72:564-579.

(55) HELGESON, H.C. 1969. Thermodynamics of hydrothermal systems at elevated temperatures and pressures. Am.J.Sci. 267:729-804.

(56) HELGESON, H.C., BROWN, T.H., LEEPER, R.H. 1969. Handbook of theoretical activity diagrams depicting chemical equilibria in geologic systems involving an aqueous phase at one atm. and 0^o to 300 ^oC. Freeman, Cooper & Co. 253 pp.

(57) HERBILLON,. A.J., PECROT, A., VIELVOYE, L. 1966. Aperçu sur la minéralogie des quelques grands groupes de sols du Vietnam. Pédologie XVI:5-16.

(58) HÖLLER, H. 1967. Experimentelle Bildung von Alunit-Jarosit durch die Einwirkung von Schwefelsäure auf Mineralien und Gesteine. Contr.Miner.Petr. 15:309-325.

(59) HORN,M.E., CHAPMAN, S.L. 1968. Clay mineralogy of some acid sulfate soils on the Guiana coast. Trans.9th. Int. Congr. Soil Sci. III:31-40.

(60) HORN, M.E., HALL, V.L., CHAPMAN, S.L., WIGGINS, M.M. 1967. Chemical properties of the coastal alluvial soils of the Republic of Guinea. Proc.Soil Sci. Soc.Amer. 31:108-114.

(61) HOWELER, R.H., BOULDIN, D.R. 1971. The diffusion and consumption of oxygen in submerged soils. Proc. Soil Sci.Soc.Amer. 35:202-208.

(62) IORDAN, E.F., PAVLOV, F.N., DIEV, N.P. 1955. (Oxidation of sulfides at low temperature under static conditions.) Trud.Inst.Khim. i Met. Akad.Nauk SSSR. Urial Filial 3:18-23 (C.A.50:13678)

(63) IRRI. 1965. Annual Rept.Int.Rice Res.Inst.Los Banos. Section Microbiology.

(64) Joint Committee on Powder difrraction standards. Philadelphia. USA.

(65) KANNO, I., HONJO, Y., ARIMURA, S., TOKUDOME, S. 1964. Genesis and characteristics of rice soils developed on polder lands of the Shiroishi area, Kyushu. Soil Sci.Plant Food 10:1-19.

(66) KAPLAN, I.R., EMERY, K.O., RITTENBERG, S.C. 1963. The distribution and isotope abundance of sulphur in recent marine sediments off Southern California. Geoch. et Cosmoch.Acta 37:297-331.

(67) KAWAGUCHI, K., KYUMA, K. 1969. Lowland rice soils in Thailand. Natural Sci. Ser. N-4. Centre for Southeast Asian Studies, Kyoto Univ. 270 pp.

(68) KEVIE, W. van der, 1972. Morphology, genesis, occurrence and agricultural potential of acid sulphate soils in Central Thailand. Thai J.Agr.Sci.5:165-182.

(69) KITTRIC, J.A. 1971. Stability of montmorillonites: I. Belle Fourche and Clay Spur montmorillonites. Proc. Soil Sci. Soc. Amer. 35:140-145.

(70) KITTRIC, J.A. 1971. Stability of montmorillonites: II. Aberdeen montmorillonite. Proc. Soil Sci. Soc. Amer. 35:820-823.

(71) KIVINEN, E. 1944. Sulfat eller alunjordar, deras egenskaper och sunpunkter på deras odling. Sv.Vall. och Mosskulturfören Tidskr. 2:152-164.

(72) KENIFETS, V.L., ROTINYAN, A.L. 1954. (Isobaric potentials of formation of sparingly soluble oxide hydrates and basic salts, and the pH of solutions in equilibrium with the solid phase.) Zhur. Obshchei Khim. 24:930-936

(73) KOMAREK, K. 1965. (The weathering of fossils containing iron disulfide.) Casopis Nārodnīho musea (Prague). 134:40-43 (C.A.63:16035)

(74) KUBISZ, J. 1964. (Minerals of the alunite-jarosite group.) Polska Akad. Nauk. Prace Geol. 22: 1-85 (C.A. 65:16688)

(75) LATIMER, W.M. 1952. The oxidation states of the elements and their potentials in aqueous solutions. 2nd ed. Prentice Hall. 392 pp.

(76) LEATHEN, W.W., BRALEY, S.A., Mc INTYRE, L.D. 1953. The role of bacteria in the formation of acid from sulfuritic constituents associated with bituminous coal. I. Thiobacillus thiooxidans. II. Ferrous iron oxidizing bacteria. Appl.Micr. 1:61-68.

(77) LJUNGGREN, P. 1960. A sulfur mud deposit formed through bacterial transformation of fumarolic hydrogen sulfide. Econ.Geol. 55:531-538.

(78) LORENZ, W.C. 1962. Progress in controlling acid mine water: A literature review. U.S.Bur.Mines.I.C. 8080. 40 pp.

(79) LYNN, W.C., WHITTIG, L.D. 1966. Alteration and transformation of clay minerals during catclay development. Clay and Clay Min. Proc.14th Nat.Conf. Pergamon. pp.241-248.

(80) MICHARD, G. 1967. Significance of redox potentials in natural waters. Conditions for application of Eh-pH diagrams. Min.Dep.(Berl.) 2:34-37.

(81) MURAKAMI, H. 1968. (Some problems on the oxidation of oxidizable sulphur. Characteristics and improvement of acid sulphate soils. Part 3.) J.Sci. Soil Man. (Jap.) 39:116-120. (Abstr.in Soil Sci. Plant Nutr.14:83-84)

(82) MUSSER, J.J., WHETSTONE, G.W. 1964. Geochemistry of water. In: COLLIER, C.R. (Ed.) Influences of stripmining on the hydrologic environment of parts of Beaver Creek Basin, Kentucky, 1955-1959. U.S.Geol.Surv.Prof.Paper 427: 25-48.

(83) PALACHE, C., BERMAN, H., FRONDELL, C. 1951. The system of mineralogy of J. D. and E.S. Dana. 7th ed. Vol.II. Wiley, Chapman & Hall. 1124 pp.

(84) PONNAMPERUMA, F.N., ATTANANDANA, T., BEYE, G. 1972. Amelioration of three acid sulphate soils for lowland rice. Proc.Int.Symp.Acid Sulph. Soils, Wageningen.

(85) PONS, L.J., van der KEVIE, W. 1969. Acid sulphate soils in Thailand. Soil Surv. Dept. 91. Land Dev.Dept. Thailand. 82 pp.

(86) POSNJAK, E., MERWIN, H.E. 1922. The system Fe_2O_3-SO_3-H_2O. J.Am.Chem.Soc. 44:1965-1994.

(87) PRATT, P.F. 1961. Effect of pH on the cation-exchange capacity of surface soils. Proc.Soil Sci.Soc.Amer. 25:96-98.

(88) PRINGLE, D.L.,DIEHL, H. 1965. The pyrite and marcasite electrodes. Proc. Iowa Acad. Sci. 72:161-168.

(89) PRUDEN, G., BLOOMFIELD, C. 1968. The determination of ferrous sulphide in soil in the presence of ferric oxide. Anal. 93:532-534.

(90) PUROKOSKI, P. 1958. Die schwefelhaltigen Tonsedimenten in dem Flachlandgebiet von Liminka im Lichte chemischer Forschung. Agrogeol. Publ.70:1-88.

(91) QUISPEL, A., HARMSEN, G.W., OTZEN, D. 1952. Contribution to the chemical and bacteriological oxidation of pyrite in soil. Plant and Soil 4:43-55.

(92) RASMUSSEN, K. 1961. Uorganiske svovlforbindelsers omseatninger i jordbunden. Thesis. Veterinaer og Landbohøjskole. København. 176 pp.

(93) RAYMAHASHAY, B.C. 1968. A geochemical study of rock alteration by hot springs in the Paint Pot Hill area, Yellowstone Park. Geoch. et Cosmoch. Acta. 32:499-522.

(94) REESMAN, A.L., KELLER, W.D. 1968. Aqueous solubility studies of high alumina and clay minerals. Am. Min. 53:929-942.

(95) RICKARD, D.T. 1972. Sedimentary iron sulphide formation. Proc. Int. Symp. Acid Sulph. Soils, Wageningen.

(96) ROBIE, R.A., WALDBAUM, D.R. 1968. Thermodynamic properties of minerals and related substances at 298.15 ^{o}K (25.0 ^{o}C) and one atmosphere (1.013 bars) pressure and at higher temperatures. U.S. Geol. Surv.Bull. 1259. 256 pp.

(97) SATO, M. 1960. Oxidation of sulfide ore bodies. I. Geochemical environments in terms of Eh and pH. Econ. Geol. 55:928-961.

(98) SATO, M. 1960. Oxidation of sulfide ore bodies. II. Oxidation mechanisms of sulfide minerals at 25 ^{o}C. Econ. Geol. 55: 1200-1231.

(99) SCHWERTMANN, U. 1961. Ueber das Vorkommen und die Entstehung von Jarosit in Marschböden (Maibolt). Naturwissensch. 48:159.

(100) SILLÉN, L.G., MARTELL, A.E. 1964. Stability constants of metal ion complexes. Spec. Publ. 17. Chem.Soc.London. 754 pp.

(101) SILVERMAN, M.P. 1967. Mechanism of bacterial pyrite oxidation. J.Bact.94: 1046-1051.

(102) SILVERMAN, M.P., EHRLICH, H.L. 1964. Microbial formation and degradation of minerals. Adv.Appl.Microbiol.6:153-206.

(103) SIMON, A., REICHELT, D. 1959. (Iron sulfides and their oxidation products.) Chem.Zvesti. 13:731-732. (C.A.54:16246)

(104) SINGH, S.S., BRYDON, J.E. 1969. Solubility of basic aluminium sulfates at equilibrium in solution and in the presence of montmorillonite. Soil Sci. 107:12-16.

(105) SINGH, S.S., BRYDON, J.E. 1970. Activity of aluminium hydroxu sulfate and the stability of hydroxy aluminium interlayers in montmorillonite. Can.J. Soil Sci. 50:219-225.

(106) SINGER, P.C., STUMM, W. 1970. Acidic mine drainage: the rate determining step. Science 167:1121-1123.

(107) SLAGER, S., van SCHUYLENBORGH, J. 1970. Morphology and geochemistry of three clay soils of a tropical coastal plain (Surinam). Versl.Landbk.Onderz. 734. Wageningen. 34 pp.

(108) SOMBATPANIT, S. 1970. Acid sulphate soils. Their nature and properties. Unpubl.Thesis. Royal Agric.Coll. Uppsala. 135 pp.

(109) SPEK, J. van der, 1950. Katteklei. Versl.Landbk.Onderz. 56.2. Wageningen. 40 pp.

(110) STARKEY, R.L. 1966. Oxidation and reduction of sulfur compounds in soils. Soil Sci. 101:297-307.

(111) STOKES, H.N. 1901. On pyrite and marcasite. U.S.Geol.Surv.Bull.186. 44 pp.

(112) STRAATEN, L.M.J.U.van, 1954. Composition and structure of recent marine sediments in the Netherlands. Leidse Geol.Meded. 19:1-108.

(113) STUMM, W., MORGAN, J.J. 1970. Aquatic chemistry. Wiley-Interscience. 583 pp.

(114) SZISZKIN, N.W., KROGIUS, E.A., LWOWICZ, P.A. 1958. (On the genetic links between basic 9-hydroxo Fe and Al sulphates and minerals of the alunite-jarosite group.) Zap. Vs. Miner. Obszcz. 87:682-686. (cit. by Brophy and Sheridan (25)).

(115) TEAKLE, L.J.H., SOUTHERN, B.L. 1937. The peat soils and related soils of Western Australia. II. Soil Survey of Herdsman Lake. J.Agric.West.Austr., 14:404-424.

(116) TEMPLE, K.L., DELCHAMPS, F.W. 1953. Autotrophic bacteria and the formation of acid in bituminous coal mines. Appl. Microb. 1:255-258.

(117) TEODOROVICH, G.I. 1961. Authigenic minerals in sedimentary rocks. Transl. from Russian. Consultants Bur. N.Y. 120 pp.

(118) VALENSI, G., van MUYLDER, J., POURBAIX, M. 1963. Souffre, de; Pourbaix, M. (Eds.): Atlas d'équilibres électrochimiques à 25 °C. CEBELCOR (Belgium). pp.545-553.

(119) VERHOEVEN, B. 1972. Acid sulphate soils in the Wieringermeer polder, a good 40 years after reclamation. Proc.Int.Symp.Acid Sulph.Soils, Wageningen.

(120) VERHOOP, J.A.D. 1940. Chemische en microbiologische omzettingen van ijzersulfiden in den bodem. Thesis. Leiden. 116 pp.

(121) VIEILLEFON, J. 1969. La pédogénèse dans les mangroves tropicales. Science du Sol 2: 115-148.

(122) VIEILLEFON, J. 1971. Contribution à l'étude du cycle du soufre dans les sols de mangrove. Ses rapports avec l'acidification naturelle ou provoqué. Cah. ORSTOM. Sér.Pédol. IX:241-270.

(123) VIEILLEFON, J. 1971. (The interest of freezedrying techniques in the analysis of waterlogged soils.) Compt.Rend.Hebd.Séances Acad.Agric.France 57: 1078-1084.

(124) VIEILLEFON, J. 1972. Sur quelques transformations sédimentologiques et minéralogiques dans les sols sulfatés acides du Sénégal. Proc.Int.Symp. Acid Sulph.Soils, Wageningen.

(125) VLEK, P. 1971. Some morphological, physical and chemical aspects of acid sulphate soils in Thailand. Soil Surv.Rept.84. Land Dev.Dept. Thailand.37 pp.

(126) VLEK,P. 1971. Enkele gevolgen van verzuring door oxydatie van pyriet. Unpubl.Rept.Agric.Univ.Wageningen. 45 pp.

(127) VOLKOV, I.I. 1961. (Free hydrogen sulfide and products of its transformation in sediments of the Black Sea.) Tr.Inst.Okeanol. Akad Nauk SSSR 50: 29-67. (C.A.56:12676)

(128) WARSHAW, C.M. 1956. The occurrence of jarosite in underclays. Am.Min. 41:288-296.

(129) WEAVER, R.M., JACKSON, M.L., SYERS, J.K. 1971. Magnesium and silicon activities in matrix solutions of montmorillonite-containing soils in relation to clay mineral stability. Proc. Soil Sci. Soc. Amer. 35:823-830.

(130) WIKLANDER, L., HALLGREN, G., BRINK, N., JONSSON, E. 1950. Studies on gyttja soils. II. Some characteristics of two profiles from northern Sweden. Ann. Roy. Agric. Coll. Sweden. 17:24-36.

(131) WIKLANDER, L., HALLGREN, G., JONSSON, E. 1950. Studies on gyttja soils. III. Rate of sulphur oxidation. Ann. Roy. Agric. Coll. Sweden. 17:425-440.

(132) WILSHAW, R.G.H. 1940. Note on the development of high acidity in certain soils of Malaya. Mal.Agric.J. 28:352-357.

(133) WINCHELL, A.N. 1907. The oxidation of pyrite. Econ.Geol.2:290-294.

Summary

The first three chapters deal with the oxidation of pyrite, the formations of acid sulphate minerals and the neutralization of sulphuric acid by silicate minerals. The emphasis is on thermodynamic equilibrium models. Where possible, the theoretical models are compared with conditions in actual acid sulphate soils, and kinetic and biological factors are taken into account. Chapter 4 shows how the various processes discussed earlier, influence soil horizon development and profile morphology.

Résumé

Les chapitres 1,2 et 3 traitent l'oxidation de la pyrite, la formation des minéraux sulfatés acides et la neutralisation de l'acide sulfurique par les minéraux silicatés. L'accent a été mis sur les modèles d'équilibres thermodynamiques. Si possible les modèles théorétiques ont été comparés avec les conditions actuelles dans certains sols sulfatés acides, compte tenu des facteurs biologiques et cinétiques. Le chapitre 4 montre l'influence des processus précités sur le développement des horizons de sol et sur la morphologie des profils.

Resumen

Los capitulos 1, 2 y 3 tratan la oxidación de la pirita, la formación de los minerales ácidos sulfáticos y la neutralisación del ácido sulfurico por los silicatos. Se hace hincapié en los modelos de equilibrios termodinámicos. En cuanto sea posible se equipara los modelos teoréticos y las condiciones en suelos ácidos sulfáticos concretos, tomando en cuenta los factores biológicos y cinéticos. El capitulo 4 muestra la influencia de los procesos susodichos sobre el desarrollo de capas de suelo y la morfología de perfiles.

Zusammenfassung

Die ersten drei Abschnitte behandeln die Pyritoxidation, die Formation sulfatsaurer Mineralien und die Neutralisation der Schwefelsäure durch Silikatmineralien. Besonders werden thermodynamische Gleichgewichts-Modelle hervorgehoben. Wo möglich, werden auch die theoretischen Modelle mit den Verhältnissen in konkreten sulfatsauren Böden verglichen mit Rücksicht auf die biologischen und dynamischen Faktoren. Abschnitt 4 zeigt die Wirkung der erwähnten Prozesse auf Horizontbildung und Profilmorphologie des Bodens.

DISCUSSION

RICKARD: How do you measure soil pH? We find that in site measurements may differ from measurements on samples.

VAN BREEMEN: Soil pH I measure by pressing a sturdy glass electrode in the wet soil (if necessary wetted with distilled water to a consistence allowing electrode insertion) and placing the reference electrode at the surface (separated from the soil by a piece of filter paper soaked in distilled water).

RICKARD: The rate of $CaCO_3$ dissolution is highly dependent on such factors as organic matter associations and dissolved Mg^{2+} concentration. These factors tend to stabilize $CaCO_3$ in undersaturated waters for hundreds of years. Is this observation pertinent to initial development of acid sulphate soils?

VAN BREEMEN: At the strong degree of $CaCO_3$ undersaturation induced by pyrite oxidation in acid sulphate soils I doubt that $CaCO_3$ dissolution is inhibited. I observed near equilibrium between calcite and solution at pH 7 to 7,5 in soil material where pyrite oxidation took place.

FRINK: If SO_4^{2-} activity in soils is constant then Fig.7 is demonstrating merely the pH dependency of the solubility of $Al(OH)_3$.

VAN BREEMEN: The SO_4^{2-} activity is only approximately constant. A plot of $\log(Al^{3+}) + 3$ pH vs. $\log(SO_4^{2-}) - 2$ pH gives a better slope (nearer to 1,0) and a better correlation coefficient than a plot of $\log(Al^{3+}) + 3$ pH vs. - 2 pH.

PONNAMPERUMA: How did you determine the activity coefficient of Al^{3+} in solutions of such high ionic strength?

VAN BREEMEN: Al-activity coefficients are calculated from experimentally determined activity coefficients of $AlCl_3$, using the "mean salt" method. Plots of Al activity coefficients vs. ionic strength (up to 1,2 molar) were curvefitted and incorporated in a computer program (see reference 19).

PONNAMPERUMA: How do you know whether hydroxy-complexes of Al were included in your assay of Al^{3+}?

VAN BREEMEN: Two hydroxycomplexes ($AlOH^{2+}$ and $Al_2(OH)_2^{4+}$) were taken into account in the computer program, as were $AlSO_4^+$ and $Al(SO_4)_2^-$. Polynuclear species were probably not present because the pH was always low.

ALUMINUM CHEMISTRY IN ACID SULFATE SOILS

C. R. Frink
Chief Soil Chemist, The Connecticut Agricultural Experiment Station,
New Haven, Connecticut, USA

Aluminum is the most abundant metallic element in the earth's crust. Moreover, hydrolysis of the aluminum ion produces a moderately strong acidic environment so that it is not surprising that many of the properties of acid soils are controlled by the chemistry of aluminum. Indeed, aluminum bonding has been described as a unifying principle in soil science (Jackson 1963). In acid sulfate soils additional acidity is produced by the oxidation of sulfides to sulfuric acid, which may also react with many aluminum compounds in soil. The venerable topic of soil acidity has been examined recently in an excellent review by Coleman and Thomas (1967). Thus, the present analysis will take a somewhat different path. First, we will consider the reactions of aluminum in aqueous solutions and then examine how these reactions may be modified in clay suspensions; then, the chemistry of aluminum in soils will be examined; and finally, we will consider the effects of aluminum on the physical properties of clays and soils.

ALUMINUM CHEMISTRY IN AQUEOUS SOLUTIONS

Hydrolysis

Chemically, the hydrolysis of aluminum in aqueous solutions has been assumed to proceed via the first-stage hydrolysis reaction:

$$Al^{3+} + H_2O = AlOH^{2+} + H^+ \qquad (1)$$

where water of hydration is omitted for convenience. Expressing ion activities as negative logarithms, the thermodynamic equilibrium constant for this reaction is given by:

$$pK = pAlOH + pH - pAl \qquad (2)$$

where the valences of the ions are omitted for convenience. There have been numerous determinations of this hydrolysis constant (Sillen and Martell, 1964,1971) with most investigators agreeing that pK is approximately 5.0. However, many feel that this reaction does not exist or that other hydrolytic species must also be considered.

A partial explanation for these different viewpoints is provided by work of Frink and Peech (1963), who showed that aqueous aluminum solutions become supersaturated with respect to $Al(OH)_3$ on dilution or addition of base. Hence, at low basicities, the first-stage hydrolysis reaction appears to be satisfactory (Frink and Peech, 1963a; Holmes et al. 1968; Raupach, 1963; Schofield and Taylor, 1954; Srinivasan and Rechnitz, 1968). At higher basicities numerous polynuclear species have been reported (Brosset et al. 1954; Fripiat et al. 1965; Matijević et al. 1961, 1964; Rausch and Bale 1964; Ruff and Tyree, 1958). These conflicting interpretations appear throughout the study of aluminum chemistry in solutions, clay suspensions, and in soils, and will become familiar topics as we proceed.

Recently, the effect of basicity on the apparent mechanism of hydrolysis has been re-examined by analysis of potentiometric titration curves of dilute aluminum salt solutions. Frink and Sawhney (1967) pointed out that these titration curves present two apparent anomalies. First, although the monomeric hydrolysis mechanism satisfactorily describes the changes in pH on dilution of aluminum salt solutions, no inflection point corresponding to the completion of first-stage hydrolysis is observed in titration curves. Second, the pH of an aluminum solution at 50% neutralization is not a constant, as is the case with other weak acids, but instead is a function of initial aluminum concentration. They proposed that the neutralization of an aluminum salt solution could be considered to proceed by stoichiometric precipitation of $Al(OH)_3$ by added base, and that the pH was controlled by first-stage hydrolysis of the aluminum remaining in solution. Discrepancies between calculated and observed pH near the equivalence point were attributed to anion penetration of the solid phase $Al(OH)_3$.

Turner (1968a, 1968b) has examined this proposal in considerable detail. His results indicate that, while the conclusions reached by Frink and Sawhney (1967) were essentially correct for rapid titrations, other reaction products including polynuclear cations were formed during slow titrations. Turner and Ross (1969) examined the solid phase formed during the neutralization of $AlCl_3$ solutions and found that its composition changed during the course of the titration and could not be represented by $Al(OH)_3$. They concluded that the initial product formed during the neutralization of $AlCl_3$ solutions is a solid phase of variable composition and that polynuclear hydroxyaluminum cations form slowly at the expense of the solid phase.

Other evidence for the occurrence of monomeric hydrolysis has been provided recently by measurements of dissociation field effect relaxation times in dilute aqueous aluminum chloride solutions by Holmes et al. (1968). Their observations agreed with earlier findings of Frink and Peech (1963a) that monomeric rather than polymeric mechanisms best described these solutions. Srinivasan and Rechnitz (1968) measured rates of formation of aluminum fluoride complexes and concluded that the simple monomeric mechanism provided the best fit to their experimental data. Sullivan and Singley (1968) analyzed titration curves of dilute aluminum perchlorate solutions and concluded that the major species present in 10^{-3}M and 10^{-4}M solutions were Al^{3+}, $AlOH^{2+}$, and $Al(OH)_3$.

Hem (1968) has examined the reaction products formed during serial titrations of aluminum salt solutions by a variety of techniques. He found crystalline gibbsite in solutions with OH/Al ratios between 2 and 3 after aging for as little as 10 days. Particle diameters were of the order of 0.1 micron and Hem (1968) feels that these crystalline products may have been overlooked by earlier investigators. He further examined various proposed polymers by considering OH^- to exist either in non-structural positions as in the monomer $AlOH^{2+}$ or in structural bridges in polymers. As a result of analyses of rates of reaction of these two kinds of hydroxyls with acid, he concluded that at equilibrium all non-structural OH^- is present as the monomer $Al(OH)^{2+}$ and that all structural OH^- is present as a polymer with formula $Al(OH)_3$. Hence, he agreed with the proposals of Frink and Sawhney (1967) that polynuclear hydroxyalyminum cations could be ignored. However, Hem (1968) does caution that equilibrium is only slowly attained and metastable complex species may exist for some time so that the concept may have limited practical usefulness.

Solid Phase and Polynuclear Species

Although considerable progress has been made in understanding the neutralization of aluminum salt solutions, neither the composition of the solid phase nor the nature of the various metastable polynuclear hydroxyaluminum species that have been proposed is known with certainty. The solubility product of gibbsite, the thermodynamically stable phase of $Al(OH)_3$, has been measured and found to correspond to $pK_{sp} = 33.5$ (Frink and Peech, 1962). However, equilibrium is established very slowly, particularly in undersaturated solutions. Kittrick (1966) found $pK_{sp} = 34.0$ for solutions aged for four years and concluded that his sample of gibbsite might be more crystalline than that of Frink and Peech (1962). Supersaturated solutions had an ion product for $Al(OH)_3$ corresponding to an apparent pK_{sp} of 31.8 (Frink and Sawhney 1967) and seeding with gibbsite had little effect.

Other precipitates of varying crystallinity and basicity have been reported by a number of workers (Hsu and Bates 1964). In their recent studies, Turner and Ross

(1969) found that the $Al(OH)_3$ precipitated during neutralization contained variable amounts of Cl^- depending on the Cl^- concentration in solution and the degree of neutralization. Singh (1969) and Singh and Brydon (1969) have identified a crystalline basic aluminum sulfate, basaluminite, with formula $Al_4(OH)_{10}SO_4 \cdot 5H_2O$ and $pK_{sp} = 117.3$, as a metastable phase formed during the neutralization of aluminum sulfate solutions. Ross and Turner (1971) have postulated that the rate of $Al(OH)_3$ crystallization is inversely proportional to the tendency for anions to penetrate the solid phase. In their studies, the tendency for gibbsite to precipitate was greatest in the presence of ClO_4^-, less in the presence of NO_3^-, and least in the presence of Cl^-. Although the exact mechanism for the crystallization of gibbsite is not resolved, these studies do suggest the role that various anions may play in the precipitation process.

The nature of the various polynuclear hydroxyaluminum cations that have been proposed is even more uncertain than the composition of the solid phase. It is evident that potentiometric methods alone are not always adequate to distinguish amongst the various species, since Brosset et al. (1954) showed that either a single species $Al_6(OH)_{15}^{3+}$ or an infinite series of complexes would fit their neutralization data equally well. Matijević, et al. (1961, 1964) studied the coagulation of aqueous sols of silver halides and proposed the species $Al_8(OH)_{20}^{4+}$. However, as Hahn and Stumm (1969) point out, specific sorption on colloid surfaces may alter the distribution of species to the point where they feel it is impossible to draw conclusions regarding the nature of a specific polynuclear species in solution. From ultracentrifugation and acidity measurements, Aveston (1965) found that two species, $Al_2(OH)_2^{4+}$ and $Al_{13}(OH)_{32}^{7+}$, provided the best fit to his experimental data. Light scattering measurements by Ruff and Tyree (1958), however, showed that the average size of the aggregates decreased on dilution or with decreasing basicity. Fripiat et al. (1965) from infrared absorption spectra found evidence for the existence of a series of polymers of the form $Al\left[(OH)_8Al_3\right]_n^{+4}$. Their assignment of frequencies to various forms of OH^- bonded to aluminum seems rather speculative, however. Rausch and Bale (1964) used small-angle X-ray scattering in 1M $Al(NO_3)_3$ solutions to measure the size of clusters from the radius-of-gyration parameter. They reported their measurements were consistent with the presence of $\left[Al_{13}O_4(OH)_{24}(H_2O)_{12}\right]^{+7}$, a species also said to be present in some solid phase basic salts. Turner (1968b) and Turner and Ross (1969) used the 8-hydroxyquinoline method developed by Okura et al. (1962) to measure monomeric aluminum ions in solution and concluded that the OH/Al ratio of the polynuclear ions was near 2.5. This basicity is close to that reported by many previous workers and probably is a reasonable approximation of the apparent basicity of many polynuclear hydroxyaluminum species. However, it is evident that the exact size and charge of these species is not constant but is a function of experimental conditions. Hence, considerable caution should be exercised in extrapolating from the results of one investigation to describe the aluminum species existing under different conditions in other investigations. Indeed, in view of the transitory nature of these various hydroxyaluminum species, it is questionable whether further efforts to identify particular ions are worthwhile.

Summary

It appears that the simple monomeric hydrolysis mechanism can be used to calculate the pH and aluminum ion activities of dilute solutions at low basicities. When base is added to these dilute solutions, a solid phase consisting of $Al(OH)_3$ with various degrees of anion substitution is formed, and at high basicities significant amounts of metastable polynuclear hydroxyaluminum cations may be present in solution in addition to simpler monomeric species. In more concentrated aluminum salt solutions, which by virtue of their acidity are considerably undersaturated with respect to $Al(OH)_3$, relatively large amounts of base can be added before precipitation occurs. Under these conditions, higher concentrations of a variety of polynuclear hydroxyaluminum species can be present in solution.

ALUMINUM CHEMISTRY IN CLAY SUSPENSIONS

Inasmuch as the chemistry of aluminum in aqueous solutions is not completely understood, it is not surprising that the reactions of aluminum in clay suspensions are the subject of some confusion and controversy. Before pursuing this subject we should consider briefly the preparation of H- and Al-saturated clays since much early work was done with mixed clays and hence misinterpreted. Coleman and Thomas (1967) have reviewed the history of the discovery that H-clays rapidly decompose to form partially Al-saturated clays. Barshad and Foscolos (1970) studied this "interchange" reaction and found that the rate of replacement of H^+ by Al^{3+} or Mg^{2+} in montmorillonite, vermiculite, and illite is directly proportional to surface charge density and MgO content. Riley and Arnold (1969) examined kaolinite, montmorillonite, and seven soils, and showed that the amount of exchangeable Al^{3+} produced was controlled by the amount of exchangeable H^+ present. In acid sulfate soils, decomposition of H-clays and their subsequent conversion to Al-clays would presumably be quite rapid.

Many methods for preparing pure H-clays have been proposed; the most recent utilizes extraction with a chelating agent followed by successive reactions with H-, OH- and H-resins (Barshad 1969). Less attention has been given to the preparation of Al-clays. Most investigators have obtained satisfactory results by treating the clay with a concentrated aluminum salt solution and removing the excess electrolyte by washing with some solvent. There are indications, however, that considerable hydrolysis occurs during prolonged washing. This question will be examined in greater detail in subsequent sections.

Hydrolysis

Considering now the effect of clay on the simple monomeric hydrolysis reaction, Ragland and Coleman (1960) reported that aluminum salt solutions undergo increased hydrolysis in clay suspensions when compared with aqueous solutions of the same pH. Frink and Peech (1963b) have disagreed with this choice of a reference solution, and concluded that hydrolysis is suppressed in clay suspensions when compared with a solution of the same total aluminum concentration. This disagreement may be largely semantic (Coleman and Thomas 1967); however, both studies show that the adsorption of hydrolytic species of aluminum on a clay surface does not alter the numerical value of the hydrolysis constant pK as shown in equation (2). Moreover, these two studies show that addition of base to an Al-clay has the same effect as addition of base to an aqueous aluminum salt solution: some form of $Al(OH)_3$ is precipitated.

Although theoretical considerations suggest that simple electrostatic adsorption of aluminum on a negatively charged surface has no effect on the mechanism of hydrolysis, adsorption by many clays appears to involve specific sorption reactions. Jackson (1963a,b) has proposed several mechanisms to describe the effectiveness of clays in promoting or enhancing the hydrolysis of aluminum. Kaddah and Coleman (1967 a,b) have recently examined the reactions of Al-saturated vermiculites in some detail. They showed that freshly prepared or aged Al-vermiculites contain predominantly trivalent aluminum as anticipated. However, extractions with various salt solutions induce variable amounts of hydrolysis, depending on the nature of the replacing cation and its concentration. At high salt concentrations interplate diffusion is unrestricted and hydrolysis is little enhanced so that primarily trivalent aluminum is exchanged. At low salt concentrations or in the presence of ions causing lattice closure, in-situ hydrolysis of surface adsorbed aluminum is greatly enhanced. According to Kaddah and Coleman

(1967 a,b) the hydrolysis product retained by the clay has a composition corresponding to $AlOH^{2+}$. Although it is not clear why this species should be specifically sorbed, consideration of equation (1) indicates that indeed such sorption would result in enhanced hydrolysis. Recent work by Kissel, et al. (1971) and by Rich (1970) indicates a similar salt-induced hydrolysis may occur in montmorillonite. Hence, prolonged washing of Al-saturated clays to remove excess electrolyte may well alter their properties significantly. Moreover, it is evident that we need to know more about the energy status of various adsorbed hydrolytic aluminum species.

Exchange

Measurements of the exchange of aluminum are complicated by hydrolysis, and, if base is added, by the precipitation of a solid phase. In this section, we will consider only the simple exchange reactions of Al^{3+} and H^+, reserving precipitation reactions for later discussion. Early studies of the exchange of H^+ and Al^{3+} ions were confounded by the difficulties of preparation of homoionic clays. Gilbert and Laudelout (1965) found the affinity for exchange of hydrogen by montmorillonite was as follows:

$$Li^+ < Na^+ < H^+ < K^+ < NH^+ < Rb^+ < Cs^+$$

although they considered the position of H^+ to be approximate owing to the tendency of the clay to decompose. Recently, Foscolos and Barshad (1969) have used new techniques in the preparation of H-montmorillonite and report that the affinity for H^+ exchange is below that for Na^+, although the differences in affinity are not great. Thus, these studies indicate that hydrogen occupies its usual place in the selectivity sequence demonstrated for common strong-acid cation exchangers (Helfferich 1962). However, since clays rapidly decompose when hydrogen-saturated, these findings are perhaps of limited practical importance.

Foscolos (1968) has demonstrated that the position of Al^{3+} in the selectivity sequence of Wyoming bentonite (with CEC = 90 me/100 g) is:

$$H^+ < Na^+ < Mg^{2+} < Ca^{2+} < K^+ < Al^{3+} .$$

For Otay montmorillonite with a higher charge density (CEC = 125 me/100 g) the sequence is:

$$H^+ < Na^+ < Mg^{2+} < Ca^{2+} < Al^{3+} < K^+ .$$

In Jeffersite vermiculite (CEC = 175 me/100 g) the sequence is:

$Mg^{2+} < Ca^{2+} < H^{+} < Al^{3+} < Na^{+}$.

Foscolos (1968) did not include K^+ in the study of vermiculite to avoid the complications of lattice collapse; however, he states that K^+ would be preferred over Al^{3+} by vermiculite. On the basis of these results, he concluded that as the surface charge density increases, univalent cations are preferentially adsorbed over ions of higher valence.

In studies of Ca:Al exchange equilibria, Coulter and Talibudeen (1968) found that Al^{3+} was preferred to Ca^{2+} by all soils and clays studied. Moreover, the preference for Al^{3+} relative to Ca^{2+} was in the order:

vermiculite >> illite > montmorillonite.

This increase in the preference for trivalent over divalent cations was attributed to increasing charge density in the series montmorillonite-illite-vermiculite, in agreement with considerations of electrical double layer theory, while findings by Foscolos (1968) seem in contradiction. Subsequently, Coulter (1969) found that for montmorillonite, Al^{3+} was strongly preferred over K^+. In vermiculite and illite, not all K^+ could be easily exchanged by Al, but, even if corrections were made for this "difficultly exchangeable K", these minerals showed preference for K^+ over Al^{3+}. The relative preference of minerals for K^+ versus Al^{3+} was in the order:

vermiculite, illite >> montmorillonite.

These findings indicate that the exchange of aluminum with other ions is not yet well understood. Miller and Brown (1969) measured activation energies of mixtures of NaCl and $AlCl_3$ and of clays and resins containing various amounts of Na^+ and Al^{3+}. They concluded that competition between the two ions for developing separate and incompatible order in the water surrounding them may lead to antagonistic effects between these ions. Similar competition between hydroxyaluminum and Ca^{+2} for exchange sites is suggested by work of Kozak and Huang (1971). These complications could likely affect measurements of exchange constants in clay systems. Corrections for hydrolysis may well be the largest uncertainty, since extraction with salt solutions enhances hydrolysis under some circumstances. Coulter (1969) and Coulter and Talibudeen (1968) assumed the presence of $Al(OH)_2^+$ in order to interpret their results. Foscolos (1968) reports that his values for exchange constants were corrected for the fact that adsorbed trivalent aluminum only exists below pH 3.0. The manner in which this correction was made, or its necessity, is not clear. These studies all suggest, however, that Al^{3+} is not as strongly sorbed as its valence would otherwise predict.

Titration Curves

As with aqueous aluminum solutions, considerable useful information has been obtained from titration curves of aluminum- and hydrogen-saturated clays. As Jenny (1961) points out, however, interpretation of the data seems to lag behind its collection. Early studies were of course confounded by the difficulties of preparing homoionic clays. Subsequent studies indicated that H-clays titrated as strong acids, Al-clays as weak acids, and that mixtures showed two buffer ranges corresponding to the neutralization of H^+ ions followed by Al^{3+} ions.

A third buffer range in the potentiometric titration of acid clays was reported by Schwertmann and Jackson (1963, 1964), which they attributed to the formation of basic aluminum compounds. Coleman and Thomas (1967) conclude that this work as well as that of Coleman and Thomas (1964) and Coleman et al. (1964) suggests that hydroxyaluminum compounds existing as coatings or interlayers are responsible for this third buffer range.

Independently, Mitra et al. (1963) reported the presence of a third buffer range in the titration of acid montmorillonite and suggested that this third range may be due to broken bond hydroxyl groups, structural hydroxyl groups, or Lewis acid sites. Sawhney and Frink (1966) examined titration curves of acid montmorillonite and also found three buffer ranges. Since the third buffer range was increased by increasing severity of acid treatment, they suggested that the weak acid titrated in this range was a complex alumino-silicate resulting from the decomposition of lattice edges. Recently, Mitra and Kapoor (1969) have reported four buffer ranges in the titration curves of acid montmorillonites. These are attributed to H^+ ions, Al^{3+}ions, basic aluminum ions, and weak acid groups assumed to be hydroxyl groups associated with aluminum at lattice edges.

A somewhat different approach has been taken by Turner et al. (1963) who assumed that two reactions occur when $Ca(OH)_2$ is added to Al-saturated clays:

$$2\ \text{Al-clay} + 3\ Ca^{2+} = 3\ \text{Ca-clay} + 2\ Al^{3+} \qquad (3)$$

$$Al^{3+} + 3\ OH^- = Al(OH)_3 \qquad (4)$$

combining the Ca:Al ion exchange constant and the solubility product of $Al(OH)_3$, they derived an equation to describe the relationship between the lime potential, $pH-\frac{1}{2}pCa$, and the percent base saturation. One difficulty with this approach is that the ion product of $Al(OH)_3$ does not appear to remain constant throughout the titration; hence allowance must be made for this variability if the prediction is to be precise (Turner and Clark 1965). Other variables, including time of reaction, accompanying anions, and temperature, are also important (Singh 1967, 1972; Turner and Brydon 1965,1967). None of these workers have observed the variety of inflection points reported by others.

Shainberg and Dawson (1967) examined a variety of titrants for acid montmorillonite, including NaOH and the sodium salts of boric, acetic, formic and nitrous acids. They demonstrated that $Na_2B_4O_7$ is a strong enough base to titrate both exchangeable H^+ and Al^{3+}, while NaOAc will titrate only exchangeable H^+ since the equivalence point with Al^{3+} cannot be detected. Titration with NaOH neutralizes exchangeable H^+ and Al^{3+}, as well as some protons attached to clay hydroxyl groups. Depending on the choice of the end point, a possible titer due to aluminate formation was also reported in the NaOH titration. Interestingly, they attribute about 14 me/100 g to hydroxyl groups in Wyoming bentonite, a value surprisingly close to the figure of 15-16 me/100 g found by Mitra and Kapoor (1969) for the fourth buffer range and attributed by them to Al-OH groups at lattice edges.

Rich (1970) titrated various exchangers with NaOH, $Ba(OH)_2$ and $Na_2B_4O_7$. He found that titration to pH 8.0 gave better estimates of acidity than did inflection points because of adsorption by the exchanger of partially neutralized hydroxy-aluminum species. He also observed, in agreement with Shainberg and Dawson (1967), that aluminate could be formed during titration with strong bases, leading to erroneously high results.

Thus, the soil acidity merry-go-round continues. Although it is not possible to reconcile all these conflicting observations, a tentative explanation will be attempted. Two groups of investigators (Schwertmann and Jackson 1963, 1964; Sawhney and Frink 1967) observed that the total potentiometric titratable acidity of acid clays in 1<u>N</u> NaCl decreased markedly on aging. They both observed three inflection points but disagreed on the interpretation of the third buffer range. Conductometric titrations (Mitra et al. 1963; Mitra and Kapoor 1969; Shainberg and Dawson 1967) do not show any decrease in titratable acidity on aging and suggest that the last buffer range in titration curves is due to lattice hydroxyls.

Hence, it is proposed that the third buffer range reported by Schwertmann and Jackson (1963, 1964) and later studied by Frink and Sawhney (1967) is in fact due to lattice hydroxyls as suggested by Mitra et al. (1963), Mitra and Kapoor (1969), and by Shainberg and Dawson (1967). The decrease in titratable acidity observed in potentiometric titrations of aged clays may then be attributed to the effect of salt on the titration of aluminum in the intermediate buffer ranges.

Sufficient evidence exists to indicate that salt may restrict the exchange of aluminum in both vermiculite (Kaddah and Coleman 1967 a,b) and montmorillonite (Rich 1970; Kissel et al. 1971). Restriction of exchange by salt apparently depends on various factors, such as time of equilibration, since it was not observed by Mitra and Kapoor (1969) when salt was added in their relatively slow potentiometric titration of aged acid clays. Neither was this restricted exchange observed in titration of fresh or aged Al-saturated montmorillonite by Frink and Sawhney (1967).

Recent studies by Schwertmann (1969) of the physical and chemical properties of various acid clays suggest that aging of concentrated suspensions at elevated temperatures leads to significant aggregation, accompanied by a decrease in exchangeable H^+ and Al^{3+} and an increase in non-exchangeable polynuclear hydroxyaluminum cations. Banin and Shaked (1969) aged dilute suspensions of H-montmorillonite at high temperatures and found them to remain well dispersed, with tactoids containing only one to two plates. They attribute this behavior to formation of some surface coating which prevents adherence of clay plates, while Schwertmann (1969) proposed that hydroxyaluminum polymers are responsible for the aggregation he observed. Both studies, however, indicated that Al-montmorillonites are well aggregated, with tactoids containing ten or more plates (Banin and Shaked 1969). The disparate effects of suspension concentration on the characteristics of aged clays suggests that the various effects of aging reported in potentiometric studies can be attributed in part to differing methods of sample preparation and hence aggregation.

Solid Phase and Polynuclear Species

As with aqueous aluminum salt solutions, a variety of solid phase aluminum compounds and partially neutralized hydroxyaluminum species have been reported in clay suspensions. The presence of clay offers an additional complication, however, since both polynuclear species and solid phase compounds may be retained by expanding layer silicates, giving rise to hydroxyaluminum interlayers or "chloritized" clays. Moreover, as Turner (1967) has pointed out, the reaction products obtained from neutralization of an Al-saturated clay are frequently different from those obtained if the aluminum salt solution is partially neutralized before it is added to the clay. Investigations of the various solid phases and polynuclear species found in clay suspensions have proceeded along two lines. In one, the aim has been to prepare synthetic hydroxyaluminum interlayered clays with properties similar to those found in soils. The second aim has been to study the neutralization of Al-saturated clays as an aid in understanding the reactions assumed to occur during the liming of acid soils.

Rich (1968) has prepared an excellent review of the occurrence,formation, and properties of hydroxyl interlayers in layer silicates; consequently the present analysis will be limited to a brief summary and review of recent work. Aluminum interlayers may be formed in both vermiculites and montmorillonites by treating them with partially neutralized Al-salt solutions. The resulting clays have greatly reduced cation exchange capacities, generally attributed to the blocking of exchange sites by sorption of hydroxyaluminum species or by precipitation of continuous solid phases in interlayer positions. The adsorption of considerable amounts of $Al(OH)_x$ by illite and kaolinite (Turner and Brydon 1967) indicates that sorption on external surfaces can also be quite pronounced. Indeed, Tweneboah et al. (1967) suggested that minerals in acid soils may be coated with aluminum "outerlayers". In vermiculites, a structure with a 14Å basal spacing is created, which resists collapse to 10Å on K-saturation or heating. In montmorillonites, a similar structure is developed which resists expansion on Mg-saturation and glycerol solvation, as well as resisting collapse to 10Å on K-saturation or heating. After aging in the laboratory, gibbsite and other forms of $Al(OH)_3$ are frequently found as separate phases, depleting some aluminum from interlayer positions. This process is apparently more rapid in montmorillonite than in vermiculite suspensions (Brydon and Turner 1972).

Many investigators have attempted to determine the OH/Al ratio of interlayer material by relating the observed changes in exchange capacity to aluminum absorbed in or extracted from interlayer positions. According to Rich (1968), the outcome of these analyses indicates that the OH/Al ratio of even one interlayer may be variable since the degree of blocking of exchange sites varies with the amount of interlayer material. Sawhney (1968) found that the apparent OH/Al ratio of interlayer aluminum in vermiculite was close to the OH/Al ratio of the particular aluminum salt solutions used in preparation of the interlayered material, but concluded that the choice of a specific polynuclear species based on charge alone was uncertain. Weismiller et al. (1967) suggested that gibbsite-like rings of structure $[Al(OH)_2(H_2O_2]_6^{6+}$ as proposed by Hsu and Bates (1964) would satisfy their observations of infrared adsorption spectra of montmorillonite containing interlayer material with OH/Al = 1.5. Little other direct evidence of the structure of interlayer material is available.

Recent studies by Colombera et al.(1971) show that the adsorption of hydroxyaluminum species by illite can be described by Langmuir adsorption isotherms at constant OH/Al ratio. This behavior, as well as other aspects of the adsorption reactions, indicated that the process is not one of exchange, but rather involves the formation of hydrogen bonds between the surface of illite and the hydroxyaluminum species similar to those formed by the sorption of hydroxy cations on silica (Stumm and O'Melia 1968). In contrast to reports by Hsu (1968) that the surface of montmorillonite is non-homogenous in its affinity for hydroxyaluminum species, Colombera et al. (1971) believe the surface of illite to be homogeneous with respect to adsorption of hydroxyaluminum species. Hence, it appears that earlier theories of the constancy of charge or of OH/Al ratio of interlayer material are probably in error. Moreover, the conclusions of Hahn and Stumm (1968) that the nature of solute species cannot be deduced from knowledge of sorbed species should certainly be kept in mind.

Considering briefly the solid phases and polynuclear species formed during neutralization of Al-saturated clays, we find less attention is given to the formation of interlayer material and more to the possible forms of $Al(OH)_3$ precipitated as a separate phase. This is certainly due in part to observations that few interlayers are formed during neutralization of dilute Al-clay suspensions (Frink and Peech 1963b; Ragland and Coleman 1960; Turner 1967). Most other studies of the solubility and identification of aluminum hydroxide have been conducted with soils and will be described subsequently.

Summary

Although theoretical considerations suggest that electrostatic adsorption by clays of the hydrolysis products of aluminum should not alter the simple monomeric mechanism, considerable evidence indicates that the presence of an indifferent electrolyte such as NaCl may well alter the reaction. Under conditions where interplate diffusion is restricted, in-situ hydrolysis is enhanced and various hydrolytic species may be specifically sorbed by clays.

When precautions are taken to prepare pure H-clays, H^+ is found to occupy its usual place in the so-called lyotropic series. The exchange of Al^{3+} is less well understood and is apparently influenced by differing charge densities of minerals, the nature of the counter ion and uncertainties in corrections for the hydrolysis of Al^{3+} itself. In general, Al^{3+} does not appear to be as strongly preferred in exchange reactions as its valence would suggest.

Titration curves of H- and Al-saturated clays have been studied for many years, but interpretation of the data has lagged behind its collection. It was formerly assumed that H-clays titrate as strong acids, Al-clays as weak acids, and mixtures of the two exhibit two buffer ranges corresponding to the neutralization of H^+ ions followed by Al^{3+} ions. Recent reports of three and four buffer ranges have shown that the reactions occurring during titration are considerably more complex. All four buffer ranges are seldom resolved in a particular titration curve, so that interpretations are difficult. It is proposed that aluminum may give rise to two intermediate buffer ranges, while the fourth buffer range, recently reported, may be due to lattice hydroxyl groups.

Both solid phase and polynuclear aluminum species are adsorbed by expanding layer silicates and may produce hydroxyaluminum interlayers or artificially "chloritized" clays. Cation-exchange capacity is reduced and lattice expansion or collapse is considerably restricted. While early investigators attempted to assign specific structures and OH/Al ratios to interlayer material, recent work suggests that its composition is continuously variable from simple monomeric aluminum through various polynuclear species culminating in the precipitation of $Al(OH)_3$.

ALUMINUM CHEMISTRY IN SOILS

Having examined in some detail the reactions of aluminum in aqueous solutions and clay suspensions, we now inquire how these reactions relate to the chemical properties of acid soils in the field. In particular, we will examine factors controlling aluminum solubility in soil solutions, the reactions involved in neutralization of acid soils and the role of aluminum interlayers.

Aluminum in Soil Solutions

Lindsay et al. (1959) measured the solubility of aluminum in $CaCl_2$ extracts of three samples of an acid soil, one amended with sulfur, one with lime, and an untreated check, and found the ion product pH-1/3pAl to remain nearly constant for any one sample as the concentration of $CaCl_2$ varied from 0.001 to 0.1 M. This constancy can be predicted from considerations of double layer theory, provided the concentrations of Al^{3+} and H^+ on the clay surface remain constant, and does not necessarily imply the presence in soil of solid phase $Al(OH)_3$. In the three soils examined, pH-1/3pAl was 2.52 in the soil at pH 4.2, 2.66 in the soil at pH 4.8 and 2.86 in the soil at pH 5.3 Corresponding values of pH-1/3pAl for gibbsite vary from 2.67 (Kittrick 1966) to 2.83 (Frink and Peech 1962) depending on the crystallinity of the product. Hence, these soils at pH 4.8 and pH 5.3 could be at equilibrium with gibbsite. Subsequent studies (Frink and Peech 1962) of the solubility of synthetic gibbsite in soil solutions showed that equilibrium was established very slowly, particularly in undersaturated solutions with values of pH-1/3pAl less than 2.67-2.83. The highest value of pH-1/3pAl for soils supersaturated with respect to gibbsite was 3.59, which was reduced only to 3.30 after equilibration with gibbsite for one month. Hence, it appears that forms of $Al(OH)_3$ more soluble than gibbsite can persist in soils for considerable periods of time.

Recently, Richburg and Adams (1970) have suggested that the apparent increase in the solubility of $Al(OH)_3$ with increasing soil pH is due to the inappropriate choice of the monomeric hydrolysis reaction, equation (1), for calculating the activity of trivalent aluminum. They report that use of the hydrolysis reaction:

$$6Al^{3+} + 15H_2O = Al_6(OH)_{15}^{3+} + 15H^+ \quad (5)$$

proposed by Brosset et al.(1954), considerably reduced the apparent dependency of the calculated ion product of $Al(OH)_3$ on soil pH. It should be noted, however, that this cannot be the sole criteria for testing the appropriateness of a proposed hydrolysis constant. Using their approach, for example, one could assign arbitrary values to the monomeric hydrolysis constant until the dependence of the ion product for $Al(OH)_3$ on pH is minimized. However, such a revised constant would then not predict the observed changes in pH on dilution of aluminum salt solutions. Since the proposed mechanism, equation (5), does not meet this criteria either (Frink and Peech 1963a), it is doubtful if it should be assumed to describe Al^{3+} activity in soil extracts. Although Richburg and Adams (1970) imply that $Al_6(OH)_{15}^{3+}$ is the sole hydrolysis product, they report that the calculated activity of Al^{3+} was not altered significantly if both the monomeric and polymeric hydrolysis reactions were assumed to proceed simultaneously. This seems consistent with the findings of Turner and colleagues (Turner et al.1968a, 1968b; Turner and Ross 1969)in their studies of titration curves of aluminum salt solutions, namely that polynuclear species may be present in addition to monomeric species, particularly at high degrees of neutralization. Thus, it appears possible that soil solutions supersaturated with respect to gibbsite, as were all soils examined by Richburg and Adams (1970), could be considered to contain polynuclear as well as monomeric aluminum ions. It also seems likely that the particular species will vary from one soil to another depending on past history as has been shown with aqueous aluminum salt solutions.

A number of partially neutralized or basic aluminum salts have been reported to precipitate from aqueous solutions and clay suspensions. Singh and Brydon (1967, 1969, 1970) have identified a crystalline basic aluminum sulfate, basaluminite, with formula $Al_4(OH)_{10}SO_4 \cdot 5H_2O$ and $pK_{sp} = 117.3$. Well-crystallized aluminum sulfates have been found in acid sulfate soils (van Beers 1962) and may perhaps be basaluminite. Richburg and Adams (1970) examined the solubility product of basaluminite in a number of soils and found it to decrease from pK = 117 in soil at pH 4.4 to pK = 112 in soil at pH 5.6. They attributed this inconstancy to use of the monomeric hydrolysis mechanism; using the polymeric mechanism, the calculated pK was reasonably constant at approximately pK = 123. Since this compound is apparently much less soluble than that studied by Singh and Brydon, the question of the appropriate hydrolysis mechanism is again raised.

Soils may contain other solid phase aluminum compounds, but their role in controlling the solubility of aluminum in soil solution is not clear. Discrete amorphous aluminum compounds similar to boehmite have been reported in some soils (de Villiers 1969). Copious precipitates of white aluminum hydroxide have been found in acid sulfate soils (van Beers 1962). Allophane, an amorphous gel containing silica and alumina in mole ratios between 0.5 and 1.3, is formed in many soils derived from volcanic ash (Coleman and Thomas 1967). Amorphous material was reported by Yuan (1969) to constitute as much as 65% of the clay fraction in a variety of soils, yet little is known of its solubility.

Although aluminum forms many soluble complexes with the hydroxyl ion, it forms few other stable complexes with ions likely present in soil solutions. However, fluoride complexes of aluminum are quite stable (Sillén and Martell 1964, 1971) and must be considered if fluoride is present in soil extracts. Hem (1968) has shown, for example, that fluoride complexes with aluminum will predominate in many natural waters below pH 6.6 in the presence of as little as 10^{-5} $\underline{M}$ fluoride. Complexes with sulfate may also be important (Turner and Brydon 1965; Richburg and Adams 1970) and should be given more consideration in analyses of soil extracts. Calculations of Hem (1968) indicate that such complexes would be particularly important in acid sulfate soils. Although knowledge of the formation of complexes of aluminum with phosphate is fragmentary (Sillén and Martell 1964, 1971), recent evidence suggests they could easily be important in strongly acid soils (Bohn and Peech 1969).

Aluminum may also form complexes or chelates with soil organic matter. Schnitzer (1969) reports some provisional studies indicating that fulvic acid complexes of aluminum are more stable than complexes of divalent cations. Aluminum was reported to occur as $AlOH^{2+}$ in complexes with metal to fulvic acid ratios of 1:1, but as $Al(OH)_2^+$ in 3:1 and 6:1 complexes. As more aluminum was added, the complex precipitated, suggesting an explanation of the movement of aluminum in podzols to the B horizon (Schnitzer 1969). Huang and Keller (1972) found the solubility of aluminum-bearing minerals to be enhanced by a number of organic acids. They also believe aluminum may be transported during weathering in organic complexes but subsequently precipitated by anions such as OH^-, PO_4^{3-} or SiO_4^{4-}. Complexes between aluminum and humic acid have also been reported (Khan 1969). According to Greenland (1971), aluminum will react with fulvic acid at pH 4.0 or below and be adsorbed in the interlayers of montmorillonite. These bonds, called "cation bridges" are rather weak and are readily broken by salt leaching. Aluminum sorbed by organic matter is believed to play an important role in soil structure and in the pH-dependent cation-exchange capacity of soils as described subsequently.

Neutralization of Acid Soils

The rationale for much of what has been discussed so far is the hope that it will aid in understanding the reactions of soil when amended with lime. Although controversy still exists over the nature of the beneficial effects of liming, we will proceed to examine the reactions of aluminum in limed soils.

One approach to the problem of predicting pH and solubility of aluminum as a result of adding lime has been taken by Turner et al.(1963) and was described briefly in a previous section. Clark and Nichol (1966) have shown that the value of the corrected lime potential follows that derived from the titration of Al-bentonite with $Ca(OH)_2$ for diverse acid and neutral mineral and organic soils. However Bache (1970) feels that correcting the solubility product of $Al(OH)_3$ does not correct a more basic problem, namely that equilibrium is not established in such titrations. He found that both $pH-\frac{1}{2}pCa$ and $pH-1/3pAl$ varied with time and solid-to-solution ratio and concluded that exchange isotherms must be measured to allow extrapolation to a point where no exchange of Al^{3+} or Ca^{2+} occurs.

A different approach to the neutralization reactions of acid soils assumes that at least three reactions occur when lime is added, and that these reactions correspond roughly to the various inflection points observed in the titration of acid clays. First, exchangeable hydrogen, if present, is neutralized; most soils contain little or no exchangeable hydrogen, however, unless free acid is present as is likely in acid sulfate soils (Dewan and Rich 1970). Next, exchangeable and non-exchangeable aluminum is neutralized over a pronounced buffer range. Although it is often assumed that this buffer range is centered at pH = 5.0, equivalent to the value pK = 5.0 for the first-stage hydrolysis constant of aluminum, the buffer range undoubtedly varies since even in aluminum salt solutions the pH of maximum buffer capacity is a function of total aluminum concentration (Frink and Sawhney 1967). The final stage of neutralization involves edge sites of minerals and weak acid groups of soil organic matter. The neutralization of soils in these latter buffer ranges, above about pH 5.5-6.0, creates additional cation-exchange capacity, commonly referred to as pH-dependent CEC. Since this pH-dependent CEC can be detected in titration curves, but is not exchangeable with neutral salts, it is also included in measurements of titratable acidity (Coleman and Thomas 1967).

The presence of pH-dependent CEC in soils has at least two important consequences: it causes large differences in apparent lime requirements depending on the method of measurement, and also affects the availability of other cations.Methods of measurement of lime requirement have been ably reviewed by Coleman and Thomas (1967). Controversy still exists, however, as to whether soils should be limed to neutralize exchangeable Al^{3+} (Kamprath 1970; Reeve and Sumner 1970) or to raise the pH to nearer neutrality+). The subject of the effect of liming on the availability of other cations, particularly potassium, is also one of some controversy. Recent evidence (Thomas and Coleman 1959; Bartlett and McIntosh 1969) suggests, however, that liming decreases potassium availability by increasing the CEC, thereby lowering the degree of potassium saturation of the exchange sites and, hence, its availability. Coleman and Thomas (1967) suggest that liming can also reduce CEC in the intermediate pH range of approximately 5.5 by precipitating aluminum and blocking exchange sites. This phenomenon has not been widely observed, however, in field studies.

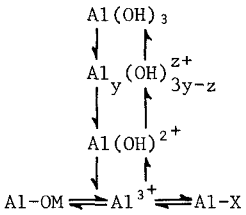
Because of the importance of pH-dependent CEC in soils, considerable effort has been devoted to its description and measurement. Since clays containing synthetic aluminum interlayers exhibit pH-dependent CEC (de Villiers and Jackson 1967b) the pH-dependent CEC of soils is often attributed in large part to aluminum interlayers or sesquioxide coatings on clay surfaces (de Villiers and Jackson 1967a; Rich 1968). Soil organic matter also contributes to pH-dependent CEC (Coleman and Thomas 1967) and its contribution frequently may be large. In addition, an association of hydroxyaluminum with organic matter is often implied, which compounds the problem of separating the various components of pH-dependent CEC.

+) Lime Requirement of Soils-Inactivate Toxic Substances or Favorable pH Range? E.O.McLean, E.J.Kamprath. Ltrs. to the Editor. Soil Sci.Soc.Amer.Proc. 34: 363-364.

McLean and his colleagues have studied pH-dependent CEC in some detail; McLean and Owen (1969) found from multiple regression analysis that in a wide variety of soils, organic matter contributed about 20% of the CEC at pH 2.5, but more than 45% at pH 8.0. They also reported that organic exchange sites unable to sorb K^+ from KCl were inactivated by non-exchangeable aluminum. Liming appeared to reactivate these sites, presumably by deprotonation of hydroxyaluminum, in agreement with earlier results by Bhumbla and McLean (1965). Fiskell (1970) measured pH-dependent CEC in surface and subsurface horizons of varying organic matter and clay content and concluded that apparent pH-dependent CEC was mainly due to hydroxyy-aluminum in interlayers and to that associated with organic matter.

Sawhney et al. (1970) proposed that contributions to pH-dependent CEC from organic matter and aluminum interlayers could be distinguished by measuring the reversibility of changes in CEC with pH. The increase in CEC from release of protons of weakly-dissociated organic matter should be eliminated by simply decreasing the pH again. Since raising the pH presumably would irreversibly precipitate aluminum interlayers or sesquioxide coatings, the increase in pH-dependent CEC from this source would be permanent. Most of the pH-dependent CEC in a number of spodosols from the Northeast was reversible and hence was attributed to weakly acidic organic matter groups. Unfortunately, aluminum bound to organic sites might also react in similar fashion, so the contribution of aluminum-organic matter complexes to pH-dependent CEC is not resolved by this technique. Sawhney, et al. (1970) did find, however, in agreement with other earlier studies, that the pH-dependent CEC was reasonably well correlated with amounts of aluminum extracted with NaOAc at pH 4.8. Subsequently, Sawhney and Norrish (1971) showed that kaolinite, halloysite, imogolite and allophane can contribute significantly to reversible pH-dependent CEC when present in soils. Irreversible components of pH-dependent CEC were shown to be very small in soils of tropical regions.

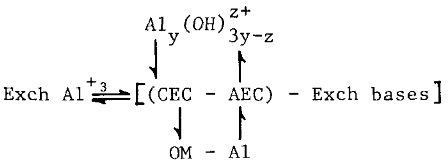
Pionke and Corey (1967) have defined "non-exchangeable acidic aluminum" as the difference between Al extracted by pH 4.8 $\underline{N}$ NH_4OAc and that extracted by 1$\underline{N}$ KCl. This "non-exchangeable acidic aluminum" reached a maximum in soils at about pH 5.0 and decreased in more acid or alkaline soils. Since this non-exchangeable acidic aluminum was correlated better with soil organic matter than with pH or clay content, they proposed it was complexed by soil organic matter according to the scheme:



where OM represents organic matter and X the clay component. Although the proposed reaction seems reasonable, the coincidence of the observed maximum in solubility with the pH of the extracting solution makes it possible that this is an artifact, i.e., the solubility of aluminum in soils more acid than the extractant might be reduced while the solubility in less acid soils would be increased.

Subsequently, Pionke et al.(1968) compared the ability of various soil properties to predict lime requirement, and ranked them in the order: pH-dependent sites on organic matter > non-exchangeable acidic aluminum > exchangeable Al^{3+} $\geq$ pH-dependent sites on clays. The regression relationship obtained accounted for nearly 90% of the observed variability in lime requirement as measured by neutralization with $CaCO_3$ to pH 6.0 in 1N KCl.

In oxisols, Reeve and Sumner (1971) have found little relationship between pH and exchangeable Al^{3+3}, a finding contrary to much earlier work. They propose that the scheme presented by Pionke and Corey (1967) be modified as follows:



where net CEC (the CEC less anion exchange capacity, AEC) and exchangeable bases control exchangeable Al^{3+} in equilibrium with hydroxyaluminum species and complexes with organic matter.

Thus, these various schemes suggest that exchangeable Al^{3+} exists in relatively small amounts in soils but is in equilibrium with a relatively large pool of non-exchangeable aluminum. Early studies attributed much of this non-exchangeable aluminum to aluminum interlayers and oxide coatings. Present evidence, however, indicates that organic matter complexes are also important. Coleman and Thomas

(1967) suggested that "neutralization of organic matter in acid soils may be no more a titration of a weak acid than is neutralization of clay", and subsequent studies indicate they may well be correct.

Aluminum Interlayers

Aluminum interlayers are found in expanding layer silicates in a wide variety of soils and sediments, yet the optimum conditions favoring their formation, even under laboratory conditions, are not known completely. Moreover, aluminum interlayers found in soils are in general more resistant to heat treatment and chemical extractants than synthetic laboratory samples. Rich (1968) is of the opinion that formation of aluminum interlayers in soils is favored by: active weathering to provide aluminum, moderate pH (4.6-5.8), low organic matter content and frequent wetting and drying. In tidal sediments in California, Lynn and Whittig (1966) found that under reducing conditions chlorite containing ferrous iron apparently was formed. Other studies (Rich 1968) indicate that magnesium may be an important component of interlayers in marine sediments.

According to Jackson (1963a) in acid soils aluminum interlayers form via the weathering sequence:

$$\text{mica} \rightleftharpoons \text{vermiculite} \rightleftharpoons \text{14A intergrade.}$$

The interlayer material may then degrade through the sequence:

$$\text{14A intergrade} \rightleftharpoons \text{Al-chlorite} \rightleftharpoons \text{kaolinite.}$$

Considerable evidence exists that these reaction sequences are indeed reasonable (Rich 1968). Less is known, however, of the reversibility of weathering sequences. Lynn and Whittig (1966) found undrained sediments contained montmorillonite, chlorite, mica and kaolinite. Sediments drained for six years developed typical cat-clay characteristics, yet the clay minerals were unaltered. After 60 years of drainage, however, all crystalline minerals showed deterioration and diffuse X-ray diffraction patterns. Chlorite had decreased the most and apparently had been converted to montmorillonite (or a high charge mica), hence reversing the weathering process. Frink (1969) reported that chloritized vermiculite transported from a watershed of acid soils into a neutral lake environment was apparently stripped of aluminum interlayers and partially converted to illite. Efforts to demonstrate dechloritization by comparison of paired wooded and cultivated soils were not successful.+)

+) Frink C.R. 1968. Aluminum interlayers in wooded and cultivated soils. Agron. Abstr. p.151.

As with clays containing synthetic aluminum interlayers, the cation-exchange capacity of soils is reduced by aluminum interlayers. Although these interlayers are often thought to be to be the source of pH-dependent CEC, we have seen that organic matter in soils also plays an important role. Changes in exchange capacity on extraction with reagents which remove aluminum have been used to measure the extent of interlayer formation (Frink 1965); however, it is likely that some of the increase found is merely a manifestation of pH-dependent CEC.

Aluminum interlayers also affect the fixation of K^+, NH_4^+, Cs^+, and Rb^+ by layer silicates. The interlayer material tends to prop open layer silicates and reduce K^+ fixation by preventing layer collapse in vermiculite and soil clays containing vermiculite (Rich 1968). Selectivity of minerals for K-size ions is also altered since they may enter partially opened mica layers without causing collapse (Rich 1968). Although most mechanisms proposed to explain the selectivity for K^+ in minerals (Sawhney 1972) suggest that aluminum interlayers should decrease selectivity for K^+, Kozak and Huang (1971) report enhanced selectivity in interlayered vermiculite and K-depleted biotite. They propose that, in addition to the "propping effect" on K^+ fixation, aluminum interlayers increase the apparent K/Ca selectivity by interfering with calcium exchange.

Summary

The solubility of aluminum in some acid soils appears to be controlled by the solubility of gibbsite. However, soils at higher pH appear to be supersaturated with respect to gibbsite. Such soils may contain more soluble forms of $Al(OH)_3$ or, perhaps, soluble polynuclear species. Soluble complexes of aluminum with phosphate, sulfate, fluoride, and organic matter may also be present in soils. Other solid phase aluminum compounds are found in soils, but their role in controlling aluminum solubility is uncertain.

The neutralization of acid soils is believed to involve at least three reactions: first, neutralization of exchangeable hydrogen, present only in very acid soils; second, neutralization of exchangeable and non-exchangeable aluminum; and third, neutralization of a rather vague collection of acids including edge sites of minerals and organic matter. This latter range corresponds roughly to pH-dependent CEC which in turn influences lime requirement and the availability of other cations. Studies of pH-dependent CEC in soils suggest that relatively small amounts of exchangeable aluminum occur in equilibrium with a relatively large pool of non-exchangeable acidic aluminum. Earlier studies associated this latter category with interlayer aluminum; present evidence indicates that complexes with organic matter should also be considered.

Aluminum interlayers reduce soil CEC and reduce the ability of vermiculites to fix K^+ and other ions of similar size and charge. Optimum conditions for their formation are moderate pH, low organic matter content, and frequent wetting and drying. Once formed, they may weather ultimately to kaolinite or, if environmental conditions change, as in draining of acid sulfate soils, they may revert to precursors in the weathering sequence.

ALUMINUM AND SOIL PHYSICAL PROPERTIES

In view of the extensive studies of the chemistry of aluminum in soils, it is somewhat surprising that little is known of the effect of aluminum on the physical properties of soils. We will begin by examining some of the effects of aluminum on physical properties of clays and then examine physical properties of acid soils in the field.

Observations of Al-saturated montmorillonite by Banin and Shaked (1969) and Schwertmann (1969) indicate that such clays are well aggregated, with tactoids containing ten or more plates. Davey and Low (1971) observed that a mixed Na-Al montmorillonite became viscous and gelation commenced in 2% suspensions, while the same behavior was not noted in pure Na-saturated clays until the suspension concentration reached 4%. The tensile strength of montmorillonite was found to increase as the valence of the saturating cation increased; however, Dowdy and Larson (1971) felt some of the tensile strength of Al-montmorillonite was due to the formation of hydrous oxides. Kidder and Reed (1972) found that macroscopic swelling of montmorillonite was greatly reduced by introduction of synthetic aluminum interlayers. Similarly, Tamura (1957) had reported that removal of aluminum interlayers from a soil montmorillonite permitted it to swell on glycerol solvation. Quigley (1969) pointed out that adsorbed aluminum causes problems in soil mechanics research, since the usual chemical pretreatments to prepare "clean" clays may remove adsorbed aluminum, making engineering test data unreliable in the field. Quigley (1969) felt that adsorbed aluminum particularly affected the measurements of Attenberg plastics limits. Thus, all of these reports suggest that aluminum may act to hold clay particles together and presumably should have some effect on soil structure.

Iron oxides have long been thought to be the primary agent cementing clay particles together providing the various kinds of structure observed in field soils. However, recent evidence suggests that aluminum may be more important than iron in many soils. Flach et al. (1969) suggest too much importance may have been ascribed to iron, due to its obvious coloration and ease of extraction, and that aluminum cementing agents should be examined more thoroughly. Deshpande et al. (1968) have reviewed earlier work and have also conducted extensive studies of the relationship between changes in the physical structure of red soils and amounts of iron, aluminum, silica and organic matter removed by various extractants. They concluded that most of the free iron oxides in such soils exist as discrete particles with little effect on soil physical properties, and that aluminum, along with minor amounts of iron and silica, plays the major role in cementation of soil particles into structural units. Saini et al.(1966) examined aggregate stability in the B-horizon of spodosols and found a better correlation of stability with aluminum oxides than with iron oxides. Reeder et al. (1967) presented evidence suggesting that aluminum is involved in creating structural stability in solonetzic soils when the pH is lowered.

Other studies have not shown aluminum to be involved in formation of some soil structures. Grossman and Carlisle (1969), for example, have reviewed available information on fragipan formation and concluded that aluminum is not the principle cementing agent in these pans. Aluminum interlayers might be expected to reduce measured clay contents of soils unless drastic dispersants are used prior to mechanical analysis. However, studies in this laboratory of the clay contents of interlayered soils described by Frink (1965) have failed to show any difference between clay content determined before or after extraction with sodium citrate. Similarly, Dixon et al.(1968) compared particle sizes determined after the conventional sodium metaphosphate dispersion and those found following a more drastic treatment with citrate-dithionite-bicarbonate. Even though some of the soils studied contained very stable aluminum interlayers, particle sizes by the two methods were nearly identical. Hence, aluminum is apparently not a universal cementing agent in all soils. These studies do emphasize, however, that continued attention should be given to the role of aluminum in soil aggregation as suggested some time ago by Jackson (1963a, 1963 b).

While it is quite likely that organic matter plays a most important role in the structure of clay soils (Boekel 1963), aluminum-organic combinations may also play some part. According to Edwards and Bremner (1967), microaggregate formation in soils involves the binding of organic matter by clay through linkage with polyvalent metals on exchange sites. Parfitt and Greenland (1970) found that soil polysaccharides were little adsorbed by Na- or Ca-montmorillonite but strongly adsorbed by Al-montmorillonite. However, Martin and Richards (1969) showed that iron and aluminum salts greatly reduced the influence of various polysaccharides on soil aggregation and hydraulic conductivity. This may be due in part to increased bonding among individual polysaccharide molecules, since the effect was much less if the soil was treated first with the polysaccharide and then with the metal. Despite considerable accumulated information on the nature of soil polysaccharides (Swincer et al. 1969) and on the nature of clay-organic complexes (Mortland 1970), the role of aluminum in binding organic matter to soil is largely unknown.

Since acid soils are generally amended with lime to improve fertility, we should consider the effect of liming on soil structure. Emerson and Dettmann (1960), from a review of earlier work and studies of their own, concluded that liming decreases attractive forces between clay particles, presumably by neutralizing trivalent aluminum, and hence tends to reduce the stability of soil crumbs. However, liming and especially the presence of free $CaCO_3$ provides enough soluble Ca^{2+} to maintain flocculation and help keep drainage waters clear. In acid sulfate soils, flocculation of silt in drainage water by soluble aluminum has a similar effect; however, the tremendous accumulation of silt rapidly fills the canals, making frequent dredging necessary (Moormann 1963). Large amounts of $Ca(OH)_2$ (several percent by weight) are sometimes added to soil to reduce swelling and shrinking and improve its mechanical properties for roads and other structures. Most earlier studies of lime soil stabilization assumed that the reaction involved dissolution of existing clay minerals and the formation of new calcium silicate and calcium aluminum hydrates (Grim 1962). Recent work by Pettry and Rich (1971) shows that clay minerals are not completely dissolved, since an acid extraction restored the original X-ray diffraction patterns. Apparently, $CaCO_3$ is a major reaction product, along with some soil-$Ca(OH)_2$ reaction products found lining the interior walls of soil voids and as intergranular bridges. These reactions would not be expected, however, as a result of normal liming of agricultural soils.

Summary

Aluminum reacts with clays and causes increased aggregation, viscosity, and tensile strength and reduces macroscopic swelling. Although iron has long been thought to be the principal cementing agent in soils, present evidence indicates that aluminum is of major importance in creating structural stability in red soils and spodosols. The nature of the cementing agent in fragipans is not known, but it does not appear to be aluminum. Although aluminum interlayers are common in many acid soils, they are not stable enough to prevent dispersion of soils for mechanical analyses. While clay-organic matter complexes may be responsible for structural stability in many soils, the role of aluminum in binding organic matter to clay is not yet clear. Liming of acid soils has been shown to reduce structural stability of soil crumbs, perhaps by neutralizing exchangeable aluminum.

SUMMARY AND CONCLUSIONS

The simple monomeric hydrolysis mechanism provides a satisfactory description of the pH and aluminum ion activity of dilute aqueous aluminum salt solutions at low basicities. When base is added, a solid phase of $Al(OH)_3$ is formed with varying degrees of anion substitution. At high basicities, significant amounts of various metastable polynuclear hydroxyaluminum cations may be present in solution. Present evidence indicates that the monomeric hydrolysis mechanism is still operative in such solutions, since there is no unequivocal proof of the superiority of any particular polymeric mechanism.

Theoretical considerations and experimental data show that the monomeric hydrolysis mechanism is not altered by simple electrostatic adsorption of hydrolysis products on clay surfaces. However, where diffusion is restricted by lattice collapse, in-situ hydrolysis is enhanced and various hydrolytic products may be specifically sorbed by clays. Studies of the exchange of aluminum are complicated by corrections for hydrolysis, but Al^{3+} does not seem to be as strongly preferred in exchange reactions as its valence might otherwise suggest. This behavior must also be attributed to specific sorption effects which are poorly understood.

The neutralization of acid clays involves several reactions: first, neutralization of exchangeable hydrogen; second, neutralization of aluminum, which may include both exchangeable and non-exchangeable forms; and third, neutralization of lattice hydroxyl groups. Titration curves may reveal three or four buffer ranges depending on how well these various reactions are resolved.

Both solid phase and soluble aluminum species may be adsorbed by expanding layer silicates, producing hydroxyaluminum interlayers. As a result, cation-exchange capacity is reduced and lattice expansion and collapse is considerably restricted. Interlayers also reduce the ability of vermiculite to fix K^+ and other ions of similar size and charge. While early investigators attempted to assign specific structures and OH/Al ratios to interlayer material, recent work suggests that the composition is continuously variable from simple monomeric aluminum through various polynuclear species culminating in the precipitation of $Al(OH)_3$. In soils, optimum conditions for the formation of aluminum interlayers are moderate pH, low organic matter content, and frequent wetting and drying.

The solubility of aluminum in some acid soils appears to be controlled by the solubility of gibbsite. However, soils at higher pH appear to be supersaturated with respect to gibbsite. Such soils may contain more soluble forms of $Al(OH)_3$, or polynuclear species of aluminum may be present. Soluble complexes of aluminum with phosphate, sulfate, fluoride, and organic matter may also be present in soils under some circumstances.

The neutralization reactions of acid soils are similar to those of acid clays but also include reactions of soil organic matter. The third or final neutralization range in soils corresponds roughly to pH-dependent CEC which in turn influences lime requirement and the availability of other cations. Studies of the pH-dependent CEC of soils suggest that relatively small amounts of exchangeable aluminum occur in equilibrium with a relatively large pool of non-exchangeable acidic aluminum. Earlier studies associated this latter category largely with interlayer aluminum, but recent work indicates that complexes with organic matter must also be considered.

Aluminum reacts with clays, causing increased aggregation, viscosity, and tensile strength but reduces macroscopic swelling. Although iron has long been thought to be the principal cementing agent in soils, it now appears that aluminum is of major importance in creating structural stability in red soils and spodosols. The nature of the cementing agent in fragipans is not known, but it does not appear to be aluminum. Although aluminum interlayers are common in many acid soils, they are not stable enough to prevent dispersion of soils during mechanical analyses. While clay-organic matter complexes are responsible for structural stability in many soils, the role of aluminum in binding organic matter to clay is not yet clear. Liming of acid soils reduces the structural stability of soil crumbs, perhaps by neutralizing exchangeable aluminum.

Despite occasional pessimism that studies of aluminum chemistry in aqueous solutions can lead to an understanding of the reactions of acid soils in the field, the record indicates that considerable progress has been made. Promising areas for further research include studies of the hydration status of aluminum ions adsorbed on clay surfaces, investigations of the nature of soluble aluminum species in supersaturated solutions with the aim of simplifying the present bewildering array of proposed polynuclear species, and an examination of the complexes of aluminum with inorganic and organic ligands present in soils.

REFERENCES

AVESTON, J. 1965. Hydrolysis of the aluminium ion: Ultra-centrifugation and acidity measurements. J. Chem. Soc. 4438-4443.

BACHE, B.W. 1970. Determination of pH, lime potential, and aluminium hydroxide potential of acid soils. J. Soil Sci. 21: 28-37.

BANIN, A. and SHAKED, D. 1969. Particle size and surface properties of acidic montmorillonite. Int. Clay Conf., Proc. Vol.1 (Tokyo, Japan), 669-682. Israel Universities Press, Jerusalem.

BARSHAD, I. 1969. Preparation of H saturated montmorillonites. Soil Sci. 108: 38-42.

BARSHAD, I. and FOSCOLOS, A.E. 1970. Factors affecting the rate of the interchange reaction of adsorbed H^+ on the 2:1 clay minerals. Soil Sci.110:52-60.

BARTLETT, R.I. and McINTOSH, J.L. 1969. pH-dependent bonding of potassium by a spodosol. Soil Sci. Soc. Amer. Proc. 33: 535-539.

BEERS, W.F.J.van. 1962. Acid sulphate soils. Int. Institute for Land Reclamation and Improvement. Bull. 3. 31 p. Wageningen, The Netherlands.

BHUMBLA, D.R. and McLEAN, E.O. 1965. Aluminum in soils: VI. Changes in pH-dependent acidity, cation-exchange capacity, and extractable aluminum with additions of lime to acid surface soils. Soil Sci. Soc. Amer. Proc. 29: 370-374.

BOEKEL, P. 1963. The effect of organic matter on the structure of clay soils. Neth. J. Agr. Sci. 11: 250-263.

BOHN, H.L. and PEECH, M. 1969. Phosphatoiron (III) and phosphatoaluminum complexes in dilute solutions. Soil Sci. Soc. Amer. Proc. 33: 873-876.

BROSSET, C., BIEDERMANN, G. and SILLEN, L.G. 1954. Studies on the hydrolysis of metal ions. XI. The aluminum ion, Al^{+3}. Acta Chem. Scan.8: 1917-1926.

BRYDON, J.E. and TURNER, R.C. 1972. The nature of Kenya vermiculite and its aluminum hydroxide complexes. Clays and Clay Minerals 20: 1-11.

CLARK, J.S. and NICHOL, W.E. 1966. The lime potential-percent base saturation relations of acid surface horizons of mineral and organic soils. Can. J. Soil Sci. 46: 281-285.

COLEMAN, N.T. and THOMAS, G.W. 1964. Buffer curves of acid clays as affected by the presence of ferric iron and aluminum. Soil Sci. Soc. Amer. Proc. 28: 187-190.

COLEMAN, N.T. and THOMAS, G.W. 1967. The basic chemistry of soil acidity. In R.W. Pearson and F. Adams (eds.): Soil acidity and liming. Agronomy 12: 1-41. Amer. Soc. of Agr.,Madison, Wisconsin.

COLEMAN, N.T., THOMAS, G.W., LEROUX, F.H. and BREDELL, G. 1964. Salt-exchangeable and titratable acidity in bentonite-sesquioxide mixtures. Soil Sci. Soc. Amer. Proc. 28: 35-37.

COLUMBERA, P.M., POSNER, A.M. and QUIRK, J.P. 1971. The adsorption of aluminium from hydroxy-aluminium solutions on to Fithian illite. J.Soil Sci.22:118-128.

COULTER, B.S. 1969. The equilibria of K:Al exchange in clay minerals and acid soils. J. Soil Sci. 20: 72-83.

COULTER, B.S. and TALIBUDEEN, O. 1968. Calcium:aluminium exchange equilibria in clay minerals and acid soils. J.Soil Sci. 19: 237-250.

DAVEY, B.G. and LOW, P.F. 1971. Physico-chemical properties of sols and gels of Na-montmorillonite with and without adsorbed hydrous aluminum oxide. Soil. Sci. Soc. Amer. Proc. 35: 230-236.

DESHPANDE, T.L., GREENLAND, D.J. and QUIRK, J.P. 1968. Changes in soil properties associated with the removal of iron and aluminium oxides. J.Soil. Sci. 19: 108-122.

DE VILLIERS, J.M. 1969. Pedosesquioxides-composition and colloidal interactions in soil genesis during the Quaternary. Soil Sci. 107:454-461.

DE VILLIERS, J.M. and JACKSON, M.L. 1967a. Cation exchange capacity variations with pH in soil clays. Soil Sci. Soc. Amer. Proc. 31: 473-476.

DE VILLIERS, J.M. and JACKSON, M.L. 1967b. Aluminous chlorite origin of pH-dependent cation exchange capacity variations. Soil Sci. Soc. Amer. Proc.31: 614-618.

DEWAN, H.C. and RICH, C.I. 1970. Titration of acid soils. Soil Sci. Soc. Amer. Proc. 34: 38-44.

DIXON, J.B., McCRACKEN, R.J., PEELE, T.C. and RICH, C.I. 1968. Particle size analysis of soils compared by sodium metaphosphate and sodium carbonate dispersion methods. Soil Sci. Soc. Amer. Proc. 32: 734-735.

DOWDY, R.H. and LARSON, W.E. 1971. Tensile strength of montmorillonite as a function of saturating cation and water content. Soil Sci. Soc. Amer. Proc. 35: 1010-1014.

EDWARDS, A.P. and BREMNER, J.M. 1967. Microaggregates in soils. J. Soil Sci. 18: 64-73.

EMERSON, W.W. and DETTMANN, M.G. 1960. The effect of pH on the wet strength of soil crumbs. J.Soil Sci. 11: 149-158.

FISKELL, J.G.A. 1970. Cation exchange capacity and component variations of soils of southeastern USA. Soil Sci.Soc.Amer.Proc.34: 723-727.

FLACH, K.W., NETTLETON, W.D., GILE, L.H., and CADY, J.G. 1969. Pedocementation: Induration by silica, carbonates and sesquioxides in the Quaternary. Soil Sci. 107: 442-453.

FOSCOLOS, A.E. 1968. Cation-exchange equilibrium constants of aluminum-saturated montmorillonite and vermiculite clays. Soil Sci. Soc. Amer. Proc.32:350-354.

FOSCOLOS, A.E. and BARSHAD, I. 1969. Equilibrium constants between both freshly prepared and aged H-montmorillonites and chloride salt solutions. Soil Sci. Soc. Amer. Proc. 33: 242-247.

FRINK, C.R. 1965. Characterization of aluminum interlayers in soil clays. Soil Sci. Soc. Amer. Proc. 29: 379-382.

FRINK, C.R. 1969. Chemical and mineralogical characteristics of eutrophic lake sediments. Soil Sci. Soc. Amer. Proc. 33: 369-372.

FRINK, C.R. and PEECH, M. 1962. The solubility of gibbsite in aqueous solutions and soil extracts. Soil Sci. Soc. Amer. Proc. 28: 346-347.

FRINK, C.R. and PEECH, M. 1963a. Hydrolysis of the aluminum ion in dilute aqueous solutions. Inorg. Chem. 2: 473-478.

FRINK, C.R. and PEECH, M. 1963b. Hydrolysis and exchange reactions of the aluminum ion in hectorite and montmorillonite suspensions. Soil Sci. Soc. Amer. Proc. 27: 527-530.

FRINK, C.R. and SAWHNEY, B.L. 1967. Neutralization of dilute aqueous aluminum salt solutions. Soil Sci. 103: 144-148.

FRIPIAT, J.J., VAN CAUWELAERT, F. and BOSMANS, H. 1965. Structure of aluminum cations in aqueous solutions. J.Phys. Chem. 69: 2458-2461.

GILBERT, M. and LAUDELOUT, H. 1965. Exchange properties of hydrogen ions in clays. Soil Sci. 100: 157-162.

GREENLAND, D.J. 1971. Interactions between humic and fulvic acids and clays. Soil Sci. 111: 34-41.

GRIM, R.E. 1962. Applied clay mineralogy. McGraw Hill Book Co., New York. 422 p.

GROSSMAN, R.B. and CARLISLE, F.J. 1969. Fragipan soils of the eastern United States. Advances in Agron. 21: 237-279.

HAHN, H.H. and STUMM, W. 1968. Coagulation by Al (III). Adv. in Chem. 79: 91-111.

HELFFERICH, F. 1962. Ion exchange. McGraw Hill Book Co., New York. 624 p.

HEM, J.D. 1968. Aluminum species in water. Adv. in Chem. 73: 98-114.

HOLMES, L.P., COLE, D.L. and EYRING, E.M. 1968. Kinetics of aluminum ion hydrolysis in dilute solutions. J.Phys.Chem. 72: 301-304.

HSU, P.H. 1968. Heterogeneity of montmorillonite surface and its effect on the nature of hydroxy-aluminum interlayers. Clays and Clay Minerals 16: 303-311.

HSU, P.H. and Bates, T.F. 1964. Formation of X-ray amorphous and crystalline aluminum "hydroxides". Mineral Mag. 33: 749-768.

HUANG, W.H. and KELLER, W.D. 1972. Geochemical mechanics for the dissolution, transport and deposition of aluminum in the zone of weathering. Clays and Clay Minerals 20: 69-74.

JACKSON, M.L. 1963a. Interlayering of expansible layer silicates in soils by chemical weathering. p.29-46. In W.F.Bradley (ed.): Clays and Clay Minerals, Proc. 11th Conf. Macmillan Co. (Pergamon), New York.

JACKSON, M.L. 1963b. Aluminum bonding in soils: a unifying principle in soil science. Soil Sci. Soc. Amer. Proc. 27: 1-10.

JENNY, H. 1961. Reflections on the soil acidity merry-go-round. Soil Sci. Soc. Amer. Proc. 25: 428-432.

KADDAH, M.T. and COLEMAN, N.T. 1967a. Salt displacement and titration of $AlCl_3$-treated trioctahedral vermiculites. Soil Sci. Soc. Amer. Proc. 31: 328-332.

KADDAH, M.T. and COLEMAN, N.T. 1967b. Salt displacement of acid-treated trioctahedral vermiculites. Soil Sci. Soc. Amer. Proc. 31: 333-336.

KAMPRATH, E.J. 1970. Exchangeable aluminum as a criterion for liming leached mineral soils. Soil Sci. Soc. Amer. Proc. 34: 252-254.

KHAN, S.V. 1969. Interaction between the humic acid fraction of soils and certain metallic cations. Soil Sci. Soc. Amer. Proc. 33: 851-854.

KIDDER, G. and REED, L.W. 1972. Swelling characteristics of hydroxyaluminum interlayered clays. Clays and Clay Minerals 20: 13-20.

KISSEL, D.E., GENTZSCH, E.P. and THOMAS, G.W. 1971. Hydrolysis of non-exchangeable acidity in soils during salt extractions of exchangeable acidity. Soil Sci. 111: 293-297.

KITTRICK, J.A. 1966. The free energy of formation of gibbsite and $Al(OH)_4^-$ from solubility measurements. Soil Sci. Soc. Amer. Proc. 30: 595-598.

KOZAK, L.M. and HUANG, P.M. 1971. Adsorption of hydroxy-Al by certain phyllosilicates and its relation to K/Ca cation exchange selectivity. Clays and Clay Minerals 19: 95-102.

LINDSAY, W.L., PEECH, M. and CLARK, J.S. 1959. Determination of aluminum ion activity in soil extracts. Soil Sci. Soc. Amer. Proc. 23: 266-269.

LYNN, W.C. and WHITTIG, L.D. 1966. Alteration and formation of clay minerals during cat clay formation. p.241-248. In W.F. Bradley (ed.): Clays and Clay Minerals, Proc. 14th Conf. Macmillan Co. (Pergamon), New York.

MARTIN, J.P. and RICHARDS, S.J. 1969. Influence of the copper, zinc, iron and aluminum salts of some microbial and plant polysaccharides on aggregation and hydraulic conductivity of Ramona sandy loam. Soil Sci. Soc. Amer. Proc. 33: 421-423.

MATIJEVIĆ, E., JANAUER, G.E. and KERKER, M. 1964. Reversal of charge of lyophobic colloids by hydrolyzed metal ions. I. Aluminum nitrate. J.Colloid.Sci. 19: 333-346.

MATIJEVIĆ, E., MATHAI, K.G., OTTERWILL, R.H. and KERKER, M. 1961. Detection of metal ion hydrolysis by coagulation. III. Aluminum. J.Phys.Chem. 65:826-830.

McLEAN, E.O. and OWEN, E.J. 1969. Effects of pH on the contributions of organic matter and clay to soil cation exchange capacities. Soil Sci. Soc.Amer.Proc. 33: 855-858.

MILLER, R.J. and BROWN, D.S. 1969. The effect of exchangeable aluminum on conductance and diffusion activation energies in montmorillonite. Soil Sci. Soc. Amer. Proc. 33: 373-378.

MITRA, R.P. and KAPOOR, B.S. 1969. Acid character of montmorillonite: titration curves in water and some non-aqueous solvents. Soil Sci. 108: 11-23.

MITRA, R.P., SHARMA, B.K. and KAPOOR, B.S. 1963. Three stages in the titration of montmorillonite in water and in acetonitrile-benzene mixtures. Ind. J. Chem. 1: 225-226.

MOORMANN, F.R. 1963. Acid sulfate soils (cat-clays) of the tropics. Soil Sci. 95: 271-275.

MORTLAND, M.M. 1970. Clay-organic complexes and interactions. Adv. in Agron.22: 75-117.

OKURA, T., GOTO, K. and YOTUYANAGI, T. 1962. Forms of aluminum determined by an 8-quinolinolate extraction method. Anal. Chem. 34: 59-63.

PARFITT, R.L., and GREENLAND, D.F. 1970. Adsorption of polysaccharides by montmorillonite. Soil Sci. Soc. Amer. Proc. 34: 862-866.

PETTRY, D.E. and RICH, C.I. 1971. Modification of certain soils by calcium hydroxide stabilization. Soil Sci. Soc. Amer. Proc. 35: 834-838.

PIONKE, H.B. and COREY, R.B. 1967. Relations between acidic aluminum and soil pH, clay, and organic matter. Soil Sci. Soc. Amer. Proc. 31: 749-752.

PIONKE, H.B., COREY, R.B. and SCHULTE, E.E. 1968. Contributions of soil factors to lime requirement and lime requirement tests. Soil Sci. Soc. Amer. Proc. 32: 113-117.

QUIGLEY, R.M. 1969. Soil mechanics research problems caused by aluminum and iron adsorption on clay minerals. Int. Clay Conf., Proc. Vol. 1 (Tokyo, Japan) 793-803. Israel Universities Press, Jerusalem.

RAGLAND, J.L. and COLEMAN, N.T. 1960. The hydrolysis of aluminum salts in clay and soil systems. Soil Sci. Soc. Amer. Proc. 24: 457-460.

RAUPACH, M. 1963. Solubility of simple aluminum compounds expected in soils. II. Hydrolysis and conductance of Al^{+3}. Aust. J. Soil Res. 1: 36-45.

RAUSCH, W.V. and BALE, H.D. 1964. Small-angle X-ray scattering from hydrolyzed aluminum nitrate solutions. J. Chem. Phys. 40: 3391-3394.

REEDER, S.W., ARSHAD, M.A. and ODYNSKY, W. 1967. The relationship between structural stability and chemical criteria of some solonetzic soils of northwestern Alberta. Can. J. Soil Sci. 47: 231-237.

REEVE, N.G. and SUMNER, M.E. 1970. Lime requirements of Natal oxisols based on exchangeable aluminum. Soil Sci. Soc. Amer. Proc. 34: 595-598.

REEVE, N.G. and SUMNER, M.E. 1971. Cation exchange capacity and exchangeable aluminum in Natal oxisols. Soil Sci. Soc. Amer. Proc. 35: 38-42.

RICH, C.I. 1968. Hydroxy interlayers in expansible layer silicates. Clays and Clay Minerals 16: 15-30.

RICH, C.I. 1970. Conductometric and potentiometric titration of exchangeable aluminum. Soil Sci. Soc. Amer. Proc. 34: 31-38.

RICHBURG, J.S. and ADAMS, F. 1970. Solubility and hydrolysis of aluminum in soil solutions and saturated-paste extracts. Soil Sci. Soc. Amer. Proc.34:728-734.

RILEY, D. and ARNOLD, P.W. 1969. Hydrogen-magnesium, hydrogen-sodium exchange equilibria and the formation of "exchangeable" aluminum. Soil Sci. 108: 414-418.

ROSS, G.J. and TURNER, R.C. 1971. Effect of different anions on the crystallization of aluminum hydroxide in partially neutralized aqueous aluminum salt solutions. Soil Sci. Soc. Amer. Proc. 35: 389-392.

RUFF, J.K. and TYREE, S.Y. 1958. Light-scattering studies on aqueous aluminum nitrate solutions. J. Amer. Chem. Soc. 80: 1523-1526.

SAINI, G.R., MACLEAN, A.A. and DOYLE, J.J. 1966. The influence of some physical and chemical properties on soil aggregation and response to VAMA. Can. J. Soil Sci. 46: 155-160.

SAWHNEY, B.L. 1968. Aluminum interlayers in layer silicates: Effect of OH/Al ratio of Al solution, time of reaction and type of structure. Clays and Clay Minerals 16: 157-163.

SAWHNEY, B.L. 1972. Selective sorption and fixation of cations by clay minerals: A review. Clays and Clay Minerals 20: 93-100.

SAWHNEY, B.L. and FRINK, C.R. 1966. Potentiometric titration of acid montmorillonite. Soil Sci. Soc. Amer. Proc. 30: 181-184.

SAWHNEY, B.L., FRINK, C.R. and HILL, D.E. 1970. Components of pH dependent cation exchange capacity. Soil Sci. 109: 272-278.

SAWHNEY, B.L. and NORRISH, K. 1971. pH dependent cation exchange capacity: Minerals and soils of tropical regions. Soil Sci. 112: 213-215.

SCHNITZER, M. 1969. Reactions between fulvic acid, a soil humic compound and inorganic soil constituents. Soil Sci. Soc. Amer. Proc. 33:75-81.

SCHOFIELD, R.K. and TAYLOR, A.W. 1954. The hydrolysis of aluminium salt solutions. J. Chem. Soc. 4445-4448.

SCHWERTMANN, U. 1969. Aggregation of aged hydrogen clays. Int. Clay Conf., Proc. Vol. 1 (Tokyo, Japan) 683-690. Israel Universities Press, Jerusalem.

SCHWERTMANN, U. and JACKSON, M.L. 1963. Hydrogen-aluminum clays: A third buffer range appearing in potentiometric titration. Science 139: 1052-1053.

SCHWERTMANN, U. and JACKSON, M.L. 1964. Influence of hydroxy aluminum ions on pH titration curves of hydronium-aluminum clays. Soil Sci. Soc. Amer. Proc. 28: 179-183.

SHAINBERG, I. and DAWSON, J.E. 1967. Titration of H-clay suspensions with salt solutions. Soil Sci. Soc. Amer. Proc. 31: 619-626.

SILLÉN, L.G. and MARTELL, A.E. 1964. Stability constants of metal-ion complexes. Special Publ. No. 17, 754 p. The Chemical Society, Burlington House, London.

SILLÉN, L.G. and MARTELL, A.E. 1971. Stability constants of metal-ion complexes. Supplement No. 1. Special Publ. No. 25, 865 p. The Chemical Society, Burlington House, London.

SINGH, S.S. 1967. Sulfate ions and ion activity product $Al(OH)^3$ in Wyoming bentonite suspensions. Soil Sci. 104: 433-438.

SINGH, S.S. 1969. Neutralization of dilute aqueous aluminum sulfate solutions with a base. Can. J. Chem. 46: 663-667.

SINGH, S.S. 1972. The effect of temperature on the ion activity product $Al(OH)^3$ and its relation to lime potential and degree of base saturation. Soil Sci. Soc. Amer. Proc. 36: 47-50.

SINGH, S.S. and BRYDON, J.E. 1967. Precipitation of aluminum by $Ca(OH)_2$ in the presence of Wyoming bentonite and sulfate ions. Soil Sci. 103: 162-168.

SINGH, S.S. and BRYDON, J.E. 1969. Solubility of basic aluminum sulfates at equilibrium in solution and in the presence of montmorillonite. Soil Sci. 107: 12-16.

SINGH, S.S. and BRYDON, J.E. 1970. Activity of aluminum hydroxy sulfate and the stability of hydroxy aluminum interlayers in montmorillonite. Can.J.Soil Sci. 50: 219-225.

SRINIVASAN, K. and RECHNITZ, G.A. 1968. Reaction rate measurements with fluoride ion-selective membrane electrode. Anal.Chem.40:1818-1825.

STUMM, W. and O'MELIA, C.R. 1968. Stoichiometry of coagulation. J. Amer. Water Works Assoc. 60: 514-539.

SULLIVAN, J.H.Jr. and SINGLEY, J.E. 1968. Reactions of metal ions in dilute aqueous solution: Hydrolysis of aluminum. J. Amer. Water Works Assoc. 60: 1280-1287.

SWINCER, G.D., OADES, J.M. and GREENLAND, D.J. 1969. The extraction, characterization and significance of soil polysaccharides. Adv. in Agron.21:195-235.

TAMURA, T. 1957. Identification of the 14A clay mineral component. Amer. Mineral. 42: 107-110.

THOMAS, G.W. and COLEMAN, N.T. 1959. A chromatographic approach to the leaching of fertilizer salts in soils. Soil Sci. Soc. Amer. Proc.23: 113-116.

TURNER, R.C. 1967. Aluminum removed from solution by montmorillonite. Can.J. Soil Sci. 47: 217-222.

TURNER, R.C. 1968a. Conditions in solution during the formation of gibbsite in dilute Al salt solutions: I. Theoretical treatment of the effect of the formation of mono- and polynuclear hydroxy aluminum ions, precipitations and crystallization on curves representing the titration of $AlCl_3$ with a base. Soil Sci. 106: 291-296.

TURNER, R.C. 1968b. Conditions in solution during the formation of gibbsite in dilute Al salt solutions: II. Effect of length of time of reaction on the formation of polynuclear hydroxy aluminum cations, the substitution of other anions for OH^- in amorphous $Al(OH)_3$ and the crystallization of gibbsite. Soil Sci. 106: 338-344.

Summary

This introductory lecture reviews and summarizes recent achievements in aluminum chemistry in relation to soil acidity. Subsequently are considered the aluminum reactions in aqueous solutions, in clay suspensions and in soils. The explanation of aluminum behaviour is difficult because of uncertainties about both the nature of the solid phase and monomeric and polynuclear dissolved species. Aluminum interactions with clay minerals, organic matter and metaloid ions further complicate this picture. All the same considerable progress has been made in distinguishing various of the aluminum species and in recognizing their very important role in soil reaction, cation exchange reactions and stabilization of soil structure, especially in acid soils.

Résumé

Cette introductoire passe en revue et résume les résultats récents de la chimie d'aluminum par rapport à l'acidité du sol. Consécutivement ont été traitées les réactions d'aluminum dans les solutions aqueuses, dans les suspensions argileuses et dans les sols mêmes. L'interprétation de la conduite de l'aluminum est difficile à cause des incertitudes autour du caractère de la phase solide et des espèces dissolues monomériques et polynucléaires. En plus l'interprétation est compliquée par les interactions d'aluminium avec les minéraux d'argiles, la matière organique et les ions métalloides. Néanmoins on a réussi à déterminer plusieurs d'espèces d'aluminium et leurs influence sur la réaction du sol, l'échange de cations et la stabilisation de la structure, surtout dans les sols acides.

Resumen

Esta ponencia da una resena de las resultas recientes en la química de aluminio relacionado al acidez de suelo. Se ha tratado consecutivamente las reacciones de aluminio en soluciones acuosas, en suspenciones arcillosas y en suelos. Es muy dificil el interpretar del comportamiento del aluminio debido a las incertidumbres relativo al caracter de la fase solida y de las especies disueltas monoméricas y polinuclearias. Luego se complica el concepto por las reacciones de aluminio antes de minerales arcillosas, materia organica y iones metaloides. Sin embargo se ha avanzado en medida progresiva en determinando especies de aluminio y reconosciendo su influencia en la reacción del suelo, los procesos de intercambio de cationes y la stabilisación de la estructura, sobre todo en los suelos ácidos.

Zusammenfassung

Diese Einleitung ist eine Zusammenfassung der letzten Entwicklungen im Gebiet der Aluminiumchemie in Beziehung zur Bodensäure. Nacheinander werden behandelt die Aluminiumreaktionen in Wasserlösungen, in Tonsuspensionen und in Böden. Die Erklärung des Aluminiumbenehmens wird erschwert durch Unsicherheiten über das Naturell der festen Phase und der aufgelösten monomerischen und polynukleären Aluminiumarten. Weiterhin wird das Bild kompliziert durch die Wechselwirkung zwischen Aluminium und Tonmineralien, organischen Substanzen und metalloiden Ionen. Trotzdem hat man wichtige Fortschritte gemacht namentlich in der Determination von verschiedenen Aluminiumarten und im besseren Kenntnis derer spezifischen Wirkungen auf die Bodensäure, Kationen-Austauschkapazität und Stabilität der Bodenstruktur.

RECOGNITION AND PREDICTION OF ACID SULPHATE SOIL CONDITIONS

R.Brinkman and L.J.Pons
Department of Soil Science and Geology
University of Agriculture, Wageningen

INTRODUCTION

Time and change in acid sulphate soils

As long as sediments or soils containing pyrite remain reduced, they are subject to little change apart from possible transformation of other sulphides to pyrite; recrystallization of pyrite, and loss of water. Such soils varying little with time can be described in terms of relatively few characteristics.

Soils containing acid sulphates are transients, the acids present being neutralized or leached out again within periods of a few years to, at the outside, a hundred years or so. From a geological viewpoint the formation and subsequent disappearance of acid sulphate soils is a virtually instantaneous process; it is also very rapid compared with most processes of soil formation. As in other sciences, analysis of transients covers a broader spectrum than analysis of phenomena that are more constant with time.

In the study of this transient phenomenon, the initial state, i.e. the nature of the supposedly potential acid soil, is only one of the aspects to be considered. Other aspects are the rate of development: the speed of oxidation in one place and the downward speed of the oxidation front, for example, as well as the rate at which acids are leached. Since an acid sulphate soil is a soil in rapid flux, even the measurement of a similarly low pH at similar times in two succeeding years may not mean the same thing twice: the acid formed in the previous year may have leached out and a similar quantity formed with the second year's seasonal oxidation, decreasing the reserve of potential acid (pyrite).

Of great practical importance in reclamation is not only the expected degree of acidity, but also the expected time span of its occurrence. Present methods of identifying and predicting acid sulphate soils take into account quantities only, and not time aspects.

Economic and social interest

The identification and prediction of acid sulphate soils is extremely important for economic reasons, but even more so for social reasons.Many times in the past as well as in the present - and in many parts of the world - much of the land in a new polder has proved unsuitable for crops because of acid sulphate conditions. This has resulted in a low standard of living or even abandonment of certain areas. Similar problems have sometimes arisen in places where drainage was improved.

The relatively short period of, say, 40 years between the development and disappearance of toxic conditions may economically and socially cripple two generations of farmers, and prevent repayment of the investments.

Other factors remaining equal, the physical quality and suitability for agriculture of clayey soils tend to increase with increasing pyrite contents in the original reduced sediment, up to the point where toxicity begins to play a part. With still higher pyrite contents, there is an abrupt drop in suitability from very high to virtually useless, at least for dry-land crops.

Sound identification is therefore necessary before one can decide whether reclamation is justified; if so, one can work out an appropriate economic management system for the expected soil conditions before embarking upon reclamation; if not, one can decide upon alternative development elsewhere.

This great economic and social interest, besides the obvious attraction of a rapid, relatively complicated, natural process occurring right under our eyes, may explain the long and venerable list of investigators studying, predicting, and identifying acid sulphate soils throughout the last two centuries.

Practical problems

The immediate causes of failure or of uneconomically low yields of upland crops on acid sulphate soils appear to be a combination of some or all of the following:

a) inhibition of root growth due to aluminium toxicity (e.g. Rees and Sidrak 1961, Cate and Sukhai 1964);

b) in severe cases also ferric iron or manganese toxicity;

c) probably also extreme acidity;

d) in combination with these three, but also after their elimination by leaching and mineral dissolution, the - perhaps temporary - low fertility level;

e) the generally very low permeability of the subsoil due to inhibited soil ripening, causing a low water storage capacity of the soil profile and hazards of temporary waterlogging and sometimes irreversible drying of peaty topsoils.

The low fertility level, which is characteristic for acid sulphate soils but not restricted to them, is due in some cases (Rhizophora muds) to the high C/N ratio of the organic matter, often occurring in high percentages; a low rate of N accumulation due to the very low microbiological activity; the very high exchangeable aluminium percentage; the precipitation of phosphate by soluble aluminium; the low contents of micro-nutrients like Cu, Mn; the generally low content of rapidly weatherable minerals; and, in severe cases, the low cation exchange capacity due to preferential acid dissolution of smectites and illite. Aluminium toxicity may also be induced or aggravated even in old leached acid sulphate soils without free (soluble) acids by cation exchange due to fertilizer applications without the addition of adequate amounts of lime. Excessive liming may induce other micro-nutrient deficiencies.

The problems for wet rice cultivation are different in kind but similar in severity. If an acid sulphate soil is reduced too long before rice is sown, the young seedlings may die due to H_2S or ferrous iron toxicity. Older plants, e.g. replanted rice, have more resistance, probably because of the oxygen flow through their roots. On the other hand, if rice is sown or transplanted on an acid sulphate soil too soon after water saturation, aluminium toxicity inhibits root growth and the seedlings may die.

Although acid sulphate soils are identified and predicted on the basis of free acids present or expected, clearly these acids are only part of the problems faced by users of acid sulphate soils.

Terms and definitions

Before embarking upon a discussion on identification and prediction of acid sulphate soils, we should delimit the subject by defining some terms.

An (actual) acid sulphate soil is a soil with one or more horizons consisting of (actual) acid sulphate materials, i.e. materials containing soluble acid aluminium and ferric sulphates in concentrations toxic to most common dry-land crops. Such materials have high proportions of exchangeable aluminium, pH (water) below 4, and many have characteristically pale yellow mottles by acid sulphates of iron, potassium-iron or sodium-iron. Some have white mottles of aluminium sulphates. The U.S. Soil Conservation Service (USDA 1970) defines a "sulfuric" horizon as a mineral or organic horizon with a pH lower than 3.5 (1:1 in water) and with yellow jarosite mottles of hues 2.5Y or yellower and chroma 6 or more (Munsell 1954 colour notation).

A potential acid sulphate soil or material is a soil or a reduced parent material which is expected by the person identifying it to become an acid sulphate soil or material upon drainage and oxidation under certain defined future field conditions. Such soils or materials generally have one or more reduced horizons or are reduced, with pyrite contents considerably in excess of any neutralizing amounts of calcium carbonate present. In sandy or peaty materials with low cation exchange capacity, the excess pyrite may be small. Whether such a soil will in fact become an actual acid sulphate soil depends upon a number of factors besides the contents of S and neutralizing components, as will be discussed below. The Soil Conservation Service (USDA 1970) specifically defines "sulfidic" materials as waterlogged mineral or organic soil materials that have 0.75 per cent (dry weight) or more total S, mostly in the form of sulphides, and less than 3 times as much carbonate ($CaCO_3$ equivalent) as sulphur (weight percentages).

The Soil Map of the World (Dudal 1968) recognizes a "Thionic" unit where recent alluvial soils contain sufficient sulphur compounds to cause acidification of the soil upon oxidation to a pH (KCl) less than 3.5 within 100 cm of the surface. This includes both potential and actual acid sulphate soils, and the depth limit would seem somewhat deep for detailed maps, but the definition does allow the grouping of potential and actual acid sulphate soils as well as shallowly reclaimed former acid sulphate soils in one unit: a distinct advantage for soil maps at a scale of 1:5 million.

If the time aspect were also taken into account in the definition and rating of acid sulphate soil, this would require specification of, for example, rainfall and its seasonal differences, expected actual evapotranspiration during development, expected soil permeability and leaching rate during and after oxidation, besides the estimations and measurements needed to predict development of acid sulphate soils as defined above.

Besides actual and potential acid sulphate soils, we will need to define two kinds of soils without acid sulphate.

A pseudo-acid sulphate soil contains one or more horizons with the characteristic yellow mottling (basic iron sulphates) commonly associated with acid sulphate conditions, but does not have a pH below 4 and does not contain free acids or more than about 60 per cent exchangeable aluminium. Such soils may or may not have been actual acid sulphate soils at some time, depending, among other things, upon their original pyrite contents and their history of oxidation and leaching.

In this paper, we will refer to other soils without actual or potential acid sulphate as non-acid-sulphate soils, for want of a better concise term. "Non-acid" cannot be used for them, since many have reactions between pH 4 and 5.

Since the term "cat clay" probably would cover both actual and pseudo acid sulphate clays with yellow mottles; may or may not include acid sulphate materials without such mottles; and generally excludes potential acid sulphate materials, we will not use the terms cat clay, cat peat or cat sand except in quotation.

The term "mud clay" which is connotative of only a subsidiary property of some potential acid sulphate clays - a property also occurring in some soft, unripened materials without or with very little pyrite - we will leave in favour of the more specifically descriptive, though longer, potential acid sulphate soil or material.

FIELD IDENTIFICATION

Sedimentary relationships and sulphur sources

For many years, acid sulphate materials were identified and predicted on the basis of mainly sedimentary relationships and considerations of possible sulphur sources.

Poelman (1973) quotes 18th century writers who recognized acid sulphate soils and materials: Linnaeus (1735) reporting that "argilla vitriolacea" is "mixta fusca, vitriolico salsa" and found under swamps; and Le Franc van Berkhey (1771) describing two kinds of acid sulphate soils, black clay material found under black peat and dark blue to black clay under black well decomposed surface layers, or under other clay layers. Many 19th century authors are quoted by Poelman, among whom van Kerckhoff (1856), reporting seven years after the establishment of the Haarlemmermeer polder that some soils there were improductive due to the presence of "sulphuric iron oxidule" and the absence of lime.

Van Bemmelen (1886), extensively quoted by van der Spek (1934), reported that under Dutch conditions acid sulphate materials appear to originate only from clays once covered by a dense reed vegetation, either where sea or brackish water could inundate the land, or where salts rise from the deeper subsoil.

Edelman (1946), writing for the practical farmer, identified acid sulphate soils by the yellow mottling and by the cover of poor, rather dense and firm, dark peat liable to dry out irreversibly. This vestigial peat covers many areas with acid sulphate material in the polders of the western part of The Netherlands. Edelman also specifically points to the relation between the presence of many Phragmites roots and potential acid sulphate soils. He suggested testing for lime content by HCl in areas with acid sulphate soils wherever it is intended to bring up subsoil material, where a thin acid sulphate layer is to be removed, or where deeper drainage is planned or considered. To find out how severe are, or will be, the acidity problems, the farmer was referred to The Netherlands Soil Analysis Laboratory.

Benzler (this symposium), too, points to the likelihood of potential acid sulphate conditions where noncalcareous, bluish black clay and peat occur mixed or in close contact in the coastal area of Lower Saxony (Germany). He recommends either laboratory sulphate determinations or a few days' observation during slow air drying of samples, wherever noncalcareous bluish black, reduced clay material occurring in association with peat is to be brought to the surface, e.g. by deepening drains.

Landform

Landform, too, has been used in prediction and delineation of potential and actual acid sulphate soil conditions. Acid sulphate soils occur in two main situations: as large, homogeneous areas with pyrite deposited together with the marine sediment or accumulated by reduction of soluble sulphates during or after deposition, and in small-scale, intricate patterns of tidal marshes alternating with generally slightly higher soils without acid sulphate.

In Sweden and Finland, along the Botnic Gulf there are large areas of marine muds with high contents of primary pyrite (finely distributed and brought in together with the sediment). These potential acid sulphate materials filled valleys and basins in the submerged moraine landscape and now are partly covered by thin sandy layers. As a result of drainage due to isostatic land rise, they have developed into extensive areas of actual acid sulphate soils.

Most other occurrences of acid sulphate soils are due to accumulation of secondary pyrite during or after sedimentation, in tidal marshes or mangrove areas, particularly in warmer temperate or tropical areas.

Moormann (1960) reports that actual and potential acid sulphate soils in the tropics occur mainly in the tidal mangrove swamps and in the marshy back swamps of the seaward side of river deltas. They may also occur in old alluvial terrace deposits. The acid sulphate soil areas in the Mekong delta mapped by Moormann and others show very clearly on aerial photographs and even on aerial photo mosaics, due to a very specific vegetation pattern. The potential acid sulphate soils of the Guyanas, too, occur largely in extensive, easily delineated back swamp areas of marine and estuarine plains, bounded by low (late Pleistocene) terraces on the landward side and separated from younger non-acid sulphate marine clays by a clear erosional coastline in most places (Brinkman and Pons 1968).

Van der Kevie (1971) states that in the Bangkok plain, the dark grey (potential acid sulphate) brackish water deposits occur in a wedge-shaped sediment body, some 0.5 m in the south to some 5 m thick in the north, over (sic) greenish grey marine sediments occurring to some 15 m depth, which in turn overlie stiff, mottled, Pleistocene clays. This is in contrast to the situation in the Guyanas coastal plain, where potential acid sulphate material appears to overlie Pleistocene material and is bordered on the seaward side by an erosion coastline separating it from sediment bodies without acid sulphate, with progressively greener reduced colours toward the sea.

In West Africa, for example in Gambia (Giglioli and Thornton 1965) and in Senegal (Vieillefon 1969), yet different physiographic relationships of acid sulphate and non-acid-sulphate materials prevail.

The instances quoted above refer to large-scale occurrences of actual and potential acid sulphate soils. These may also occur in intricate patterns, however, either associated with non-acid-sulphate soils or in an association of more and less severe conditions. An example of an association with non-acid soils is reported by Bennema (1953). Studying reduced subsoils in an area of old Holocene marine clay in the western part of The Netherlands, Bennema found percentages of S, mainly as FeS_2, generally between 1.5 and 3, and $CaCO_3$ percentages from 0 to 18. The $CaCO_3$ content is closely related to the physiography, relatively high-lying sandy broad tidal creek ridges having the highest percentages and low-lying, level, soft basin clays between ridges being generally noncalcareous. The differences are probably due to decalcification of the sediments during deposition by higher CO_2 pressures in the reduced environment of the basins, the $Ca(HCO_3)_2$ formed being removed mainly by the tidal flood water. Pyrite contents in the basins tend to be slightly higher than in the ridges, probably due mainly to the longer periods available for sulphate reduction and to the higher proportion of organic matter available. This has resulted in an intricate pattern of calcareous soils and acid sulphate soils, very well related to elevation and detailed landforms.

Allbrook (this symposium) found slight depressions in coastal areas of north-west Malaya useful indicators of possible acid sulphate soils; van Wijk (1951) and Driessen and Ismangun (this symposium) used landform as one of their indicators in southern Kalimantan (Indonesia); and Grant (this symposium) reports that the acid sulphate soils in and near the Pearl River estuary (Hong Kong) occur below 5 metres above sea level.

Vlek (1971) as well as van Breemen, Tandatemiya and Chanchareonsook (this symposium) found a very close correlation between small differences in elevation and the occurrence of near-surface soil horizons with potential acid sulphate in the Bang Pakong land development area, Thailand coastal plain. All subsoils were potential acid sulphate material in this area.

Apart from potential and active acid sulphate soil formed naturally in Holocene, marine or estuarine landscapes, at the present surface or buried e.g. by Holocene peat, other occurrences merit mention. For example Palmer and Williams (this symposium) described man-made surface occurrences of acid sulphate material (colliery spoil).

Hesse (1960, pers. comm.) investigated potential acid sulphate muds in papyrus swamps near Lake Victoria far above sea level. Chenery (1954) describes acid sulphate soil material developed in papyrus swamps in Uganda, at some 2000 m elevation, the sulphur compounds being derived from Precambrian shales. This, besides demonstrating that acid sulphate soils do not necessarily occur at sea level, suggests that potential acid sulphate soil materials may have existed since Precambrian times.

Older landscapes (Pleistocene surface configuration, Pleistocene and Tertiary materials e.g.) have in fact been found containing subsurface layers rich in pyrite, that may develop into acid sulphate material upon exposure. In the neighbourhood of the bauxite excavations near Onoribo in the old (late Pleistocene) coastal plain of Surinam, a large area with a reduced potential acid sulphate layer at 3 to 4 m below surface was identified (Brinkman and Pons 1964, unpublished data; Veen 1970). The now deacidified, young pleistocene soils, probably developed from this potential acid sulphate material show now a normal natural vegetation or an occasional cultivation, but in sterile ditch banks and especially clearly in the long profiles excavated in the bauxite mine acid sulphate phenomena occur. Yet older materials were investigated by Buurman and van Breemen (this symposium), who studied Tertiary marine acid sulphate materials occurring under a thin cover of non-acid sulphate material.

Poelman (this symposium) quotes similar occurrences and besides these, describes "cat sand" - a term coined by Wind and Steeghs (1964) - from various sandy valleys in The Netherlands. He considers sulphate seepage from pyrite-rich Tertiary marine clays outcropping in the adjacent hills and immobilization by reduction in the waterlogged, peaty surface of the sands in the valleys to be the cause of pyrite accumulation in the potential "cat sand" occurring near Ootmarsum and elsewhere in the east of The Netherlands.

Clearly, no general predictions about the occurrence of potential acid sulphate materials can be made on the basis of sedimentary or physiographic relationships alone. Within many specific sedimentation areas, however, very clear and specific relationships have been recognized, which can be used in the identification and prediction of acid sulphate conditions. Their nature is within the subject of another session of this symposium.

Vegetation

Vegetation, too, has been used extensively for identification and delineation of actual and potential acid sulphate soil areas, for example Rhizophora mangle (S. America) or racemosa (W. Africa) where the environment is brackish (Hart 1959; Thornton and Giglioli 1965, also quoting Hesse 1961, Tomlinson 1957, Rosevear 1947, Doyne and Glanville 1933) or, in temperate climates, a dense reed vegetation in brackish swamps.

In fresh-water areas, the combination of Blechnum serrulatum, Imperata brasiliensis and certain Cyperaceae (Evans and Cate 1962) or Blechnum fern, Montrichardia arborescens, Scleria and Rhynchospora spp. (razor grass), and Tabebuia insignis v. monophylla (white cedar) (Applewhite 1965, Brinkman 1966) is characteristic in northern South America. In fresh-water swamps in Eastern Asia, potential acid sulphate soils are indicated by Melaleuca with different associates (van Wijk 1951), Melaleuca, sedges and rushes (Allbrook, this symposium) or Melaleuca and Fimbristylis (Driessen and Ismangun, this symposium). Acid sulphate soils are even called "gelam" (=Melaleuca) soils locally. This tree has a very wide ecological amplitude, however, and also occurs on poorly drained, acid sandy soils rich in quartz as well as on brackish potential acid sulphate soils.

Tidal brackish-water vegetations are causally related to the accumulation of pyrite, through sulphate reduction and sulphide accumulation in the root mass produced (this root mass in the soil might be a better indicator than the vegetation, incidentally). The fresh-water vegetation only shows a correlation with the occurrence of acid sulphate soils.

Soil characteristics

Besides sedimentary relationships, landforms and vegetation, specific directly observable soil characteristics have been used in identifying actual and potential acid sulphate soils. The peculiar yellow colours of mottles (and soft tubular aggregates) in actual acid sulphate materials which were already mentioned, are indicative in many cases, especially in combination with observed extreme acidity; dying of plants; and presence of soluble sulphate. The yellow mottles by itself are not a certain criterion, however.

Van der Spek (1934, p.502) reports the occurrence of a yellow efflorescence in the tubular pores made by old reed vegetation, while the bluish-grey clay quite close to the pore reacted strongly with HCl. Van der Spek (1950) found examples of yellow-mottled "cat-clay" material in the north of The Netherlands, which had a neutral reaction, presumably by leaching with water containing some calcium bicarbonate. The yellow material had the composition $4Fe_2O_3.5SO_3.13 \pm 2\ H_2O$. Na or K were not determined. This yellow material isolated from the soil also had a neutral reaction.

Maschhaupt (1922, pers. comm. quoted in v.d.Spek) and van Wallenburg (this symposium) found similar material in the west of The Netherlands. Also Verhoeven's data (this symposium) clearly indicate the presence of jarosite ("cat clay") stains in horizons which are not now acid sulphate soil material, but most probably were, 40 years ago. The characteristic yellow staining, therefore, may not be used by itself to determine the presence of acid sulphate material. Similar conclusions were reached in Suriname where Pons (1963) proposed the term "pseudo cat clays", and in (then British) Guyana, where the Soil Survey Project recognized the same materials. Buurman and van Breemen (this symposium) also found jarosite persisting even in materials with a pH well above 5 and nearly base-saturated (Ca + Mg) at present.

Pons and van der Kevie (1969) found in the coastal plain of Thailand that greenish grey reduced soil colours, Munsell (1954) notation 5GY 4/1 and greener, which upon first oxidation develop mottles 5G 4/1, correlate with absence of potential acid sulphate conditions; and that grey colours N4, 10YR 3 and 4/1, 2.5Y and 5Y 4 and 5/1 may be used to predict acid sulphate conditions. Colours 5Y and 5/1 may indicate borderline cases. Pons en van der Kevie consider that very easily weatherable minerals, probably chlorites (glauconites or chamosites?), cause the greenish hues, and that their decomposition buffers acids formed from pyrites, thus preventing development of acid sulphate materials. This is based upon their observation that soils with much free iron and much secondary silica but without acid sulphate developed from greenish materials rich in pyrite, while grey materials with similar pyrite contents developed into acid sulphate soils. The materials were all noncalcareous.

In the coastal plain of (then British) Guyana, Brinkman et al. (1963, unpublished data) found colours 5 BG 5/1 and greener indicative of the absence of potential acid sulphate conditions, and colours 5 GY 5/1 and 4/1 and greyer indicative of potential acid sulphate soils. They considered the greenish colours to be correlated with low pyrite contents, but not necessarily indicative of high neutralizing capacity.

Buurman and van Breemen (this symposium) found jarosite occurring in glauconite-rich Miocene clay in western Germany. Deeper horizons contain much pyrite in the ground mass, in aggrotubules or in glauconitic material.
Matrix hues are mainly 2.5Y to 7.5Y. In the Senegal coastal plain, Vieillefon (this symposium) found indications of formation of green minerals in reducing conditions in material, likely to become acid sulphate soil after oxidation. Clearly, the greenish colours may not be taken as a generally applicable "green light".

The soft, "buttery" nearly liquid ("unripened") subsoil consistence of many potential acid sulphate materials has been used as an additional criterion (Applewhite 1955; Brinkman 1966; Pons 1956; Pons and van der Kevie 1969; van Wallenburg, this symposium); also used are characteristics like high organic matter content or grey subsoil colours with dark grey to black specks or mottles with partially decomposed organic remains (the same authors, also Allbrook, this symposium, and Driessen and Ismangun, this symposium); the characteristic fibrous material throughout soft clays consisting of the partly decomposed roots of a former Rhizophora vegetation (Giglioli and Thornton 1965); the partly decomposed remnants of reed in soft clays (van Bemmelen 1886; Edelman 1946); and the presence of hydrophobic peaty or organic surface horizons (Edelman 1946; van Wallenburg, this symposium; van Wijk 1951). This last criterion is correlated with acid sulphate conditions, but is not necessarily a cause or an effect.

The smell of H_2S when the soil is disturbed has been found indicative (Fleming and Alexander 1961; Allbrook, this symposium); as well as the rapid and drastic drop in pH upon air drying (many authors, e.g. Fleming and Alexander 1961; Thornton and Giglioli 1965; soil surveys by Applewhite 1965 and Brinkman 1966; Benzler this symposium; and van Breemen and Tandatemiya, this symposium).

The HCl field test to determine absence or low contents of carbonates has been used by many; the sodium azide or sodium azide-soap test for presence of sulphides by several (van Andel and Postma 1954; Pons and van der Kevie 1969; Edelman 1971; van Wallenburg, this symposium); electrical conductivity and its increase after air drying by a.o. Fleming and Alexander (1961); and, on the borderline between field and laboratory, pH measurement after oxidation by H_2O_2 by van Beers (1962), and a semiquantitative test for sulphates after and before H_2O_2 oxidation by Poelman (this symposium).

Westerveld and van Holst (this symposium) consider that actual acid sulphate peat and sand are difficult to recognize in the field by visual characteristics, since the characteristic straw-yellow mottles are absent. (It would seem possible, however, to recognize them by simple pH measurement or by a rapid field test for sulphates.) Potential acid sulphate sand may be expected (Westerveld and van Holst) where sandy soils in valleys and depressions have a very humous or peaty or peat topsoil and show black or blue-black specks or mottles associated with remnants of organic matter. They are recognized by the sodium azide test or the pH drop after oxidation by H_2O_2 or by air drying. The latter two tests and the presence of blue-black mottles or layers indicate potential acid sulphate peat. (For laboratory confirmation of the expected degree of acidification, Westerveld en van Holst use total sulphate and total Ca determined after oxidation with a HNO_3-HCl, 3:1 mixture.)

In most places, in coastal plains as well as elsewhere, field identification rests upon a combination of the indications mentioned, each of which taken by itself might not be very certain, but which, in the aggregate, allow fairly accurate diagnosis. Most authors point out that visual observation of landscape, vegetation and soils alone can be very misleading. They use field tests or a combination of field tests and laboratory determinations for a greater degree of confidence in identification and prediction of acid sulphate materials. Within the boundaries of a given sedimentary, climatic and vegetation environment, however, fairly few and simple criteria can be used with confidence in most cases, after their relationships to acid sulphate occurrence have been established.

METHODS OF ANALYSIS AND ESTIMATION

General

Where other factors are equal - for example the envisaged drainage system; climate; sedimentary history - contents of pyrite or sulphides and calcium carbonate may be used to estimate the expected relative severity of acid sulphate soil conditions after the envisaged drainage. This is of use especially where data are available on earlier reclamation objects from similar materials.

Out of the many methods available to determine total sulphur and its various fractions in the laboratory, those combining extreme simplicity and speed are of prime importance for predicting acid sulphate soil conditions and for possible application in the field. If the methods automatically take into account the total acids formed upon oxidation as well as the possible neutralizing substances present, so much the better. A precision of better than 10 per cent or so would not be required in any case. In view of the characteristically irregular occurrence of pyrites in many potential acid sulphate soils, either the sampling error would be appreciable, or a large sample of perhaps a few kilos would have to be dried, ground and split, which would defeat the objects of simplicity and speed.

Van der Spek (1934) already comments upon the difficulty of obtaining average samples for analysis of potential acid sulphate soils, due to the inhomogeneous distribution of the pyrite aggregates.

Pons (1963 and this symposium) calls attention to the fact that pyrite occurs in two main forms: "primary" pyrite, which is formed (during or after sedimentation) through reduction by "primary" organic matter deposited together with the mineral fraction of the sediment; and the "secondary" (and tertiary, a distinction not relevant here) pyrite, formed through reduction by "secondary" organic matter which is added to the sediment by plant growth after deposition. The primary pyrite is evenly and finely distributed throughout the reduced sediment, while the secondary pyrite generally occurs irregularly concentrated in part-decayed remnants of roots or other pieces of vegetative matter. In most cases, at least in warm temperate or tropical climates, only the secondary pyrite may occur in proportions giving rise to acid sulphate materials. The irregular distribution then limits the precision attainable in estimating pyrite content from a small sample, as commonly used in field estimation as well as in laboratory analysis.

The relation between contents of primary pyrite (generally low, not dangerous) and organic matter is quite close, but where high proportions of secondary pyrite occur (in the majority of potential acid sulphate soils), the relationships tend to break down (e.g. Pons 1963, Brümmer 1968).

Two practical points should be considered in the analysis or estimation of potential acid sulphate materials, which are often wet and contain a great deal of water.

1. If the moisture from wet (reduced) soil samples is allowed to evaporate by air drying, considerable changes occur which may not be desired before analysis. Rasmussen (1961) found that (rapid) oven drying of samples in the presence of $CaCO_3$, H_2SO_4 and $Fe_2(SO_4)_3$, or without additions, caused only small losses of pyrite, which would make it possible to analyze dried samples with little loss

of accuracy. Van Breemen (pers. com.) recommends rapid freeze drying and prefers this to oven drying.

2. In the field, one might like to run some quick analyses along the lines of one of the methods mentioned. To obtain a known weight of soil one would have to first dry the material; or dry a separate sample to determine the water content of the analyzed material; or know the proportion of water by other means. The approximate water content of such soil materials can be arrived at quickly by estimating the "ripening class" (Pons and Zonneveld 1965) described below, estimation of approximate clay and organic matter percentages, and use of the following formula:

$$A = 20 - \frac{L + H}{5} + N\ (L + 3H)$$

A = water percentage of dry soil

N = "N value", a figure derived from ripening classes, tabulated below

L = clay percentage

H = organic matter percentage

DESCRIPTION OF SOIL CHARACTERISTICS (squeeze test)	RIPENING CLASS	N VALUE
Stiff wet, very hard dry	very ripe	0.4
Firm wet, hard dry; not possible to squeeze through fingers	ripe	0.7
Medium consistency. Squeezed between fingers with difficulty	nearly ripe	0.7-1.0
Somewhat soft mud. Easily lost between fingers when squeezed	half ripe	1.0-1.4
Soft mud, very easily lost between fingers when squeezed	nearly ripe	1.4-2.0
Very soft mud, more or less fluid, dripping through fingers without squeezing	unripe	2.0

Still higher water contents (of liquid muds) are less easily estimated, but these occur only rarely. For field estimations, the above formula and table would give adequate precision in many cases.

Similar results can be obtained still more quickly by using the simpler formula (Smits et al. 1962): $A = 20 + N\ (L + 3H)$.

Rapid oxidation methods

Beaton, Burns and Platou (1968) summarized more than 500 references on analysis of sulphur compounds and total sulphur, out of which one method appears attractive for our present purpose: oxidation by H_2O_2 and subsequent alkalimetric titration (Murakami 1960, Yoneda 1961). Many authors have tried to simulate the development of acid sulphate soils by rapid oxidation.

Van Beers (1962) developed a simple and straightforward field method for the prediction of acid sulphate soil conditions after drying (after drainage). He treats about 5 ml soil with about 20 ml H_2O_2 30 per cent, heating if the mixture is not spontaneously heated sufficiently to complete the decomposition of H_2O_2. After complete decomposition of H_2O_2 the pH is determined, electrometrically by preference, or with an indicator clearly distinguishing between pH 4.3 and 2. The slight acidity of the usual commercially available H_2O_2 did not noticeably influence the results, mainly due to buffering by the soil. The method automatically takes into account the amount of rapidly acting neutralizing components that may be present, $CaCO_3$ in the first place.

Incomplete oxidation with H_2O_2 may give intermediate acid products from organic matter, but probably these are further oxidized to non-acid simple compounds if oxidation is allowed to go to completion. Concentrated, 30 per cent H_2O_2 would be indicated, therefore, as well as heating until most of the liquid has evaporated after the reaction appears complete. Only in soils with much manganese (mottles or iron-manganese nodules) it is difficult to ensure complete oxidation since in this case H_2O_2 is rapidly decomposed katalytically. A "boiling" effect was also observed in very peaty soils. In these two cases, the operator should make sure that the H_2O_2 will not pop in his direction.

Van Beers suggests a tentative limit of pH 2.5 after oxidation by H_2O_2 for the dangerous potential acid sulphate soils. At first sight this would seem somewhat low, since e.g. roots of germinating rice fail to develop at soluble Al concentrations as low as about 16 ppm (Evans and Cate 1962). In equilibrium with amorphous $Al(OH)_3$ this is the case already about pH 4. The pH limit suggested by van Beers may work well in practice, however, since part of the acids formed during the drying process after the installation of a drainage system are leached out, and since slower acting neutralizing compounds (possibly dolomite, clay minerals) also have an effect. The latest soil classification by the U.S. Soil Conservation Service (USDA 1970) also suggests pH measurement before and after boiling with concentrated H_2O_2 as a field test for "sulphidic" materials, but does not specify limits for either the drop in pH or the resultant pH.

Cate and Sukhai (1963) suggest laboratory identification of potential acid sulphate soils first by Walkley-Black carbon figure (which includes ferrous sulphides), excluding from suspicion samples with less than 0.5 per cent Walkley-Black carbon. Their next criterion, for samples above this limit, is the increase in water-soluble sulphate after thorough oxidation with H_2O_2 or, more simply, the increase in conductivity after such oxidation. This increase would then have to be compared with the amount of rapidly neutralizing materials present, in the case of British Guyana coastal clays mainly comprising exchangeable bases. This procedure would only yield rough approximations. If more precision is required, Cate and Sukhai (1963) suggest H_2O_2 oxidation with subsequent washing to remove the bulk of the salts, followed by a determination of exchangeable cations. This they consider should approximate the end result of all of the complex ion exchange equilibria that can be involved in draining a coastal clay.

Since acid sulphate sand is difficult to recognize visually, Poelman developed a field test to estimate sulphate content after and before oxidation by H_2O_2, which is described in an appendix to his paper in this symposium.

In British Guyana, the Soil Survey Project in 1962 suggested two field test units, one with rapid oxidation, the other with HCl and lead acetate test paper (unpublished data Brinkman). The procedure of the first one follows: Air-dry material, 1 day or longer. Shake about 1 g air-dry soil with 1 N KCl solution (5 ml or more) and let stand. Decant clear supernatant into second bottle and add 1 drop phenolphtalein and 1 drop 0.5 N NaOH solution. If the solution becomes pink and does not develop a coloured precipitate: very probably not acid sulphate soil material. The number of drops of NaOH solution needed to turn the decanted liquid pink is a very rough indication of the severity of acid or potential acid sulphate conditions. This method could be made semiquantitative by first boiling with concentrated H_2O_2 and evaporating to almost dry. 40 drops of NaOH required would be equivalent to roughly 100 me excess acid per 100 g soil material.

Slow oxidation methods

None of the rapid oxidation procedures, discussed so far may be expected to take into account the slow neutralization by soil components other than lime.

The Soil Conservation Service (USDA 1970) states that a sample of sulfidic material, if dried in the shade for about two months with occasional remoistening, becomes extremely acid. Bloomfield (this symposium) proposes replacement of this procedure by storing moist soil material for some weeks in a thin polythene bag. Both procedures may be somewhat too rapid for neutralization by soil components other than lime to have its full effect.

Pons (1956) measured pH after 6 months of oxidation in a number of potential acid sulphate and non-acid sulphate materials from the Old (Holocene) Sea Clay landscape in The Netherlands. He found the approximate relation pH (water) = 5.3 + (me Ca/100 g - me S/100 g)/60, with a standard deviation of roughly 0.5 pH unit. The data ranged from about 200 me excess S/100 g to about 100 me excess Ca/100 g. This suggests that almost all of the acid formed in excess of the lime content was neutralized, probably by clay minerals.

Van Breemen (this symposium) found that with oxidation under laboratory conditions extending over a period of months, the bulk of the acid formed in soil systems does not remain in solution, but is in fact neutralized by dissolution of clay minerals. The field pH after drainage of acid sulphate soils appears to be invariably 1 to 2 units higher than pH after laboratory drying and rewetting of samples (van Breemen et al., this symposium).

The pH differences between material drained and oxidized under field conditions and oxidized rapidly or slowly in the laboratory indicate that some 90 to 99 per cent of the acid formed in the laboratory is not formed, eliminated or neutralized under field conditions, by one or a combination of: incomplete oxidation; leaching by rain or inundation water; and neutralization by dissolution of slow acting carbonates (dolomite?), by decomposition of silt or sand minerals (e.g. Ca feldspars, biotite?) or by decomposition of clay minerals (smectites, illite, chamosites). In view of these uncertainties, high precision in routine measurements for the prediction of acid sulphate soil conditions would not be meaningful until the degree of influence of these modifying conditions can be accurately predicted or, better still, controlled.

For present practical purposes, however, a set of tentative pH limits can be suggested for identification of potential and actual acid sulphate soils on the basis of different oxidation tests, as tabulated below.

	tentative limit (pH water)
Incomplete oxidation by rapid air drying, 1 day (uncertain and indicative only)	4
Rapid complete oxidation by H_2O_2	2.5
Slow oxidation under moist conditions, a few weeks to six months	3.0-3.5
Slow oxidation of soils in the field after drainage (including leaching effects where present), one to several years	4.0

Chemical methods of sulphide estimation and pyrite extraction

A simple field test for all active sulphides in soil material with HCl and lead acetate paper was developed by Neckers and Walker (1952), as summarized below: Put 2-3 g of material in a 20 by 150 mm test tube, mix with 1 g of granular c.p. zinc (20-30 mesh). Insert a spiral of copper wire halfway down the tube to disperse bubbles. Add 2-3 ml (one eyedropperful) of 6 N HCl. Wait 5 sec., then place a small circle of test paper impregnated with lead acetate over the mouth of the tube. Remove after 5 seconds. Slight tan coloration: very weak. Tan: weak. Brown with tan edge: moderate. Black with silvery cast: very strong. Relationships with total sulphur were: very weak about 0.06 per cent; weak 0.09 - 0.13 per cent: moderate about 0.2 per cent; and very strong more than 2 per cent.

For possible use in identifying potential acid sulphate soil material it might be useful to decrease the standard amount of soil to 1 g, in order to bring the "moderate" reaction in the neighbourhood of 0.7 per cent total sulphur.

Rashig (1915), quoted by Feigl (1931), first recorded to our knowledge the katalytic action of sulphides (and thiosulphates and rhodanides) on the liberation of nitrogen gas from a sodium azide-iodine solution.

Van Andel and Postma (1954) used this method for rough semi-quantitative estimation of sulphides in sea bottom sediments, observing the degree of effervescence by a binocular microscope. Their highest intensity of reaction ("strong") corresponded with about 0.25 per cent total S.

Edelman (1971) adapted the method to the range in pyrite contents of interest for the prediction of acid sulphate materials and eliminated use of the microscope. His procedure follows.

In a test tube, add 1 ml concentrated soap solution (liquid detergent) and about 0.5 ml Na azide solution (dissolve 1.27 g sublimated iodine and 2.4 g KJ in 8 ml water, dilute to 100 ml, add 3 g NaN_3 and dissolve; keep in brown bottle; prepare new solution frequently). Add sample material equivalent to 0.2 g dry soil, stir carefully, to avoid making bubbles, three times in 1 minute. The N_2 gas, formed by katalytic action of any sulphides present, makes foam. The quantity of foam after 2 minutes is an indication of the sulphide surface area present. For a few samples from Thailand the following relation applied.

foam 2 cm high	1.4 per cent sulphide S
foam 0.3 cm high at margin and covering whole surface of liquid	0.8
foam 0.3 cm at margin, not covering centre	

of liquid surface	0.4
no foam	0.0

Since the reaction is katalytic, coarse pyrite crystals would have less effect than an equal content of finer pyrite crystals or aggregates. Other sulphides or organic sulphur compounds present might cause an exaggerated reaction: especially finely-divided FeS, or organic matter with a low C/N ratio and a relatively high S content. Within a specific sedimentary region, however, the size of pyrite crystals, the kind of organic matter and other modifying factors might be relatively constant. After standardization within specific areas, this method would seem to have promise as a very rapid and simple field estimate.

A specific extraction method for pyrite was worked out by Petersen (1969), consisting of successive extraction of a soil sample in a Soxhlet apparatus, first 15 hours with 20 per cent HCl and then 15 hours with 68 per cent HNO_3. Iron contents were determined by titration after elimination of organic matter involving two evaporations and heating in an electric oven. The iron contents of the second extract showed 99-103 per cent recovery of added pyrite; a standard deviation of 0.05 per cent pyrite (single determination); and calculated pyrite figures of 0.09 and 0.17 per cent for pyrite-free samples.

X-ray diffraction and fluorescence methods

X-ray diffraction has also been used to determine pyrite or total S in the laboratory.

Rasmussen (1951) measured pyrite concentrations in soil materials by X-ray diffraction with MgO as an internal standard. For samples requiring less precision, MgO was omitted and a correction factor applied dependent upon the percentage loss on ignition: approximately constant (1.0) for ignition losses up to 40 per cent, and then increasing roughly proportionately to 1.7 at ignition losses of 80 per cent (graph based on few observations).

Petersen (1969) measured pyrite in soils by an X-ray diffractometer method with internal MgO standard and correction for quartz interference, by measuring integrated intensities over the strongest lines of quartz, pyrite and MgO. Good agreement was obtained with the chemical method (Soxhlet extraction), but with a standard deviation of 0.3 per cent pyrite (single determination).

Total sulphur determinations in soils by X-ray fluorescence were compared with other methods and found satisfactory by Tabatabai and Bremner (1970), and determination of total S (and total Ca) in soil samples presents no difficulties in, for example, the X-ray fluorescence routine of the laboratory of the Dept. of Soils, Wageningen University. Besides sulphide S, total sulphur includes a generally small amount of S in stable organic compounds, as well as acid sulphates and (neutral) calcium sulphate. Total Ca includes, besides Ca in carbonates, calcium sulphate, calcium in mainly sand and silt minerals (Ca feldspars, for example) and exchangeable Ca. In order to arrive at an indication of the maximum total acidity to be expected after complete oxidation, one would need to know the oxidizable ferrous iron content in addition to total S and Ca. This would defeat the object of speed and simplicity. Even then, the presence of different S and Ca compounds, non-reactive or acting very slowly, make the results only approximate. However, rapid X-ray fluorescence methods could produce the data needed to identify "sulphidic" materials according to the USDA (1970) definition if it is known that the materials are reduced (contain S mainly in sulphide form) and if the approximation of carbonates through total Ca is accepted (if gypsum is absent).

If X-ray fluorescence measurements include Mg besides S and Ca, this would provide a rough measure of the slower-acting neutralizing compounds. That might allow more accurate prediction of the soil development after drainage under field conditions than on the basis of S and Ca alone.

Microscopic estimation of pyrite

Microscopic methods for identification and estimation of pyrite in soil materials have been in use for a long time.

Harting (1852), as quoted by Poelman (1972a) described pyrite from the soil below Amsterdam, recognizing mainly coherent groups of dark greenish black more or less rounded bodies, 30-100 microns diameter, occurring in layers with organic remains, and some larger crystals of cubic or pentagon dodecahedral shape.

Eswaran (1967) described and illustrated a gradual change from round pyrite bodies to angular crystals in the reduced zone of an acid sulphate soil in Malaysia.

Love and Amstutz (1965) gave a detailed description of round pyrite aggregates ("framboids") and Rickard (this symposium) summarized data on their formation.

Van der Spek (1934) first mentioned, to our knowledge, the metallic lustre of the groups of round black pyrite aggregates occurring in partially decomposed plant remains and in diatom remnants, which is used as a determining characteristic by the Dept. of Soil Science and Geology, Wageningen Agricultural University.

Van Bemmelen (1886) found a relation between the content of ferrous sulphides and microscopically observed pyrite. The pyrite occurred as black round aggregates, mostly in groups, and locally clearly cubic.

This needed to be distinguished from brownish black or reddish brown round aggregates which were also present. These occurred mainly in materials with yellow ferric sulphate efflorescence; were dissolved in HCl, in contrast to the black, true pyrite, aggregates; and did not show a relation to the content of ferrous sulphides.

Pons (1964) developed a method for microscopic semi-quantitative estimation of pyrites in soil materials, which was modified by Slager (1967).

The original method showed good correlations for samples from Suriname and (British) Guyana with oxidizable S determined by two chemical methods (SO_4 increase after oxidation by H_2O_2 and strong acids respectively) in the range from 0.5 to 2.5 per cent pyrite S. Standard deviations of single estimations compared with chemical data were of the order of 0.3 and 0.2 per cent S respectively. Standard deviations of single estimations by the modified method were between 10 and 20 per cent of estimated percentage (no chemical data were available). The method with slight further modifications is described below.

A quantity of material containing about 1 g dry soil is suspended in 10 ml water by shaking in a small plastic tube or bottle with some 5 steel balls, 4-5 mm diameter, added to speed dispersion. Immediately after shaking, a drop of suspension (0.05 ml) is placed on a microscope objectglass by a small pipette. Most of the water is evaporated by gentle heating and a drop of glycerine is added. A homogeneous suspension is made by stirring with a needle, and covered by a coverglass of known surface area. In the preparation, pyrite bodies are recognized as spheres, clusters of spheres or - more rarely - angular fragments, opaque in transmitted light, or very bright metallic green in incident mercury light (Slager and co-workers, pers. comm.). Pyrite bodies are counted in size classes diameters 2-6; 6-10; .... 58-62; ... microns. These would be equivalent to 1; 2; .... 15; ... units of an ocular micrometer (10 mm in 100 divisions) with a 25x objective magnification. Counting should cover all pyrite bodies the centre of which lies within strips of, for example, 400 microns wide and 10 mm long. Factors for calculation follow.

mg FeS_2 in pyrite sphere of D microns diameter equals:

$$5.0 \times \pi/6 \times D^3 \times 10^{-9} = 2.6 \times 10^{-9} \times D^3$$

mg S in pyrite sphere of D microns diameter equals:

$64/120 \times 5 \times \pi/6 \times D^3 \times 10^{-9} = 1.4 \times 10^{-9} \times D^3$

Weight percentage of FeS_2 or S equals:

$20 \times B/A \times$ (total milligrams FeS_2 or S counted)

B is surface of cover glass and A is total surface of strips counted, both in square mm.

MODIFYING CIRCUMSTANCES

Pyrite oxidation

There have been some statements in the literature that pyrite may persist in oxidized soils almost indefinitely. Their degree of relevance to the development of acid sulphate soils can be inferred from published findings and experiments, some of which are summarized below.

Quispel, Harmsen and Otzen (1952) found that oxidation of pyrites was significantly slowed but not stopped by high pH or high levels of phosphate in solution, presumably by their depressing effect on Fe solubility. Harmsen (1954) found significant amounts of total sulphidic S (exceeding 0.25 to 0.4 per cent) in some well aerated, old cultivated, strongly calcareous soils (14-16 per cent $CaCO_3$). In less calcareous soils he did not find more than 0.21 per cent sulphidic S, and often much less. Hart (1962) considers that the relatively slow oxidation of part of the pyrite is due to a relatively coarse particle size, not to an inherently greater resistance to oxidation. He considers time periods of 1 to 2 months, not years.

These are the three sources quoted by Starkey (1966) for his statement that appreciable amounts of pyrite may still be found in dry land many years after it was reclaimed and cultivated. According to the data in Harmsen (1954), this only applies in soils with an appreciable excess of calcium carbonate over that needed for neutralization of potential acid. In other cases the amounts of pyrite remaining after 1 or 2 seasons of intensive oxidation are expected to be small.

Liming potential acid sulphate material with sufficient $CaCO_3$ to neutralize most of the acid that could form by oxidation slowed sulphur oxidation to about 10-20 per cent of the value without liming in an experiment (Hesse 1961) where the pH remained above 7 throughout, while in a related experiment where the pH remained between 6 and 7, sulphate production was as high as in the unlimed samples with final pH values of 3.3 or higher.

Rasmussen (1961) found rates of pyrite oxidation highest in moist materials without $CaCO_3$ or H_2SO_4 additions. Such additions decreased the rate by more than 90 per cent, but did not stop oxidation. (Pyrite in dry material did not oxidize at a measurable rate.)

Van der Spek (1934) found a very small proportion (less than 0.1 per cent) sulphide or free S after oxidation of acid sulphate soil materials under field conditions (determined on material with yellow efflorescence from a ditch side).

Pons (1960) states that pyrite in sediments rich in calcium carbonate is oxidized very slowly, disappearing over a period of centuries; but that in acid soils almost all of the pyrite is oxidized rapidly, with exception of a very small amount remaining almost indefinitely.

Harmsen (1962) discusses oxidation experiments on a mangrove soil material with about 4 per cent oxidizable sulphur and 0.5 per cent $CaCO_3$, indicating that pyrite will oxidize in a soil at widely different pH, but at widely differing rates, both pH dependent and time-dependent. The latter is explained by the presumed difference in size of pyrite particles, only coarse ones remaining after a long period of oxidation.

Studies by Wiklander, Hallgren and Johnsson (1950) a.o. show that lime speeds up the oxidation from S to sulphate, whether the pH is above 7 or below. Only the pyrite oxidation seems to be slowed down by a soil reaction above neutrality, therefore.

It seems clear from these studies that most of the pyrite found in soils with less than the equivalent amount of lime may be expected to be oxidized in the course of months or at the most a few years, if sufficient oxygen is present. The presence of oxygen in a potential acid sulphate soil after drainage is not necessarily assured, however.

Bloomfield (this symposium) found that in a year of leaching an undisturbed potential acid sulphate soil core with a total of 1000 mm distilled water, about 16 per cent of total S was removed. Oxygen could diffuse to the bottom of the soil column, but at what rate is not stated. Bloomfield also quotes earlier work showing that much residual pyrite remained in a Malayan acid sulphate soil after 5 years severe leaching. In both cases, possibly the moisture content during leaching remained too high for optimum pyrite oxidation. This would be suggested by the locally high pH near the bottom of the soil cores. Another part explanation may be that much of the pyrite oxidized and transformed into basic iron sulphates occurred along pore walls in the soil core, and that leaching water moved preferentially through pores. This would also explain the very acid effluent compared with the less acid soil reaction.

It would seem considerably easier to eliminate sulphates from a soil in a strongly seasonal (monsoon) climate than in a perennially wet one like in Malaya, which might hamper efficient oxidation. Climate, too, would need to be taken into account, therefore, when attempting predictions of the severity of acid sulphate conditions after drainage.

Even in climates where non-acid sulphate soils can be drained and will ripen rapidly, drained acid sulphate soils are often underlain at a characteristically shallow depth by soft, unripened or partly ripened, reduced pyrite-containing material. Drains only exert a very low suction on soil water, while ripening requires high suctions. Slow evaporation from the surface with saturated flow through the soil mass will eventually bring about ripening and oxidation; and a very porous "sponge" structure of many root channels in the reduced material may speed up the desiccation; but living roots with their high suction maintained by transpiration are most effective for rapid ripening. Where potential acid sulphate soils occur without sponge structure (without considerable tubular porosity), the oxidation front moves down slowly after drainage, since most plant roots cannot live when acid sulphate conditions develop in the upper horizons. Also, the soluble acids are leached out very slowly in this case. On the other hand, in potential acid sulphate soils with sponge structure, after drainage the root channels rapidly become coated with jarosite or iron hydroxides, their walls develop an extremely acid reaction (high proportions of exchangeable aluminium) and their stability is high (Pons 1963). Vlek (1971) found a very good correlation between permeability and jarosite content. Detailed structure and permeability profiles of potential acid sulphate sulphate soils will need to be known, therefore, in order to predict the nature and speed of soil development after drainage.

Besides these factors, the way in which the pyrite is distributed in the soil material has considerable influence on the effects of its oxidation. If pyrite is evenly distributed (primary pyrite or secondary pyrite associated with fine root remnants for example), much of the acid formed upon oxidation may attack soil components, while leaching may account for a relatively small proportion. If pyrite is distributed heterogeneously through the soil, mainly in large root remnants for example, a larger proportion of the acid formed upon oxidation is leached out through the root channels, which at the same time become stabilized, and the leaching is more rapid as well. Where the pyrite distribution is more heterogeneous, the limit between the formation of acid sulphate soils and pseudo acid sulphate soils may be expected at higher pyrite percentages, therefore; and if acid sulphate soils are formed, they may be expected to change into pseudo acid sulphate soils more rapidly than where the pyrite is more homogeneously distributed through the soil material.

Neutralization of acids

Besides the oxidation of pyrite, the neutralization of the acids formed in different conditions will need to be considered in the prediction of the severity of acid sulphate conditions. One neutralizing component is dealt with rather simply. Calcium carbonate neutralizes equivalent amounts of acids rapidly and at pH levels near neutral.

After dissolution of calcium carbonate present, (and part of any dolomite) and probably concurrently with further dissolution of dolomite if present, further acids formed displace exchangeable basic cations while the pH drops from near neutral to about 4. Acids equivalent to somewhat more than half the cation exchange capacity can thus be adsorbed before there is a hazard of toxicity, since most reduced sediments containing appreciable pyrite are base saturated.

When dissolution of carbonates and adsorption of acids have been taken into account, further acids formed still do not depress the soil reaction to the levels one would expect if the remaining soil components would be inert. To obtain an indication which minerals might neutralize acids in different conditions we summarized some very approximate estimates in the following table. Van Breemen (this symposium) deals with acid dissolution of minerals in more detail.

Calcium carbonate stands out in neutralizing speed and, with dolomite, in neutralizing capacity. The common clay minerals either act very slowly or at a very low pH or both. Dissolution of montmorillonite is suspected by van Breemen (pers. com.) to be responsible for much of the neutralization observed below pH 4 in some acid sulphate soils in Thailand. Mg chlorite could play a part in keeping the pH above or about 4 where pyrite oxidation is very slow. Field evidence from Thailand suggests that the same may be the case with chamosites and/or glauconites ("green minerals"), but for these we have no pH or speed data. Their neutralizing capacity is less than that of Mg chlorite, but similar to that of e.g. montmorillonite.

NEUTRALIZING CAPACITY OF DIFFERENT SOIL MINERALS

MINERAL	APPROXIMATE NEUTRALIZING CAPACITY NEAR OR ABOVE pH 4[1], me/100g	APPROXIMATE BUFFERING pH	NEUTRALIZING OR BUFFERING SPEED[4]
Ca carbonate	2000	8-7	very high
dolomite	2500	7-6?	moderate
Mg chlorite	<1800[2]	>7	low?
chamosites	450-600[3]	?	?
glauconites	125-250[3]	?	?
vermiculite	<1500[2]	?	?
montmorillonite	<350[2]	4-3	moderate
beidellite	<400[2]	4	low
illite	<450[2]	>4	very low
kaolinite	0[2]	<3.5	very low
plagioclase	500[2]	8-6	very low

[1] disregarding contributions from ferrous iron and aluminium

[2] calculated from compositions quoted in Scheffer and Schachtschabel (1960)

[3] calculated from compositions quoted in Porrenga (1967)

[4] strongly dependent upon degree of crystallization

Soluble salts and leaching of acids

Salts (chlorides and sulphates) in the soil solution would not be expected to participate directly in neutralization, but they are beneficial in two other ways. Salts in the leaching water are a very efficient leaching agent for acids, since they displace acid cations from the exchange complex. Also, as long as the soils are still reduced, the salts aid in maintaining a degree of structure stability and porosity, thus indirectly aiding the leaching of acids after oxidation. Besides neutralization, the degree of leaching before oxidation is an important factor in the prediction of acid sulphate conditions.

Hesse (1961) oxidized saline fibrous mud (marginal potential acid sulphate material) from Sierra Leone without leaching salts, and after leaching salts with fresh water, in one experiment starting from fresh (reduced) mud, in a second starting with previously air-dried material. No total S figures were quoted, but the material contained at least about 0.7 per cent S and apparently no calcium carbonate. Leaching salts from fresh mud decreased the final sulphate content found after subsequent moist oxidation but lowered the pH by about 1.5 unit (to pH 3.2) compared with mud oxidized while saline (pH 4.6). Clearly, buffering by soluble salts kept the clay from becoming dangerously acid. Leaching salts from previously dried mud, in which about half of the sulphur had been oxidized to sulphate by that time, decreased the final sulphate S content after moist oxidation to some 0.1 per cent, and kept the pH as high as 4.8 (well above the danger zone). These experiments suggest that, in fact, the degree of leaching, and the difference between leaching before or after part oxidation, have a dominant influence on the severity of the eventual acid sulphate problems.

Harmsen (1962) in oxidation experiments on a mangrove soil material with about 4 per cent oxidizable sulphur and 0.5 per cent $CaCO_3$, found that where the soil in the field was allowed to oxidize by drainage under conditions of periodic tidal inundation, the pH did not fall into the danger zone, while the topsoil drained without the benefit of saline inundation water attained a pH as low as 2.3.

Pons (1963) reports results of slow air drying of potential acid sulphate materials without and with prior desalinization by leaching. The final pH of the saline samples was about 0.5 to 1.5 units higher than of the desalinized ones, in spite of the salt effect. The sea water must have caused some buffering, therefore. In addition, during subsequent leaching by drainage, the salt present would increase the proportion of acid leached out, by competition with the acid cations for exchange sites. These two factors could explain why noncalcareous sediments high in pyrite, both in Suriname and in Guyana, if drained and oxidized in saline conditions, hardly ever develop into true acid sulphate soils. They often show jarosite-yellow mottles and streaks along old root channels, presumably by strong very local acidification ("pseudo acid sulphate soils"), but this merely increases their structure stability and permeability, and does not impair their productivity.

CONCLUSION

There is no single, commonly accepted method for the identification and prediction of acid sulphate soils, and different methods are appropriate in different conditions.

It is clear that data on pyrite or total sulphur and calcium carbonate contents are not sufficient by themselves to predict the occurrence and severity of future acid sulphate soil conditions after drainage. In addition, one would need estimates of the contents of exchangeable bases or c.e.c. and base saturation percentage; of salts if any; and of 2:1 clay minerals. Apart from this, one would need to know whether acid waters from elsewhere would be liable to flood the area to be used; whether seepage, or very slow permeability of the reduced soil, would hinder or prevent efficient drainage and oxidation; whether seepage water would contain sulphur compounds; whether sea water would be available for short-term flooding; if irrigation water to be used contains calcium bicarbonate; and whether the climate and envisaged drainage can ensure efficient oxidation by allowing the rapid development of a permeable, ripened, soil structure.

Although they may cause tremendous problems at certain times and for certain periods, acid sulphate conditions are not permanent soil characteristics. A number of variables that need to be taken into account in predicting the expected severity of acid sulphate conditions can be modified by man to either minimize the severity of the acid sulphate conditions or to speed the soil through its acid sulphate stage to a productive situation. That, however, is the subject of another session of this Symposium.

REFERENCES

ANDEL, Tj. van, POSTMA, H. 1954. Recent sediments in the Gulf of Paria. Verh. Kon.Ned.Akad.Wetensch., afd.Natuurk. (Proc.Royal Neth.Acad.Sciences, dept. Physics.) 1st series, XX, No.5 (Sulphides, pp.101-102). North Holland Publ.Co., Amsterdam.

ANDRIESSE, J.P., SIM, E.S. 1968. Report on soil investigations in the proposed Sungai Sarawak padi scheme area. Report 125. Res. Branch, Dept. of Agric., Sarawak. 37 pp. Maps. Mimeographed.

APPLEWHITE, C.C. 1965. Semi-detailed soil survey of the Mahaica-Mahaicony-Abary area. Report of the Soil Survey Project of British Guyana. IV. FAO, Rome.

BEATON, J.D., BURNS, G.R., PLATOU, J. 1968. Determination of sulphur in soils and plant material. Techn.Bull.14. The Sulphur Inst., Washington & London.

BEERS, W.F.J. van. 1962. Acid sulphate soils. ILRI Bull. 3. 31 pp. Veenman, Wageningen.

BEMMELEN, J.M.van. 1886. Contributions to the knowledge of the alluvial soil in The Netherlands. (Dutch). Kon.Akad.v.Wetenschappen, Amsterdam. (Quoted extensively in: van der Spek, 1934).

BENNEMA, J. 1953. Pyrite and $CaCO_3$ in polder Mijdrecht. (Dutch). Boor en Spade 6:134-148. Sticht. voor Bodemkartering, Wageningen.

BRINKMAN, R. 1966. Semi-detailed soil survey of the Canje area. Report of the Soil Survey Project of British Guyana. V. FAO, Rome.

BRINKMAN, R., PONS, L.J. 1968. A pedo-geomorphological classification and map of the Holocene sediments in the coastal plain of the three Guianas. Soil Survey Papers 4. Soil Survey Institute, Wageningen.

BRÜMMER, G. 1968. Investigations on the genesis of marshes. (German). Thesis. Kiel. Inst. Pflanzenernähr. & Bodenkde. Chr.Albrechts-Univ.

CATE, R.B., SUKHAI, A.P. 1963. Salt, acidity and base status in the coastal clays of British Guiana. Proc. Congress Agric. Res. Guianas Panamaribo. 1963. Landbouwproefstation Suriname. Bull. 82:133-139 (1966). Repr. in: Report on the Soil Survey Project of British Guiana. II:43-49. FAO, Rome. Undated (1966).

CATE, R.B., SUKHAI, A.P. 1964. A study of aluminium in rice soils. Soil Sci.98: 85-93. Repr.in: Report on the Soil Survey Project of British Guiana. II: 25-39. FAO, Rome. Undated (1966).

CHENERY, E.M. 1954. Acid sulphate soils in Central Africa. Trans.Int.Congr.Soil Sci. (5th). 4:195-198.

DOYNE, H.C., GLANVILLE, R.R. 1933. Some swamp rice growing soils of Sierra Leone. Trop.Agric. (Trin.) 10:132-138.

DUDAL, R. 1968. Definitions of soil units for the soil map of the world. With addendum May '68 and Key, September '70. World Soil Resources Reports 33. FAO/UNESCO, Rome.

EDELMAN, C.H. 1946. Cat clay. (Dutch). Groenten en Fruit, No.32-33, 1-4. Repr. in: Boor en Spade 1:172. Stichting voor Bodemkartering, Wageningen 1948.

EDELMAN, Th. 1971. Preliminary investigation of the possible use of the "soap-azide method" for rapid field estimation of pyrite content in soil. (Dutch). Internal report. Dept.Soil Sci. & Geol. Agric.Univ.Wageningen. 2 pp. Mimeo.

ESWARAN, H. 1967. Micromorphological study of a "cat-clay" soil. Pedologie (Ghent) 14:259-265.

EVANS, H., CATE, R.B. 1962. Studies in the improvement of "problem" soils in British Guiana. World Crops, November 1962. Repr.in: Report on the Soil Survey Project of British Guiana. II:17-22. FAO, Rome. Undated (1966).

FEIGL, F. 1931. Qualitative Analyse mit Hilfe von Tüpfelreaktionen. Akad.Verlagsgesellschaft. Leipzig, pp.282-284.

FLEMING, J.F., ALEXANDER, L.T. 1961. Sulphur acidity in South Carolina tidal marsh soils. SSSA Proc. 25:94-95.

BERKHEY, J.le Franc van. 1771. Natural History of Holland. (Dutch). p.339 ff. Intema en Tieboel, Amsterdam.

GIGLIOLI, M.E.C., THORNTON, I. 1965. The mangrove swamps of Keneba, lower Gambia river basin. I. Descriptive notes on the climate, the mangrove swamps and the physical composition of their soils. J.Appl.Ecol.2:81-103.

HARMSEN, G.W. 1954. Observations on the formation and oxidation of pyrites in soil. Plant & Soil 5:324-348.

HART, M.G.R. 1959. Sulphur oxidation in tidal mangrove soils of Sierra Leone. Plant & Soil 11:215-236.

HART, M.G.R. 1962. Observations on the source of acid in empoldered mangrove soils. I. Formation of elemental sulphur. Plant & Soil 17:87-98.

HARTING, P. 1852. The soil under Amsterdam investigated and described. (Dutch). J.C.A.Sulphe, Amsterdam.

HESSE, P.R. 1961. The decomposition of organic matter in a mangrove swamp soil. Plant & Soil 14:249-263.

KEVIE, W. van der. 1971. Acid sulphate soils in Central Thailand. FAO_UNDP Seminar on Soil Survey and Soil Fertility Research. New Delhi. FAO, Rome. Document AGL:TSSF/71/16).

LINNAEUS, C. 1735, 1768. Systema Naturae. XII. Vol.III. Gen.52, Sp.11.

LOVE, L.G., AMSTUTZ, G.C. 1966. Review of microscopic pyrite from the Devonian Chattanooga Shale and Rammelsberg Banderz. Fortschr.Miner.43:273-309.

MOORMANN, F.R. 1960. Acid sulphate soils in the tropics. In: Res.on acid sulphate soils and their amelioration by liming. Min.of Rural Affairs. Agron.Lib., Saigon 1961, 3-15.

MOORMANN, F.R. 1963. Acid sulphate soils (cat clays) of the tropics. Soil Sci. 95:271-275.

MUNSELL. 1954. Munsell soil color charts. Munsell Color Co. Baltimore, Md.

MURAKAMI, Hideyuki. 1960. A method of semi-quantitative determination of oxidizable sulfur in polder soils by hydrogen peroxide. Shimane Agr.Exp.Sta.pp. 276-279. Ref. in Beaton, Burns and Platou, 1968.

NECKERS, J.W., WALKER, C.R. 1952. Field test for active sulfides in soil. Soil Sci. 74:467-570.

PETERSEN, L. 1969. Chemical determination of pyrite in soils. Acta Agric.Scand. 19:40-44.

POELMAN, J.N.B; 1973. The scientific history of the cat-clay phenomenon. (Dutch). In preparation for: Boor en Spade, Stichting voor Bodemkartering, Wageningen.

PONS, L.J. 1956. Some aspects of the improvement of pyrite-containing old marine soils in The Netherlands. Proc.Int.Congr.Soil Sci. (6th). 2:727-734.

PONS, L.J. 1960. Occurrence and formation of pyrite in various marine deposits in The Netherlands and explanation of the genesis of the "knip" phenomenon. (Dutch). Int. report 2342. Sticht. voor Bodemkartering, Wageningen. 37 pp. Mimeographed.

PONS, L.J. 1963. Pyrites as a factor controlling chemical "ripening" and formation of "cat-clay", with special reference to the coastal plain of Suriname. Congr.Agric.Res.Guianas. Paramaribo 1963. Bull.Agric.Exp.Sta.Paramaribo, Suriname. 82:141-162.

PONS, L.J. 1964. A quantitative microscopical method of pyrites determination in soils. In: Jongerius, A. (ed.): Soil Micromorphology. Trans.2d Int.Working-meeting on Soil Micromorphol. Elsevier.

PONS, L.J., ZONNEVELD, I. 1965. Soil ripening and soil classification. Initial soil formation in alluvial deposits and a classification of the resulting soils. Int.Inst.Land Reclam. and Improvement. Publ.13. Wageningen.

PONS, L.J., KEVIE, W. van der. 1969. Acid sulphate soils in Thailand. Studies on the morphology, genesis and agricultural potential of soils with cat clay. Soil Survey Report 81, 65 pp. Soil Survey Div., Land Development Dept., Min. of Nat.Dev.Bangkok.

PORRENGA, D.H. 1967. Clay mineralogy and geochemistry of recent marine sediments in tropical areas. Thesis. Amsterdam.

QUISPEL, A., HARMSEN, G.W., OTZEN, D. 1952. Contribution to the chemical and bacteriological oxidation of pyrite in soil. Plant & Soil 4:43-55.

RASCHIG, F. 1915. Ber.Dtsch.Chem.Ges. 48:2088. (Quoted in Feigl, 1931.)

RASMUSSEN, K. 1961. Transformations of inorganic sulphur compounds in soil. (Danish. Engl.summary.) Thesis. Kgl.Veter.and Agric.Univ.Copenhagen.

REES, W.J., SIDRAK, G.H. 1961. Inter-relationship of Al and Mn toxicities towards plants. Plant & Soil 14:101-117.

ROSEVEAR, D.R. 1947. Mangrove swamps. Farm & Forest. Ibadan. pp.23-30.

SCHEFFER, F., SCHACHTSCHABEL, P. 1960. Lehrbuch der Agrikulturchemie und Bodenkunde. Vol.I. Bodenkunde. 5th ed. Enke, Stuttgart.

SLAGER, S. 1967. Backgrounds and methods of pyrite investigation. (Dutch). Soil Survey Dept. Ministry of Development, Panamaribo. 13 pp. Mimeographed.

SMITS, H.A.J., SCHREVEN, D.A., BOSMA, W.A. 1962. The physical, chemical and microbiological ripening of the soils in the Lake IJssel polders. (Dutch). Van Zee tot Land 32.

SPEK, J. van der. 1934. Contributions to the knowledge of acid soils in the Dutch coastal area. (Dutch). Versl. Landbouwk. Onderz. 40:409-503.

SPEK, J. van der. 1950. Cat clay. (Dutch). Versl.Landbouwk.Onderz.56:2

STARKEY, R.L. 1966. Oxidation and reduction of sulphur compounds in soils. Soil Sci. 101:297-306.

TABATABAI, M.A., BREMNER, J.M. 1970. Comparison of some methods for determination of total sulfur in soils. SSSA Proc. 34:417-420.

THORNTON, I., GIGLIOLI, M.E.C. 1965. The mangrove swamps of Keneba, lower Gambia river basin. II. Sulphur and pH in the profiles of swamp soils. J.Appl.Ecol.2:257-269.

TOMLINSON, T.E. 1957. Relationship between mangrove vegetation, soil texture and reaction of surface soil after empoldering saline swamps in Sierra Leone. Trop.Agric. (Trin.) 34:41-50.

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

VEEN, A.W.L. 1970. On geogenesis and pedogenesis in the old coastal plain of Surinam (South America). Thesis. Amsterdam. Publ.14. Phys.-Geogr.& Pedol. Lab. Univ. of Amsterdam.

VLEK, P. 1971. Some morphological, physical and chemical aspects of acid sulphate soils in Thailand. Soil Survey Report 84. 37 pp. Soil Survey Div., Land Development Dept. Min. of Nat. Dev. Bangkok.

VLEK, P. 1972. Acid sulphate soils: reactions during their oxidation from pyrite muds. (Dutch). Colloquium. Dept.Soil Sci.& Geol., Agric.Univ.Wageningen. 8 pp. Mimeographed.

VIEILLEFON, J. 1969. Pedogenesis in tropical mangrove areas: an example of a chronosequence. (French). Sci. du Sol 2:115-148.

WIKLANDER, L., HALLGREN, G., JONSSON, E. 1950. Studies on gyttja soils. III. Rate of sulfur oxidation. Lantbrukshogsk. Ann. (Uppsala) 17:425-440.

WIND, G.P., STEEGHS, B.H. 1964. Cat Sand. (Dutch). Landbouwk.Tijdschr. 76: 150-157.

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.123:1-49. Bogor.

YONEDA, S. 1961. Studies on polder soils in Japan. 16. Rapid method for determining oxidizable sulphur and change of soil reaction of sea muds and polder soils. Sci.Rept.Faculty Agr.Okayama Univ.17:39-46.

Summary

The existing methods for identification and prediction of acid sulphate soil conditions are critically reviewed. Comments pertain to dependability of results, practicability of procedures and consistency of concepts in the light of up to date information on nature and behaviour of acid sulphate soils. Subsequently are discussed field identification and analytical methods. Some little known but expedient techniques are described in detail. Special emphasis is given to chemical tests on potential acid sulphate soil material for prediction of conditions following drainage. The often heterogeneous material requires high sampling density which implies quick and simple analytical techniques. The usual methods reproduce or indicate readily occurring oxidation, acidification and neutralizing processes in the soil sample within a closed system. For dependable interpretation of the test results, modifying field conditions should be taken into account, in particular mass transportation in open systems and intensity factors. It is concluded that no single of the existing methods has general applicability for the objective in consideration and it is recommended that different combinations of geographic, morphometric and analytic methods be applied to suit different situations.

Résumé

Cet introductoire passe en revue critiquement les méthodes permettantes l'identification et la prognose de l'état sulfaté acide du sol. Les méthodes existantes ont été jugées pour sûreté, possibilité practicable et logique de la conception vu l'information actuelle sur le caractère et la dynamique des sols sulfatés acides. Discussiés sont successivement l'identification dans le terrain et les méthodes analytiques. Quelques techniques peu connues mais très pratiques ont été expliquées en détail. Attention spéciale a été donnée à l'analyse chimique des roches mère sulfuriques dans l'intention de pronostiquer l'état du sol après drainage. Il faut une échantillonnage intensive à cause de l'hétérogénéité des matériaux et par conséquent méthodes analytiques rélativement rapides et simples. Les méthodes usuelles sont indicatrices du cours des processus d'oxidation, acidification et neutralisation comme ils avancent couramment dans l'échantillon dans un système fermé. Pour une interprétation sûre des résultats il faut les corriger pour les effets modifiants des conditions actuelles dans le terrain, tenant compte surtout du transport des matériaux dans les systèmes ouverts et des différences en intensité des processus.La conclusion est qu'on ne peut pas attribuer à aucune des méthodes existantes utilité générale pour l'objet en question, et qu'il faut utiliser dans chaque situation une combinaison assortissante de méthodes géographiques, morphologiques et analytiques.

Resumen

Se da una resena crítica de los métodos para la identificación y el pronóstico de ácidos sulfáticos en suelos. La crítica toca a la certeza de resultas, la conveniencia del procedimiento y la lógica del concepto, dada la información recién sobre la naturaleza y el desarrollo de los suelos ácidos sulfáticos. Consecutivamente son tratados la identificación en el campo y los métodos analíticos. Algunos procedimientos poco conocidos pero muy convenientes han sido descritos detallados. Se presta atención especial a las experiencias químicas con muestros de suelo sulfurico, al fin del pronosticar el desarrollo despuès del drenaje de ácidos sulfáticos. Porque normalmente la materia es muy heterogénica, se necesita una grande cantidad de muestras y puès procedimientos analíticos rápidos y sencillos. Las experiencias usuales reproducen o indican los corrientes procesos de oxidación, acidificación y neutralización transcurriendo en muestras de suelo dentro sistema cerrado. Para el interpretar de las resultas se necesita cargar en cuenta las modificaciones débidas a las condiciones concretas en el campo, sobre todo los efectos de traslación de materias en sistemas abiertos y de diferencias en intensidad de los procesos. Se concluye que ningun de los métodos existientes tiene conveniencia general para el objeto perseguido, y se recomenda la aplicación para cada situación, de una propiada combinación de métodos geográficos, morfológicos, y analíticos.

Zusammenfassung

Die Methoden für die Identifizierung und Vorherbestimmung sulfatsaurer Bodenverhältnisse werden kritisch bewertet. Zuverlässigkeit, praktische Anwendbarkeit und theoretische Ausgangspünkte der Methoden werden geprüft und verglichen mit den neuesten Anschauungen über die Natur und das Verhalten sulfatsaurer Böden. So wird behandelt die Identifizierung im Felde und die analytischen Verfahren. Einige wenig bekannten, doch geeigneten Verfahren werden ausführlich beschrieben. Besondere Aufmerksamkeit bekommen die chemischen Versuche mit sulfidhaltigem Ausgangsmaterial zur Vorherbestimmung sulfatsaurer Bodenverhältnisse infolge künftiger Entwässerung. Die Heterogenität dieser Ausgangsmaterialen erfordert meistens eine Kombination intensiver Probenentnahmen mit einfachen Schnellanalysen. Die üblichen Verfahren bezeichnen den fertigen Verlauf der Oxidation, Versauerung und Neutralisation in Bodenproben innerhalb eines geschlossenen Systems. Für die zuverlässige Vorherbestimmung sollen die Ergebnisse der Versuche korrigiert werden für zusätzliche Wirkungen reeler Feldverhältnisse, besonders des Massentransports im offenen System und der Intensitätsdifferenzen für verschiedene Prozesstufen. Die Konklusion ist, dass keine einzelne der üblichen Methoden allgemeine Anwendbarkeit hat für das beabsichtigte Zweck, und es wird empfohlen für verschiedene Lagen entsprechende Kombinationen von geographischen, morphologischen und analytischen Verfahren anzuwenden.

PHYSIOGRAPHY, CLASSIFICATION, AND MAPPING OF ACID SULPHATE SOILS

W. van der Kevie
Food and Agriculture Organization of the United Nations

Introduction

Though acid sulphate soils may occur in inland areas (Chenery 1954), they are usually restricted to areas relatively close to the sea, where they have formed on marine and estuarine deposits. They have been described in various parts of the world, from cold temperate climates to the humid tropics, but it seems that they have their largest extent in tropical deltas.

For the classification and mapping of acid sulphate soils, it is necessary to know under which conditions they form and to understand the relation between their occurrence and landscape features such as vegetation and land forms.

Sedimentation environment

All acid sulphate soils have developed from sediments that have a high content of sulphides which have been fixed and accumulated by reduction of sulphates from the sea water. Such sediments occur mainly in narrow coastal zones of swampy land which are regularly flooded by sea water. At places where big rivers debouch into the sea and where deltas are formed, large areas of swamp land under the daily influence of brackish water may extend quite far inland. For instance Giglioli and Thornton (1965) reported the penetration of brackish water in the Gambia river to be 115 miles upstream and a swamp area with brackish water deposits extending to about 100 miles inland.

In the tropics littoral swamps consist of almost flat land covered with regular belts of Avicennia and Rhizophora mangroves with mixed forest of low, salt-tolerant trees or grasslands on the land side of the swamps.

If the swamps extend farther inland, more complicated vegetation patterns may occur, with different species on the banks of the tidal channels and farther away from them. For instance in semi-humid tropical climates in West-Africa, the tidal streams are bordered by galleries of Rhizophora racemosa which are within the limits of daily flooding with brackish water. Farther away from the channels, on slightly higher land, Avicennia nitida is found (Giglioli and Thornton 1965) while the highest land between the tidal streams, which has been silted up so high that flooding only occurs at high tides during the rainy season, is barren or has very scanty vegetation of Sesuvium. Similar vegetation patterns, but with different species of mangrove trees, occur in Southeast Asia. On the low mud flats along the coast, and along the lower courses of rivers and tidal channels, Avicennia marina is mainly found, while farther upstream on the banks of tidal channels there is a mixed forest of other Avicennia species (officionalis and alba), Sonneratia (alba and caseolaris), Rhizophora (mucronata and apiculata), Bruguiera (gymnorrhiza, parviflora, sexangula) and Nipa palms (Nipa fruticans). On the higher land, which is flooded at spring tides only, there are more trees, such as Xylocarpus (mekogensis and obovatus), Cereops, and Lumnizera, and many non-mangrove trees such as Heritiera, Combretum, and Thespesia. In monsoon climates like that of Central Thailand, barren flats partly covered with Sueda maritima are found on tidal land that is only flooded in the rainy season. Grasslands with sedges and rushes may occur on the land side of mangrove swamps. Brackish water marshes in temperate climates are normally not covered with forest, but carry a vegetation of grasses, reeds, and other low herbaceous vegetation.

The deposition of sediments and the formation of soils is closely related to the vegetation pattern. Not only is there a relation between kind of vegetation on the one hand, and elevation, flooding conditions, and salt content of flood water and sediments on the other, but there is also a relation between the presence of a high content of sulphides in the sediments and other factors which are often related to the kind of vegetation:

a) a permanent, highly reducing environment
b) a sufficient supply of sulphur
c) high content of organic matter

The optimum environment for accumulation of sulphides is thus an area at some distance from moving water (a) - thus not near the sea shore or on the banks of rivers and tidal channels - which is regularly flooded by salt water or brackish water (b), and where the sediments are permanently saturated (a). In such an environment Rhizophora-Bruguiera forest thrives (with or without Nipa palms, which grow in slightly brackish environment in Southeast Asia) and its dense fibrous root system provides a high content of organic matter (c) that can be used by sulphate-reducing bacteria for their energy supply.

Avicennia and Sonneratia species, which are more salt tolerant than Rhizophora-Bruguiera and Nipa, grow on the better drained and more saline parts of the swamp area - on the mud flats along the sea shore and on the banks of the tidal channels. Avicennia is also found on the higher very saline areas that are only flooded at spring tides. The root systems of Avicennia and Sonneratia are not so dense as those of Rhizophora and Bruguiera and sulphide accumulation in soils under the former vegetation is consequently much less. In some of the higher areas under Avicennia forest however, high concentrations of sulphides may occur due to the fact that Avicennia is here a secondary forest following Rhizophora, which died because of high salinity and drought.

In the formation of potentially acid sulphate soils, it is not only the concentration of sulphides that is important, it is also the content of neutralizing components that will prevent a strong acidification after oxidation of the sulphides upon drainage.

One of the main neutralizing components is calcium carbonate and its occurrence is largely determined by the quality of the river water that mixes with the sea water in the swamp area. However, even with a considerable supply of lime from river water, precipitation of $CaCO_3$ may be limited if the carbon dioxide tension is high, (formation of soluble $Ca(HCO_3)_2$). This is true in very poorly drained sediments with a high organic matter content, where the conditions for production and preservation of CO_2 are favourable. At the same time these are conditions that are also favourable for the fixation and accumulation of sulphides. It is therefore understandable that sediments that have very high contents of both sulphide and calcium carbonate will only be found in those mangrove swamps that are flooded by river water with an extremely high calcium carbonate content, as may occur along coastal areas with limestone hills.

Other important neutralizing components are easily weatherable iron silicate minerals such as chlorite and chamosite, which can be formed on shallow sea bottoms. These minerals have a green colour and if the organic matter content in the sediments is relatively low, these minerals may give the sediments a typical greenish-grey colour. Greenish-grey sediments are therefore often found in the better drained parts of the swamp area, thus along rivers and tidal channels and in the higher silted up areas carrying only sparse vegetation. There are, however, many brackish swamp areas where these minerals do not occur in the sediments.

Coastal Swamps are usually dissected by rivers and tidal channels. The rivers may have low levees of sediments that are slightly lighter textured than the backswamp deposits. In areas where the rivers are draining hilly or mountainous land not far from the coast, the levees may be more pronounced. Very little sulphide will be accumulated in these levee sediments due to relatively good drainage.

Very inconspicuous levees occur along tidal channels that have no hinterland other than the swamp area itself. Yet drainage is also relatively good along these channels due to the daily tides, and very little sulphide is accumulated in the sediments bordering these channels. However, as the swamp areas extend into the sea by accretion, the tidal channels may eventually silt up and drainage of the former levees wil deteriorate. The original vegetation will change and a considerable quantity of sulphides could still accumulate in the levee deposits.

Some of the mangrove swamp areas in the humid tropics are characterized by the presence of large mounds built up by mud lobsters (Thallasima anomale) (Andriesse and Sim 1968, Pons and Van der Kevie 1969). These lobsters bring up reduced unripe soil material from the subsoil and build it into mounds that may be as high as one metre. Many of the mounds are 100 to 200 cm wide at the base and some overlap to form even bigger mounds. The soil material of these mounds is exposed to aeration and oxidation and if the material contains sulphides it will rapidly become extremely acid. The mounds occur in varying densities. In mangrove swamps in Sarawak for instance, it is normal to find 500 to 1500 mounds per ha but even more than 5,000 per ha may occur (van der Kevie[1] 1969). These mounds will gradually erode and flatten and the activities of the lobsters thus cause the soil to mix thoroughly, resulting in surface soils that are very acid.

In other swamps, such as in Central Thailand, where these lobsters do not live, perhaps because of higher salinity, no high mounds will be found, though crabs may build up low hills 10 to 20 cm high. In these swamp deposits it is normal that the surface soil is considerably less acid or potentially acid than the subsoil with its high content of organic matter caused by decomposition of fibrous roots.

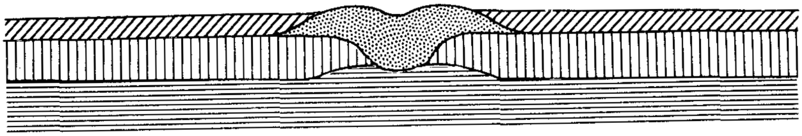
Land forms

After the sulphide-containing sediments of the brackish water swamps have been drained - either naturally by coast accretion or sea level subsidence, or artificially by reclamation - the soils will slowly ripen and acid sulphate soils will be formed. The environment will change as other vegetation replaces the salt-tolerant species and most of the tidal channels silt up. Natural ripening may occur in a brackish environment, as often happens in semi-humid climates with a pro-

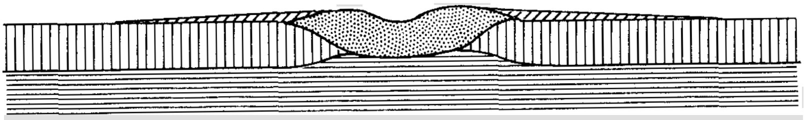
---

[1] W. van der Kevie (FAO). Report on a visit to the proposed Sungai Sarawak Padi Scheme Area. 18-27 June 1969.

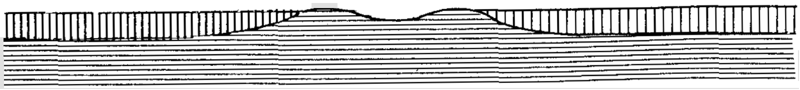
a. Upstream of area with acid sulphate soils



b. In the middle of area with acid sulphate soils



c. Downstream of area with acid sulphate soils



▒ river loam and sand

▥ brackish water clay

▨ river clay

▤ marine clay

Fig. 1. Three schematic cross sections of the Chao Phraya river in Thailand, streaming through an area with acid sulphate soils

nounced dry season, or in a completely fresh water environment as happens in humid tropical areas and perhaps also in temperate climates.

The acid sulphate soils occur in almost flat plains, either as small inclusions in otherwise nonacid marine soils (van der Kevie and Yenmanas 1972) or as nearly homogeneous areas with only narrow strips of nonacid soils along rivers and some of the former tidal creeks. If not used for cultivation, these soils are normally covered with grasses, rushes, and sedges (monsoon climate), or fresh water swamp forest and reeds (humid tropics and temperate climates). In humid climates organic matter may accumulate on the surface and the acid sulphate soils may be covered by peat (van Wijk 1951, FAO 1966).

In the inland part of areas containing acid sulphate soils, riverine sediments may be deposited on top of acid sulphate soils as the coast line progresses. Along large rivers with high silt loads, conspicuous natural levees will be formed, and in the backswamp areas too riverine clays may cover acid sulphate soils. In very humid climates, this deposition of river sediments may occur before the brackish water sediments are ripened, resulting in river soils overlying soft, only slightly acid mud clays, containing pyrites (van 't Woudt[1] 1969). After being drained these mud clays will become extremely acid, while the overlying river sediments will also acidify because of acids rising to the surface.

Figure 1 shows three schematic cross-sections of a river (here the Mae Nam Chao Phraya in Thailand) streaming through a delta. In the upstream areas, acid sulphate soils with unripened mud clay subsoils are covered by thick layers of riverine deposits. Along the rivers natural levees of fine loamy texture occur and these are several metres higher than the back swamps where 2-3 m thick layers of fine river clay are found on top of acid sulphate soils. The unripened subsoils are dark grey and have a very high pyrites content. At greater depth these pyrites clays are in turn underlain by greenish-grey marine deposits having relatively low contents of pyrites and organic matter.

Somewhat more downstream, acid sulphate soils are exposed over large areas, but along the river low and narrow levees of fine loamy texture occur while a wide zone of backswamp area on both sides of the river consists of a thin layer of riverine clay over acid sulphate soils. The riverine clays here may have red mottles and are rather acid because of acidification from below. As the river water contains calcium, fine gypsum crystals will be formed in these soils.

---

[1] B.D. van 't Woudt: Report on swamp development in Southeast Kalimantan. FAO, October 1969.

In the downstream part of the area containing acid sulphate soils. where the river contains very little silt, the levees are inconspicuous and consist of ripe, nonacid, brownish mottled, grey soils formed on greenish-grey deposits. These are the sediments that were relatively well drained and covered with Avicennia-Sonneratia vegetation during deposition. Thus the areas with acid sulphate soils that still have some relief in the upstream parts are nearly flat in the downstream areas.

A very conspicuous landscape feature in the area with acid sulphate soils in Thailand is the presence of many so-called wallows, which are shallow rounded or sub-rounded depressions about 50 cm deep and with a diameter of 10 to 50 m. Some of them hold water throughout the year but most dry out for a few months in the hot season. Their origin is not well understood. They have been referred to as elephant wallows (Pendleton 1947). It is more probable, however, that they have another origin. During sedimentation local concentration of vegetation may have caused a deficit of inorganic sediments in small areas, which resulted later in the formation of depressions after decomposition of the organic matter. The higher carbon content and dark colour of the soils in these wallows may be an indication of such an origin. However, these depressions have certainly been deepened considerably in recent times by water buffaloes using them as wallows during the dry season. Several kilograms of wet soil will be removed from a wallow as it sticks to the buffalo's skin each time he rolls in the mud. Afterwards, as the mud dries, it will crack and peel off somewhere else.

One important aspect of acid sulphate soils is their age. There are very young soils that have formed on pyrites-containing sediment of recently reclaimed swamp areas; there are old holocene acid sulphate soils (Brinkman and Pons 1968; van der Kevie 1971) formed on sediments that were deposited during a rising sea level; and there seem to be even pleistocene acid sulphate soils on low terraces surrounding the younger flood plain (Brinkman and Pons 1968). All these soils have a different appearance. The young soils are ripened to shallow depth and can be extremely acid with pH values of 2 to 3. The older soils are usually less acid and may be much deeper, particularly in climates with a pronounced dry season. They may have red and purple mottles, together with yellow mottles of jarosite. The pleistocene soils have a very firm consistence and no reduced mud clay is found in the subsoil.

Classification

Many soil scientists regard as acid sulphate soils only those soils that contain cat clay (strongly acid clay with yellow jarosite mottles) at some depth in the profile. Others consider also nonacid mud clays with a high sulphide content, as these soils may acidify considerably after drying out and oxidation of the sulphides to acid sulphates (Moormann 1963).

In Thailand the term "acid sulphate soil" is used for acid soils that are already physically and chemically ripened and which have a high sulphate content and a cat clay horizon at some depth; the term does not cover the unripe "potentially acid sulphate" soils of the coastal swamps (van der Kevie 1971).
In the FAO/UNESCO Soil legend for the Soil Map of the World (FAO/UNESCO 1968) the name Thionic Gleysols was used, which was later changed to Thionic Fluvisols (FAO/UNESCO, 1970). The latter, according to its definition, includes soils that have a thionic horizon containing an amount of sulphides and/or elementary sulphur which is sufficiently high to cause acidification of the soil upon oxidation to a pH (KCl) of less than 3.5 within 100 cm of the surface (FAO/UNESCO 1968).

Not until the last edition of the Comprehensive Soil Classification System of the USDA (1970) were the acid sulphate soils classified in a separate great soil group. Before that they were included in various great groups of the Aquepts (and Aquents for the potentially acid sulphate soils). However, the latest draft of the American classification introduced the great soil group of Sulfaquepts, which comprises very acid soils that have a sulfuric horizon with yellow jarosite mottles and a pH (1:1 water) below 3.5 in some layer of the upper 50 cm of the profile. In Thailand and other intertropical regions therefore most acid sulphate soils will be classified as Typic Sulfaquepts or Sulfic Tropaquepts, but other subgroups and intergrades such as Histic Sulfaquepts and Histic Sulfic Tropaquepts may occur in wet equatorial climates where acid sulphate soils are covered with a layer of peat or muck. Sulfohemists, having a sulfuric horizon within 50 cm of the surface (pH /1:1 water/ is less than 3.5), are the acid sulphate soils that are mainly organic. They are permitted to have any fiber content because of the relative importance of the sulfuric horizon (thus no soils are classified as Sulfofibrists or Sulfosaprists). These soils are rare and probably occur only in the wet tropics. They are all considered to be typic. In monsoon climates with a strongly pronounced dry season Vertic Sulfic Tropaquepts may occur, having cracks in the dry season that are more than 1 cm wide at a depth of 50 cm. OOutside the tropics Sulfaquepts and sulfic subgroups of Haplaquepts and Humaquepts occur.

The potentially acid mud clays occurring in swamp areas would have to be classified as Typic Sulfaquents if they have a pH (1:1 water) of dried soil that is below 3.5 in the upper part of the profile (within 50 cm from the soil surface if the n-value is > 1, and within 30 cm if the n-value is 0.7 or less). The actual soil reaction in the field, however, is normally only slightly acid to mildly alkaline.
The presence of a histic epipedon or a buried Histosol is not considered important compared with the acidifying effects of drainage and aeration and therefore no histic subgroup is distinguished. However, potentially acid sulphate soils that are dominantly organic are classified as Sulfihemists. They have sulfidic materials within 1 m of the surface. Sulfic Hydraquents include very soft swamp soils (saline or fresh) that contain sufficient sulphides to produce a pH (1:1 water) below 4.5 in the upper 25 cm or more, or have larger (as yet undefined) amounts of sulphides between 50 cm and 1 m. Sulfic Tropaquents and Sulfic Fluvaquents are similar soils, respectively in and outside the tropics, that are more ripe - having lower n-values (< 0.7) - in the upper part of the profile. Sulfic Haplaquents are mentioned in the American classification though they are not known to occur in the U.S. and it is doubtful whether they exist anywhere else because of their low organic matter content. No provision is made in the American classification at subgroup level for saline acid sulphate soils. Dost (Harza Eng. Co. Int. 1969) in his soil studies in Guinea proposes the use of "halic" subgroups. Various soils indeed have a salic horizon (containing at least 2 per cent salt if horizon is more than 30 cm thick) and "Halic" Sulfaquents or "Halic" Sulfic Hydraquents would be common soils in coastal swamps. Somewhat more inland in areas with a strongly pronounced dry season "Halic" Sulfaquents or "Halic" Sulfic Tropaquepts may occur but also Sulfic Halaquepts.

In the FAO/UNESCO soil legend no separate units have been established for already physically and chemically ripened acid sulphate soils and most of them (both Sulfaquepts and sulfic subgroups of Tropaquepts, Haplaquepts and Humaquepts) should be placed in the Thionic Fluvisols, together with the potentially acid sulphate soils (Sulfaquents and part of the Sulfic Hydraquents, Tropaquents and Fluvaquents). Part of the less potentially acid soils should be placed in the Gleyic Solonchaks or Dystric Fluvisols, depending on salinity.

Correlation between the American subgroups and units of the World Soil Map is somewhat difficult as definitions for sulfidic (U.S.) and thionic (FAO/UNESCO) materials do not have the same limits. In Tab. 1a/1b an effort has been made to place the various acid and potentially acid sulphate soils in the American classification, and to correlate them with units of the World Soil Map. Though this list of soils does not claim to be complete and concedes that other subgroups may occur elsewhere to a small extent, it nevertheless includes the main ones.

The American classification requires that sulfuric horizons have yellow jarosite mottles. Most acid sulphate soils do indeed contain jarosite mottles, but in some areas there are very acid soils, high in sulphur, that do not have these mottles. Such soils were identified in Sarawak (Andriessen and Sim 1968; van der Kevie[1] 1969). Though jarosite may have been present originally, at least in the surface, it may have been hydrolyzed to ferric oxides (van Breemen[2] 1969). Therefore a definition that only includes requirements for acidity and sulphur content may be preferable.

Of great importance in recent years are the efforts that have been made to classify and subdivide the various kinds of acid sulphate soils, since the term "acid sulphate" unnecessarily frightens workers in agriculture. Though some of these soils are really extremely poor and entirely unsuitable for agricultural use without reclamation or special practices of soil improvement, others (such as most of the Sulfic Tropaquepts in Thailand) are producing reasonably good crops of paddy.

Mapping

Soil surveying in areas containing acid sulphate soils or potentially acid sulphate soils is in principle the same kind of work and uses similar methods as surveys in other areas. There are, however, some special problems in the identification and mapping of these soils.

First of all, it is the acidity in acid sulphate soils that is the main characteristic determining the place of the soil in the classification system at great group or subgroup level and this is not easily measurable in the field. It can be measured with a portable pH-meter or a pH test kit with a pH indicator. Many of the commonly used indicators, however, do not show a clear colour change at pH levels below 4.5 and it is desirable to develop an indicator that shows a colour change at the critical pH levels 4.0 and 3.5. Another problem is that classifi-

---

[1] W. van der Kevie (FAO): Report on a visit to the proposed Sungai Sarawak Padi Scheme Area. 18-27 June 1969.

[2] N. van Breemen: Some notes on soil conditions in the proposed Sungai Sarawak Padi Scheme Area (preliminary report of a visit to the area, 14-20 December 1969), Agricultural University, Wageningen.

cation is based on pH-values that are measured on dry soil. Therefore soils may have to be dried first before the pH is measured or a correlation has to be found between pH of fresh soil and dry soil, which may be done in acid sulphate soils if the moisture content of the soil is fairly constant during the period of survey.

The occurrence of yellow jarosite mottles is of course an easily visible characteristic to help identify acid sulphate soils. However, there are soils with jarosite, having a pH of 4.5 to 5.0, and it has been mentioned already that there are also soils, though they are probably very rare, which are very acid but lack jarosite mottles. Yet even in these soils jarosite may be found in freshly dug ditches and in other places where relatively fresh soil has been excavated and exposed to aeration.

Mapping potentially acid sulphate soils is even more difficult as it is based on characteristics that, though inherent, will only show clearly after drainage and ripening. There are various field and laboratory methods of estimating potential acidity, such as drying of the soil before pH measurement and oxidation of sulphides with hydrogen peroxide (H_2O_2). The content of sulphides present as pyrites may also be determined chemically or microscopically (Pons 1970). All these methods require extensive sampling and much work that cannot be done at the boring site. There are, however, other ways of recognizing the presence of potentially acid soil in the field, particularly in reconnaissance surveys. The kind of vegetation is a very important feature in the recognition of both acid and potentially acid sulphate soils, as it is related to the sulfide content of the sediments or acidity of the soils. Van Wijk (1951) based his soil survey in South Kalimantan on vegetation patterns and found very good relations between plant growth and soil type. For instance, many acid sulphate soils in the area are covered with a low forest of predominantly Melaleuca cajuputi (Gelam in Malay). The relation is so clear that these soils are sometimes called Gelam soils in Malaysia (Coulter 1952). Aerial photos are of course indispensable for the recognition and mapping of the various vegetation types.

Another indication of potential acidity is the occurrence of dense fibrous organic matter in the soil, which normally contains a high content of pyrites. Soil colour too is important. Dark grey soils with a high organic matter content are often potentially acid, and greenish grey soils are mostly not. Calcium carbonate content is important as a neutralizing compound and can be estimated by its reaction with hydrochloric acid (HCl).

Another helpful feature in identifying potentially acid soils is the occurrence of yellow or olive-yellow mottles of jarosite on lobster mounds or in other places where subsurface soil has been exposed to aeration.

Yet it is extremely difficult in swamp areas to map more or less homogeneous mapping units as there is much variation in potential acidity and soils not far from each other may have a pH of dried soil that differs by 2 or more pH units. In such areas soil associations have to be mapped. Even in detailed surveys it is difficult to make a distinction between, for instance, Typic Sulfaquents and Sulfic Hydraquents, and mapping units may contain both great groups in addition to smaller inclusions of Typic Hydraquents or other Aquents.

Performing surveys in swamp areas is an arduous task because of poor accessibility. Normally the only access is by boat but one has to reckon with the tides as small channels may run dry at low tides. Landings have to be made and the surveyors have to walk along traverses at right angles to the major hydrography as vegetation and soil conditions often change in this direction. This is very tiring work as the soils may be very soft, while in mangrove swamps the stilt and air roots of the trees make normal walking impossible. The many vicious mosquitoes make work in these swamps even more unpleasant and surveyors are advised to wear gloves and netting over their heads.

In areas with already ripened acid sulphate soils accessibility is often much better and in cultivated areas in monsoon climates, where the soils dry out deeply during the dry season, it is often possible to drive by car to any place where one wants to go. These areas are flat, and land forms and land use are very homogeneous. Air photo interpretation in such areas is of little help and borings have to be made at regular distances. In combination with other soil properties, the presence and depth of cat clays and the pH are major criteria for distinguishing between soil units. Other important factors are kinds of mottles, presence of gypsum, ripening stage, colour and depth of A-horizon, and flooding conditions.

As certainly not all areas containing soils known as acid sulphate soils consist of useless and unproductive land, soil surveys in such areas can be of great benefit as they will indicate soils that can be used for agriculture (mainly rice in the tropics). In already cultivated areas soils with different degrees of acidity can be mapped and such soil maps will be of value in further research on methods of improving these soils and in making recommendations for lime and fertilizer applications or other soil amendments.

Table 1a. Placement of potentially acid sulphate soils in the American classification, correlated with units of the Soil Map of the World (FAO/UNESCO)

Climatic zone	USDA	Main characteristics	World Soil Map	Main characteristics
World-wide	Typic Sulfaquents	pH (1:1 water) of dried soil < 3.5 within 50 cm if $n > 1.0$; within 30 cm if $n < 0.7$	Thionic Fluvisols	pH (KCl) of dried soil < 3.5 within 100 cm
World-wide	Sulfic Hydraquents	pH (1:1 water) of dried soil < 4.5 in upper 25 cm, or more acid between 50 and 100 cm $n > 0.7$ between 20 and 50 cm	Thionic Fluvisols	Some that are less acid than Sulfaquents but sufficiently acid to be included in Sulfic Hydraquents; non-saline
			Gleyic Solonchaks	Salic horizon and saline at some time of the year; part that meets acidity requirements for Sulfic Hydraquents but not for Thionic Fluvisols
			Dystric Fluvisols	Not sufficiently acid for Thionic Fluvisols but meets requirements for Sulfic Hydraquents; non-saline
Wet tropics and monsoon	Sulfic[1] Tropaquents	Acidity requirements of Sulfic Hydraquents but $n < 0.7$ between 20 and 50 cm	Thionic Fluvisols Gleyic Solonchaks Dystric Fluvisols	see above
Temperate	Sulfic Fluvaquents	Same as Sulfic Tropaquents		
World-wide	Typic Sulfihemists	Sulfidic materials within 100 cm; pH (1:1 water) of dried soil < 3.5	Thionic Fluvisols	see above

[1] Subgroups not recognized in American classification

Table 1b. Placement of acid sulphate soils in the American classification, correlated with units of the Soil Map of the World (FAO/UNESCO)

Climatic zone	USDA	Main characteristics	World Soil Map	Main characteristics
World-wide	Typic Sulfohemists	pH (1:1 water) < 3.5 within 50 cm	Thionic Fluvisols	pH (KCl) of dried soils < 3.5 within 100 cm
World-wide	Typic Sulfaquepts	pH (1:1 water) < 3.5 within 50 cm	Thionic Fluvisols	see above
Wet tropics and monsoon	Sulfic Tropaquepts	pH (1:1 water) < 4.0 between 50 and 150 cm and/or 3.5 to 4.0 within 50 cm	Thionic Fluvisols Humic Gleysols Dystric Gleysols	see above pH(KCl) ≥ 3.5; umbric or O horizon pH(KCl) ≥ 3.5; ochric A horizon
Wet tropics	Histic Sulfic Tropaquepts	Acidity like Sulfic Tropaquepts Histic epipedon	Thionic Fluvisols Humic Gleysols	see above pH(KCl) > 3.5; O horizon
Monsoon and semi-arid	Vertic Sulfic Tropaquepts	Acidity like Sulfic Tropaquepts; cracks (1 cm) at 50 cm when dry	Thionic Fluvisols Humic Gleysols Dystric Gleysols	see above pH(KCl) ≥ 3.5; umbric or O horizon pH(KCl) ≥ 3.5; ochric A horizon
Humid temperate	Sulfic[1] Humaquepts	Acidity like Sulfic Tropaquepts; Umbric or Histic epipedon	Thionic Fluvisols Humic Gleysols	see above pH(KCl) ≥ 3.5; umbric or O horizon
Temperate	Sulfic Haplaquepts	Acidity like Sulfic Tropaquepts; Ochric epipedon	Thionic Fluvisols Dystric Gleysols	see above pH(KCl) ≥ 3.5; ochric A horizon
Monsoon and semi-arid	Sulfic[1] Haplaquepts	Acidity like Sulfic Tropaquepts; Sodium saturation > 15 in half or more of upper 50 cm; mostly saline in some part of the year	Thionic Fluvisols Gleyic Solonchaks	see above pH(KCl) ≥ 3.5; salic horizon and/or saline at some time of the year

[1] Subgroups not recognized in American classification

REFERENCES

ANDRIESSEN, J.P. and SIM, E.S. Report on Soil Investigations in the Proposed Sungai Sarawak Padi Scheme Area. Report No. 125. Research Branch, Department of Agriculture, Sarawak, Malaysia.

BRINKMAN, R. and PONS, L.J. 1968. A pedo-geomorphological classification and map of the Holocene sediments in the coastal plain of the three Guianas. Soil Survey Paper No.4, Netherlands Soil Survey Institute, Wageningen, The Netherlands.

CHENERY, E.M. 1954. Acid Sulphate Soils in Central Africa. Trans. 5th Intern. Congr. Soil Sci., Leopoldville.

COULTER, J.K. 1952. Gelam soils, a study of their sulphur content. Journ. of Malay Agric. No. 35.

FAO. 1966. Report on the Soil Survey Project. British Guiana. FAO/UNSF. Rome, Italy.

FAO/UNESCO. 1968. Definitions of soil units for the Soil Map of the World. World Soil Resources Report No. 33, FAO. Rome, Italy.

FAO/UNESCO. 1970. Key to Soil Units for the Soil Map of the World. Soil Resources, Development and Conservation Service, FAO. Rome, Italy.

GIGLIOLI, M.E.C. and THORNTON, J. 1965. Mangrove swamps of Keneba, Lower Gambia river basin. Journal of Appl. Ecology 2, Lackwell Scientific Publications. Oxford, U.K.

HARZA ENGINEERING COMPANY INTERNATIONAL. 1969. Etude d'un programme d'aménagement hydro-agricole des terres rizicultivables de la Basse-Guinée. Vol.II, Pédologie.

MOORMANN, F.R. 1963. Acid sulfate soils (cat-clays) of the tropics. Soil Sci., Vol.95, No.4.

PENDLETON, R.L. 1947. The formation, development and utilization of the soils of the Bangkok Plain. The Siam Society, Natural History Bulletin. Vol. 14(2). Bangkok, Thailand.

PONS, L.J. and VAN DER KEVIE, W. 1969. Acid Sulphate Soils in Thailand; studies on the morphology, genesis and agricultural potential of soils with cat-clay. Soil Survey Report No.81, Dept. of Land Development, Bangkok, Thailand.

PONS, L.J. 1970. Acid sulphate soils (soils with cat-clay phenomena) and the prediction of their origin from pyrites muds. Fysisch Geografisch en Bodemkundig Laboratorium "From Field to Laboratory" Publ. No.16. Amsterdam, The Netherlands.

UNITED STATES DEPARTMENT OF AGRICULTURE. 1970. Soil Taxonomy of the National Cooperative Soil Survey (preliminary). Soil Conservation Service. Washington D.C., USA.

VAN DER KEVIE, W. 1971. Acid sulphate soils in Central Thailand. Regional Seminar on Soil Survey and Soil Fertility Research in Asia and the Far East. New Delhi. February 1971. World Soil Resources Report No.41, FAO. Rome, Italy.

VAN DER KEVIE, W. and BANCHONG YENMANAS. 1972. Soil Survey of the Southern Central Plain. Soil Survey Division, Department of Land Development. Bangkok, Thailand.

VAN WIJK, C.L. 1951. Soil Survey of the tidal swamps of South Borneo in connection with the agricultural possibilities. Landbouw No. 123. Wageningen, The Netherlands.

Summary

Acid sulphate soils have their largest extent in tropical deltas. A major part of these soils is going through highly dynamic initial phases of soil formation. Their mapping and classification therefore requires understanding of the actual soil properties in a genetical context. For the deltas of southeastern Asia the morphometric properties of acid sulphate soils are described and explained by interaction between sedimentary soil material and changing sedimentary environment, hydrological regime, succession of vegetation and surface configuration. The placing of acid sulphate soils in the world wide classification systems of FAO/UNESCO and USDA (United States Department of Agriculture) is discussed and the relative taxonomic units of both systems are correlated (Tables 1a and 1b). The methods of distinguishing acid sulphate soils in the field for mapping purposes are shortly reviewed.

Résumé

La majorité des sols sulfatés acides se trouve dans les estuaires tropicaux. Ces sols sont souvent dans une phase d'évolution initiale hautement dynamique. Alors, leur levé cartographique et leur classification demandent l'interprétation génétique des propriétés actuelles. Les propriétés morphologiques des sols sulfatés acides d'Asie sud-ouest ont été descrites en les explicant à travers de l'intervention mutuelle de l'ambiance sédimentaire, les régimes hydrologiques changeants, les successions de la végétation et la configuration de la superficie ainsi que la roche mère sédimentaire des sols. La position des divers sols sulfatés acides dans les systèmes de classification de la FAO/UNESCO et du USDA (Ministère d'Agriculture des Etats Unis) est discutée. La corrélation des unités taxonomiques concernantes tous les deux systèmes a été présentée dans les Tableaux 1a et 1b. Enfin les méthodes de levé cartographique et les crittères de distinction dans le terrain ont été discutés brèvement.

Resumen

Los suelos de sulfatos ácidos encuentran en mayoría en los deltas tropicales. Sobre todo son suelos en un estado inicial de desarrollo, caracterizado por un fuerte dinamismo. Por eso su levantamiento cartográfico y su clasificación requieren conocimiento de las propriedades de suelo en relación con los procesos de desarrollo. Se describe los suelos ácidos sulfáticos en los deltas de Asia sudeste, explicando sus cualidades en fonción del ambiente fisiográfico (cambios hidrológicos, cadenas de vegetación, relieve de los aluviones). Pués se discute colocación de varios tipos de suelos de sulfatos ácidos dentro los sistemas de clasificación de la FAO/UNESCO y del USDA (Ministerio de Agricultura de los Estados Unidos). En las Tables 1a y 1b se presenta la relación entre las unidades taxonómicas respectivas. Al fin se trata unos aspectos prácticos del levantamiento en el terreno de los suelos de sulfatos ácidos.

Zusammenfassung

Die sulfatsauren Böden sind hauptsächlich in den tropischen Delta- und Küstenebenen verbreitet. Am meisten befinden sich solche Böden in den dynamischen Anfangstadien ihrer Entwicklung. Ihre Kartierung und Klassifikation erfordert daher eine gründliche Kenntnis der Bodeneigenschaften in genetischer Hinsicht. Die Eigenschaften der schwefelsauren Böden in den Küstenebenen Südasiens werden vom genetischen Gesichtspunkt aus beschrieben. Die lokalen Variationen werden aufgeklärt auf Grund der gegenseitigen Wirkung von Änderungen in den Ablagerunsverhältnissen, Wasserbewegungen, nachfolgenden Vegetationen, Höhe der Aufschlämmung und Zusammenstellung des alluvialen Ausgangsmaterials. Die Unterbringung der schwefelsauren Böden innerhalb der Bodenklassifikation von FAO/UNESCO und der von USDA (Amerikanische Klassifikation) wird ausführlich behandelt. Die diesbezüglichen taxonomischen Einheiten beider Systeme werden verglichen in Tafeln 1a und 1b. Schliesslich werden einige praktische Fragen der Kartierungsmethodik besprochen.

DISCUSSION

COULTER: Are remote sensing techniques, e.g. sequential monitoring by satellite, likely to have any application in mapping potential and developed acid sulphate soils?

VAN DER KEVIE: Probably in as much as vegetation types and moisture conditions are related to the occurrence of acid sulphate soils and can be detected by remote sensing techniques.

ZONNEVELD: Are there plants that contribute to acid sulphate soil formation not just by producing large amounts of organic matter but also by accumulating sulphur?

MOORMANN: Melaleuca leucodendron can accumulate S in its tissues; however, it grows also in areas poor in sulphur. It is not an indicator for soils rich in sulphur.

VAN DER KEVIE: The indicator value of Melaleuca depends on its being very tolerant to acidity, not to its contributing to pyrite accumulation.

VAN BREEMEN: In reduced conditions sulphide accumulation (inorganic and microbiologically) is more probable than preferential uptake of SO_4 by higher plants.

THE EFFECT OF EXTREME SOIL ACIDITY ON THE NUTRIENT UPTAKE AND PHYSIOLOGY OF PLANTS

I. H. Rorison
Nature Conservancy Grassland Research Unit,
Department of Botany, University of Sheffield, United Kingdom

INTRODUCTION

Since the eighteenth century botanists have been aware that the chemical nature of soil affects plant growth and distribution. One of the earliest causal considerations was made by Unger (63) in his book "Über den Einfluss des Bodens auf die Verteilung der Gewächse, nachgewiesen in der Vegetation des Nordöstlichen Tirols". He described the different floras which occurred on calcareous (calcicole) and on acidic soils (calcifuge) in the Kitzbühl district of Austria. At that time, and for most of the C19, the main differences in the soils were considered to be physical, calcareous soils being drier and warmer than acidic ones. It was noted that several species which are indifferent to soil type in Southern Europe tend to be limited to dry calcareous soils at the northern limits of their distribution (16). Even in the early C20 scientists in Britain were stressing physical aspects of the problem, such as water relations and root morphology (61). However, with the rapid development of experimental techniques at the beginning of the C20, interest turned towards the chemical properties of soils and in particular to the influence of pH and of calcium ions. Paul (45), in a classic experiment with Sphagnum species, showed that they were killed in a solution containing 80-90 mg/l $CaCO_3$ whereas a solution fifteen times stronger, of $CaSO_4$, could be tolerated without damage.

There followed a spate of work on the failure of certain species to survive calcareous soils (57). The most complete review of the subject up to that time was written by Mevius (42). Gradually characteristics of calcareous soils were itemized, dryness, high Ca level, and lack of available iron being the most prominent. The influence of high pH on the availability of NPK and the trace elements Mo, Bo, Cu, and Zn was reported later when micro-analytical techniques became widespread (16).

While botanists were concerned with calcareous soils, agronomists were tackling the problems concerned with the failure of crop plants in acidic soils. Liming and thereby raising pH was the simple corrective, but what were the underlying causes? Aluminium toxicity (24) and the depression of P uptake by Al in acid solution (39) were the factors most studied.

Fe and Mn toxicities were other possibilities, as were deficiencies of almost all essential nutrients in the inevitably leached acidic soils. The major factors were reviewed by Hewitt (25).

Initially the problem was considered only in relation to well aerated soils, but later similar problems, with variations, were encountered in waterlogged soils, where Mn and, particularly, Fe^{2+} (35, 41) could be considered major factors.

It wasn't until the 1950s that botanists began to concentrate on the cause of failure of calcicole species in acidic soil conditions (16) and on the importance of the role of Al (50). At this time too the value of comparative experiments utilizing a range of species of varying degrees of tolerance to acidic conditions began to be realized. There were then also stirrings of the idea that tolerance and susceptibility might be controlled by the same mechanisms developed to differing degrees in tolerant and susceptible species (50).

More recently the effects of aluminium (12) and ferrous iron (27, 41) have been elaborated and the relationship between mechanisms of response to both elements has been explored by Grime and Hodgson (22) and Hodgson (27).

It may be concluded that the edaphic factors which affect the growth and distribution of plants are both chemical and physical. To understand the physiological mechanisms involved in the plant it is important to consider both plants which are tolerant of acidic conditions and those which are not. This consideration will now be made with respect to acid sulphate soils, whose range of conditions depending on time, depth in profile, amount of $CaCO_3$ added, amount of leaching etc., makes general knowledge of the calcicole-calcifuge problem applicable in many cases.

FACTORS ASSOCIATED WITH ACID SULPHATE SOILS

Hewitt (25) presented a list of factors, and those best documented in contributions to this Conference are underlined:

1. Direct effect - injury by hydrogen ions
2. Direct effect due to low pH
    - (a) Physiologically impaired absorption of Ca, Mg, and P
    - (b) Increased solubility and toxicity of Al, Mn, Fe etc.
    - (c) Reduced availability of P - Al x P interaction
    - (d) Reduced availability of Mo

3. Low base status
   - (a) Ca deficiency
   - (b) Deficiencies of Mg, K and possibly Na
4. Abnormal biotic factors
   - (a) Impaired nitrogen cycle and fixation
   - (b) Impaired mycorrhizal activity
   - (c) Increased attack by soil pathogens, e.g. club root
5. Accumulation of soil organic acids or other toxic compounds due to unfavourable oxidation reduction conditions

The physical condition of the soil has a major influence on the way chemical factors influence the nutrition of plants. Drainage as it affects aeration and soil moisture content is a key factor.

The drier the soil, the more sulphur is oxidized to sulphate, the lower the pH drops, the higher the concentration (in solution) of hydrogen, aluminium, and ferric iron ions (Fig.1).

The levels to which any of these components rise or fall depends upon the chemical nature of the parent material and upon the solubilities of the metals involved. Sparling (59) produced a set of curves for the solubilities of cations likely to cause injury to plants, using data from Britton (8) (Fig.2). The relationship between solubility and pH is for single salts in solution, and therefore the position of the curves is likely to shift to the left if less soluble salts, e.g. phosphates, and different combinations of metals occur.

It is of immediate interest that Fe^{3+}, Al^{3+}, and Fe^{2+} become insoluble at, approximately intervals of 2 pH units so that above pH 3.0 Fe^{3+} is unlikely to be toxic, above 5.0 Al, above pH 7.0 Fe^{2+}. This narrows the field of potential toxins, and the degree to which they operate in different acid sulphate soils may be judged from the papers of Verhoeven (I-7) and Ponnamperuma et al. (V-3).

THE RESPONSE OF PLANTS

Having established the range of chemical and physical conditions in the soil, it is next important to note that there is a wide range in the response of plant species to these conditions (Fig.3) and it is vital to design experiments which include (a) a wide enough range of levels of any variable (3) (Fig.4) and (b) a number of species which between them respond to the range of the variables (53) (Fig.5).

By this means it should be possible to measure the extent to which plants respond, then ultimately to identify the physiological pathways by which tolerance and susceptibility come about.

pH

Although the distribution of calcicoles and calcifuges is significantly related to soil pH, neither H^+ nor OH^- ions are generally considered to be toxic to plants between pH 4-8. The evidence for this rests largely on the oft-quoted work of Arnon and Johnson (5) and Olsen (44), who used mainly crop plants grown in solution culture media. In their media and those of subsequent workers (26) nutrient levels were high and it may be that plants tolerate high H^+ concentrations only so long as the concentration of other cations is high and potentially toxic polyvalent metals are in low concentration. pH drift has also been a problem in investigations concerning culture media, especially where nitrate nitrogen is present. An upward drift in these becomes more difficult to arrest, the more rapid plant growth becomes.

Definitive experiments employing constantly flowing solutions with monitored pH are required before an accurate assessment of the part played by the hydrogen ion in the rooting medium can be made.
pH is influenced by the form of certain nutrients in the soil and in turn can affect the solubility of nutrients. Two nutrients whose form affects pH are nitrogen and calcium.

Nitrogen

The many heterotrophic organisms which produce ammonium nitrogen from organic matter operate over a wide range of pHs. The two autotrophic micro-organisms, Nitrosomonas and Nitrobacter, which are largely responsible for the nitrification of ammonium to nitrite, and of nitrite to nitrate, both function poorly or not at all at low pH (28).

As a result, NH_4-N tends to build up in acidic soils and when plants take it up there is an efflux of hydrogen ions. In media of higher pH where NO_3-N predominates, uptake by plants results in an efflux of bicarbonate ions.

The innate buffering capacity of soils tends to minimize the resulting pH drift, but in culture solutions it can be considerable if unchecked.
Several publications record the relative tolerance of plants to NH_4-N and to NO_3-N and relate it to the nitrogen supply of the soils in which they are normally distributed (6, 17).

It has been shown that the strictly calcifuge species Deschampsia flexuosa grows very poorly with NO_3-N at pH 7,2 and that the calcicole Scabiosa columbaria fails completely at pH 4,2 when supplied with NH_4-N (Table 1). There is no shortage of nitrogen in the tissues of affected plants and the exact mechanism of growth inhibition is not known. An excess of NH_4-N may be toxic directly. It is also associated with reduced uptake of essential mono- and divalent-cations (K in particular) in susceptible species.

Differential uptake of nitrogen from a NH_4-NO_3 mixture may lower or raise pH in the immediate vicinity of a plant root if the species is selective with respect to nitrogen supply. At critical pHs below 5.0 this could lead to increased solubility of Al, Mn, and even Fe^{3+}, thus increasing the possibility of toxicity. Alternatively the possibility of toxicity could be reduced (20).

Calcium

Apart from areas around gypsum deposits, calcium mainly occurs in the soils as $CaCO_3$ and thus its concentration influences pH. It has been possible to distinguish between the effect of $CaCO_3$ and Ca ions on plants by the addition of salts to acidic soils, for example

Acid soil treatments	Effect on plant growth (other than calcifuges)
+ $CaSO_4$	Nil or deliterious
+ $CaCl_2$	Nil
+ NaOH	Beneficial chemically (not physically)
+ $CaCO_3$	Very beneficial

These results show that for many species the benefit of $CaCO_3$ is additive due to both the Ca ion and the ensuing rise in pH. Too high a level of calcium can cause a depression in the uptake of both potassium and magnesium in some plants but this is not normally a problem in acidic soils.

According to plant physiologists (9, 67) Ca is characterized by its relatively high content in the plant, coupled with a requirement for survival which is not much higher than that of a trace element. However, much depends upon the balance of ions, including trace elements, employed.

It has been shown (29) that the calcifuge species

Juncus squarrosus, grown in culture solution at constant pH, had a low optimum requirement of c. 10 mg/l Ca and made less growth at higher concentrations. The calcicole Origanum vulgare had an optimum at c.400 mg/l Ca. It failed to grow below 20 mg/l and tolerated up to 500 mg/l (Fig.6). Even if a basic level of Ca is present in an acidic soil, its uptake and long-distance transport may be inhibited by aluminium and other polyvalent cations (14), see p. 237.

Phosphorus

Inorganic phosphorus occurs as sparingly soluble salts of aluminium, iron, manganese, and calcium and its availability to plants varies with pH. Organic phosphorus occurs in several forms and may be more mobile than the inorganic form due to its movement in micro-organisms and fungal hyphae, which subsequently decay (23).

Whereas a plant's tolerance of other major elements may extend to concentrations of one or two orders of magnitude, its response to phosphorus may be over as many as five, e.g. 10^{-3} - 10^{-7} M (52) (Fig.7).

P supply may fall below the minimal requirement of plants grown in acidic soils for a variety of reasons which are discussed on p. 229.

Polyvalent ions

In addition to deficiencies of major elements the presence of polyvalent cations in toxic ionic form is a major cause of failure of most plant species in soils of pH less than 5.0.

Aluminium

Aluminium is not only a major constituent of most mineral soils but also a major soil toxin in the pH range 3.5 to 4.5, and we normally accept Schofield's edict (56) that however leached an acidic soil may be the predominant exchangeable cation is aluminium.

The degree of tolerance or susceptibility of species, at least in the Sheffield region where it has been studied extensively, is closely related to the pH of the soils in which they are distributed (22).

Tolerance was measured in the first instance by determining the aluminium concentration required to cause 50% inhibition of root extension in young seedlings (68). Fig.8 shows a range of responses with the calcifuge grass Deschampsia flexuosa as the most tolerant species at 0.48 mM Al and Bromus erectus, a calcicole, one of the least tolerant at 0.02 mM Al.

Despite such a correlation it has not always been possible to relate absolute amounts of exchangeable aluminium in the soil with plant tolerance, mainly, I suspect, because it is the balance of ions rather than the absolute amounts which is critical and because other elements may be contributing to the response, e.g. NH_4-N. The first symptom of aluminium toxicity is the stunting of the root systems, whose laterals become peg-like or, in extreme cases, fail to penetrate the cortex of the primary roots. Purpling of cotyledons and older leaves, implying phosphorus deficiency, is another early symptom (50).

The problem has been to relate these symptoms to physiological processes. Aluminium can directly affect cell division (12). It can affect the uptake and absorption of phosphorus (11, 51), and of several essential cations, including Ca (14, 43) and K (14). It can also disrupt the activities of proteinaceous enzymes located in the cell wall (71) even before it starts to affect sensitive internal sites at the mitochondria and the nucleus.

The major direct effect of aluminium so far suggested relates to cell division and there is evidence (12) that it causes total or partial failure of cell division, probably by interference with DNA synthesis in the S period of the mitotic cycle. It is also feasible that cell elongation is inhibited by the development of cross linkages between Al and pectin in cell walls in regions of the root where division has just taken place (49). A more recent suggestion (71) is that enzymes concerned with the synthesis of wall material may be inhibited by specific metal attack and that structural modifications in the enzymes could confer differential metal ion sensitivity.

Aluminium and phosphorus

The inhibition of phosphorus uptake and absorption by aluminium also has a drastic effect on the growth of susceptible species.

Some precipitation of aluminium phosphate may occur outside the root altogether, and more is possible in the intercellular spaces of the cortex. This may still leave enough P for the plant to survive (49).

Disturbances in P metabolism may be detected at two levels: the first at the surface of root cortical cells, where adsorbed Al appears to fix P; the second is within the cell, where the build-up of phosphorylated intermediates is altered

(12, 51) and respiratory metabolism depressed.+)

Decisive progress in interpretation of these pathways still awaits a suitable isotope, or other analytical method, for determining aluminium. Some possible mechanisms of tolerance are examined on p. 233.

Iron

In well aerated soils of pH less than 3.5, ferric iron is likely to be toxic to plants; above pH 3.5 its solubility is very low and toxicity is unlikely. Ferrous iron is soluble to around pH 6.0 under reducing conditions and can reach toxic levels in marshland and waterlogged soils. Most workers report difficulties in keeping iron in the ferrous state in solution culture, but several comparative studies have been attempted. When a range of plants was grown in nutrient solutions containing Fe^{2+}, calcifuges including Deschampsia flexuosa showed a high requirement and calcicoles including Scabiosa columbaria a low requirement for iron measured in terms of root extension (27). This was probably a reflection of their relative resistance to iron toxicity since calcifuges, marsh plants (27), and plants tolerant of waterlogged soils (41) so far tested are tolerant of concentrations of up to, 1 mM Fe^{2+}.

At circum-neutral soil pHs, iron is barely available to plants (indeed in solution culture pH > 6,0 it is best supplied as an EDTA salt) and calcifuges exhibit chlorosis symptoms, which are assumed to be caused by iron deficiency.

Laboratory experiments in which iron was supplied in chelated form have shown no adverse effect on calcifuge seedling growth of either pH or a wide range of calcium concentration (50). However, chlorosis symptoms are produced by lowering or removing inorganic iron supplies in culture solutions. The degree to which recovery occurs on the re-introduction of iron varies with the species.

Some calcifuges take longer to recover than calcicoles. It may be (a) because calcifuges have a higher Fe requirement or (b) that calcifuges' ability to take up and utilize Fe is poorer. Certainly in root extension tests (22) Scabiosa columbaria had the lowest Fe^{2+} requirement for maximum elongation.

Gas/soil solution contents

Apart from unbalanced nutrient supply, chlorosis is also associated with relative

---

+) Norton and Harris, private communication

O_2 and CO /HCO_3^{2-} concentrations in the soil atmosphere and soil solution, HCO_3^{2-} concentration increasing with increasing pH.

It has been shown (69) that root growth of Deschampsia flexuosa is adversely affected by high HCO_3^{2-} concentrations in solution and that, at least in short term, 4-hour periods, HCO_3^{2-} (at the sort of concentrations likely in calcareous soils) brings about a partial inhibition of isotopic ^{59}Fe uptake into both root and shoot. Neither of these effects occurs in the calcicole grass species Koeleria cristata and Arrhenatherum elatius.

Whether calcifuge and marsh species have a high iron requirement or are merely inefficient in taking it up, it is relatively more available under acidic and under anaerobic conditions than at high pH.

Manganese

Manganese is soluble in one form or another over a wide pH range (28) and in acidic culture solutions it can be more toxic than equivalent strengths of aluminium (54). However, unlike aluminium, its toxicity in acidic soil conditions can be ameliorated by the presence of several other elements which occur at relatively high levels in acid sulphate soils, including silica (46, 64), Al, Fe, and NH_4 (28). Manganese toxicity is also reduced in soils with adequate calcium (60). Therefore, only in localized areas of high concentrations are there authenticated cases of toxicity in acidic soils which are directly or solely due to manganese.

Sulphate

Although it is a major component of acid sulphate soils, an excess of sulphate ions is not normally thought to have any influence on plant growth and nutrition (26). It is the anion most used in culture solutions in which cation levels are to be varied, and Bollard (26) reports no effect on the response of a range of species in solutions in which the sulphate concentration ranged from 6 to 224 ppm.

It may be taken up quite rapidly into plant roots, but much of it remains in the inorganic form and its absorption into sulphur-organic compounds is very slow (7).

If it occurs at even higher concentrations and prevents the uptake of either nitrate or phosphate ions, it may well cause a reduction in plant growth, but I have found no experimental evidence of this. When it reaches molar concentrations, its effect could be osmotic but is more likely to be due to the formation of dilute H_2SO_4.

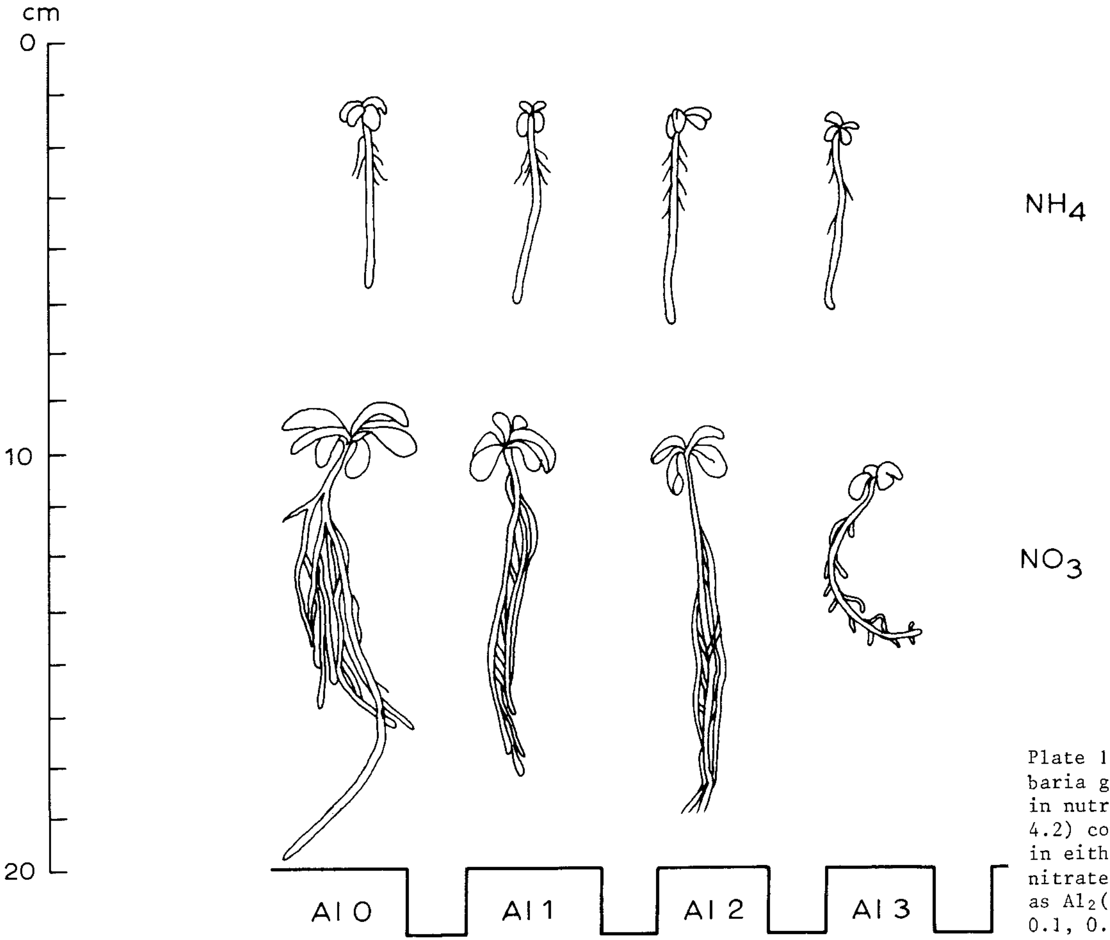


Plate 1. Scabiosa columbaria grown for two weeks in nutrient solutions (pH 4.2) containing nitrogen in either the ammonium or nitrate form and aluminium as $Al_2(SO_4)_3$ 18 H_2O at 0, 0.1, 0.5 and 1.0 mM

MECHANISMS OF TOLERANCE

From the foregoing experimental evidence it can be seen that an excess of several elements individually can be lethal to some species and yet tolerated by others. The effect of these elements can be controlled external to the plant by altering the soil pH or, in the case of manganese, by altering the balance of cations in the soil solution. The major problem is to identify and isolate the individual factors operating in the field, where the complexity of the situation makes measurements very difficult.

Almost as difficult is the execution of laboratory experiments designed to simulate field conditions. The number of variables, including the range of response among species, make it necessary to operate a series of experiments in controlled environmental conditions (53).

Aluminium is usually considered to be the major toxin, but with some calcicole species, e.g. Scabiosa columbaria, it adds nothing to the toxic effect of NH_4-N at pH 4.2 (Plate 1).

It is however, the toxic component of acid sulphate soils which has received the most attention, and it is this component for whose mechanism of operation in plants there is most experimental evidence.

Some of this evidence will now be discussed, together with evidence from heavy metal studies (2, 47).

Aluminium, location and action

Gross analysis of root and shoot of susceptible species shows a build up of Al in the root, and only above a certain Al concentration in the root is there a significant increase in Al concentration in the shoot (Rorison, unpublished).

Early histochemical work (40) suggested that Al is concentrated in the cortical cells of the root and heavily localised in the protoplasm and nucleus. The uncertainty about these results is (a) whether any movement of Al occurred within the tissues between cutting and staining, (b) whether polyvalent ions other than Al were stained by the haematoxylin reaction employed.

The vital questions remain: where exactly is the Al located? Is it superficially adsorbed onto cell walls and/or incorporated into the protoplasm and/or dumped in the vacuole? Also, how does it affect the growth of the plant and what are the differences in reaction between susceptible (calcicole) and tolerant (calcifuge) plants?

Electron probe analysis

The use of electron probe x-ray microanalysis for the detection of elements in plant tissues promised rich rewards (36). As with other elaborate methods there have been initial technical problems, mainly concerning the preparation of sections.

Two attempts have been made to use the technique to identify the positions of accumulation of aluminium in plant roots (48, 66), and neither has added much to our basic knowledge of the problem. Rasmussen (48) allowed his tissues to thaw and air dry before the analysis, and contamination was therefore possible before the tissue was scanned. He confirmed the restriction of Al to the root cortex, but gave no evidence of exact location. Waisel et al. (66), using plants grown in solutions of pH 9.5, produced results expected of aluminium in the anionic form, i.e. like nitrate it was concentrated in the protoplasm. Had susceptible species been raised under acidic conditions, the aluminium would probably have been found, like its fellow cation in the above experiment, calcium, adsorbed onto the cell walls. The critical experiments remain to be done.

Isotopic substitutes

The lack of a suitable isotopic form of aluminium has been a major restriction in the determination of its precise location and activity.

However, recent work with scandium ^{46}Sc has shown it to be similar in its action to aluminium (13). Autoradiographs of freeze-dried sections of onion (*Allium cepa*) roots showed that ^{46}Sc and, by implication, aluminium, penetrate the meristematic cells rapidly and in advance of any observable effects on the activity of the meristem. The rapid movement of scandium among dividing cells with primary walls, contrasts markedly with its slow migration across the differentiated cortex. Differentiation and secondary wall formation in the cortical cells appeared to increase the scandium binding capacity of the walls, thus restricting the progress of the ion through the free space. After development of the endodermis there is no sign of entry into the vascular tissues - thus supporting the view of movement only through the cortical free space and very slow transport to the shoots.

So we now have the picture of aluminium (a) entering meristematic cells of the root tip and preventing cell division; (b) moving through the intercellular spaces of the cortex and being adsorbed onto cell wall surfaces. From this position it can affect the absorption of calcium (14) and phosphorus (10, 51, 71).

There are, however, two points to bear in mind:

1. The inhibitory effect of a number of polyvalent ions on cell division in many species (10, 38) suggests an absence of cation specificity at this point, i.e. iron, aluminium, and possibly manganese could be involved at the nucleus.

2. Contrarily, most workers (2, 47, 62) report strict specificity in tolerance to polyvalent ions, e.g. in races of *Agrostis tenuis*.

Specificity

This implies that in a particular race or species the potentially toxic effect of one polyvalent ion is not realized.

Metal ions could be prevented from reaching the nucleus by several means (Fig.9). They could be prevented from entering the cell by adsorption or chelation on the cell wall or in the intercellular spaces.

This implies a specific binding mechanism involving either a specific chemical complex or a specific geometrical spacing of fixed charged sites ensuring goodness of fit.

Adsorption

Evidence supporting adsorption on the walls of expanding and mature cortical cells is strong. Negatively charged carboxyl chains of pectin molecules provide the sites (32) and they could be adequate to cope with the inflow of polyvalent ions if the root was growing quickly enough and the concentration of polyvalent ions in the external solution was below a critical level (27, 55). It is important to remember that we are dealing with a dynamic system in which the rate of growth and development of tissues in a species could strongly affect its degree of tolerance.

The relationship between tolerance and the cation exchange capacity (CEC) of roots has been invoked (65) but the arbitrariness of the method of its determination, the overwhelming differences in CEC between the roots of dicotyledonous and monocotyledonous plants, and the absence of any proven relationship between CEC and salt absorption make it difficult to confirm.

It may be that it is the spatial pattern of the carboxyl exchange sites rather than their quantity that is critical (33) and that other complexing agents play an even more vital role. The primary walls of meristematic cells may be too open and have insufficient exchange capacity to adsorb all the potentially toxic polyvalent ions (13) and therefore in tolerant species one must think of other mechanisms for rendering them harmless. Evidence is beginning to accumulate that binding complexes in the cell wall can contain both sugar and amino-acid components (31).

Complexing

When aluminium is complexed with EDTA it is taken up from acidic solutions by susceptible species without toxicity symptoms developing (19, 49). We know that the affinity of individual polyvalent cations for the sites on any given ligand grouping depends on their concentration, charge, and crystal radius. Al^{3+} = 0.51 A, Fe^{3+} = 0.64 and Fe^{2+} = 0.76 (1) are of sufficiently different size to allow a spatial "net" to operate. For example, although Al may have a large water shell, it could form tight co-ordination compounds with either the carboxyl side-chains or with hydroxyls of the cell wall and the resulting complexes may still be sufficiently positively charged to attract a large number of anions including phosphate (14). When ions are of approximately the same size, e.g. Fe^{2+} = 0.76, Zn^{2+} = 0.74 and Cu^{2+} = 0.72, selection would depend on the avidity of the ions for the complexing agent and on its configuration. For example, Fe^{2+}, Fe^{3+} and Al^{3+} form regular octahedral complexes and Zn^{2+} mainly tetrahedrals, while Cu^{3+} forms only irregular planar complexes.

There are many substances both in the protoplasm and in the intercellular fluids which could complex aluminium and indeed any polyvalent metal.

Carboxylic acids such as malic, citric and oxalic are obvious candidates and the suggestion of Small (58) that calcifuges have organic acid buffer systems and calcicoles phosphate buffer systems had some attraction. However, the carboxylic acid content of plants varies in many ways and seems more related to the maintenance of ionic balance (15, 37) than to the complexing of polyvalent ions.

Amino acids and proteins are other possible complexing agents and differences in their configuration could lead to specific complexing. Albert (1) reports that if the chelating groups are not close enough, or there is not the right steric configuration to allow the formation of strong complexes, small metallic cations cannot be gripped. This applies particularly to aluminium which has the smallest crystal radius of any common metal.

Another feature of ligand-metal interaction is that the bound metal may considerably change the reactivity of the organic ligand by inter alia increasing the liposolubility of the ligand and hence helping it to penetrate into a living cell. In this way aluminium in a non-reactive form might pass through the protoplasm and even be dumped in the vacuoles of cortical cells.

The complexing mechanism may be highly efficient in dealing with a specific heavy metal which is potentially toxic but also essential to the plant in trace amounts. It need not cause a deficiency because there will be some local competition in the root between systems requiring the element and the complexing agents. Some complexed metal may also move through the plant and be dissociated by enzymatic activity at sites where it is required (e.g. in the leaf). Synthesis of necessary proteinaceous complexes can be rapid. The raw materials are available in the cell wall and in the plasmalemma. Synthesis may be triggered off by an increased external concentration of the element to be "filtered". The problem of identifying specific complexes and their mode of synthesis remains.

Aluminium and phosphorus uptake

Aluminium complexed either at sites on the cell wall or by extracellular compounds is prevented from interfering with phosphorus uptake in two ways.

It is unlikely to inhibit the activity of phosphatic enzymes in the cell wall (71) and it will not reach the mitochondria and interfere with phosphorylation. Interference with phosphorus uptake and absorption has been shown by several workers (11, 51). In each case not only was the percentage of phosphorus esterification reduced but also the pattern of incorporation was altered (Table 2) implying effects both inside and outside the cell.

Aluminium and calcium

There are many reports of decreased concentrations of calcium in the shoots of plants that are suffering from aluminium toxicity. Recently a precise investigation of uptake and transport of calcium in barley seedlings was made by Clarkson and Sanderson (14) in an effort to reveal the nature of the inhibition. They used ^{85}Sr as a carrier free tracer added to solutions of $CaCl_2$ to infer quantitative estimates of calcium absorption. ^{46}Sc was used to infer the distribution of aluminium in the root.

They found that aluminium, scandium and iron inhibited the uptake of calcium from culture solutions of pH 4.0-4.2. The non-exchangeable fraction of labelled calcium was unaffected by treatment, but each polyvalent ion reduced the amount of calcium held in the water free space and the Donnan free space of the roots. ^{46}Sc and, by inference, aluminium were concentrated on the epidermis and the outer rank of cortical cells and it was suggested that the peripheral location of polyvalent cations allowed them to control the entry of calcium into the free space - presumably by repulsion of like charges. If sufficient calcium chloride was added to the external medium this inhibition of calcium movement was overcome even though the toxic effect of the aluminium treatment on root growth was not. Also this polyvalent ion effect was not restricted to calcium but was applicable to cations of lower valency, such as potassium.

It is of interest that the non-exchangeable fraction of calcium was unchanged by any treatment, since Woolhouse (70) reports leakage of potassium from the root tips of susceptible species following exposure to high concentrations of aluminium. This implies disruption of the semi-permeability of the plasmalemma which could be expected to lead to freer movement of aluminium or other polyvalent ions into the protoplasm and of cations of lower valency outwards. However, it is not yet known if or how aluminium modifies the permeability of membranes to other ions and further research is needed.

Mechanisms of tolerance to iron

Little is known either of the mechanisms of toxicity or tolerance of iron in plants. According to Kliman (34) all iron enters the plants as Fe^{2+}. This implies that in well aerated soils plants, or more likely their associated rhizosphere organisms, must have enzyme systems at the periphery of the root which are capable of reducing Fe^{3+}.

Fe^{2+} and Fe^{3+} are probably inactivated in the plant, like aluminium, by adsorption and complexing (18) and even by precipitation with phosphorus (35) but no mechanisms have yet been identified.

The situation is complicated because iron, unlike aluminium, is an essential element. The root extension of calcifuge and marsh plants is certainly stimulated by higher concentrations of iron than those of calcicoles (27) but is has yet to be confirmed that this can be equated with a higher requirement for iron in growing plants.

In plants of waterlogged soils tolerance to Fe^{2+} has been related to two physiological factors: the evolution of oxygen from the roots of Menyanthes trifoliata causing a precipitate of ferric oxide at the epidermis (4) and the lowering of transpiration rate, which in Erica cinerea reduces the build-up of iron in root tissues (30).

CONCLUSION

The nutrition and physiology of plants growing in very acidic soils are affected in two main ways. The soils are essentially leached of nutrients and the uptake of the remainder and their incorporation into physiological systems of the plant is inhibited, to a greater or lesser extent, by polyvalent cations. Polyvalent cations also operate directly at specific sites of metabolic acitivity.

At pHs of less than 3.5, Fe^{3+} and H^+ are likely to be highly inhibitory, then up to pH 5.0 aluminium and ammonium ions may be the major inhibitors. Above pH 5.0,Fe^{2+} can be toxic and, locally over a wide pH range, high concentrations of other heavy metals may also be toxic.

Plants differ in their response, from the very tolerant to the highly susceptible, and the mechanism(s) of their tolerance of polyvalent metals have still to be identified experimentally. More is known of the minimal requirements for nutrients, which, in plants adapted to extremely acidic soils, are often low. Failure of growth is first manifest in the stunting of roots and this may be brought about in a number of ways. Inhibition of cell division can be achieved by any of a number of polyvalent metals, but before the nucleus can be reached, several sensitive sites of metabolism, at the cell wall, at the plasmalemma, and in the organelles of the protoplasm could be reached and affected.

All physiological and some genetical evidence (2) points to strict specificity in metal tolerance among races and species of plants and the "filtering" mechanism to ensure specificity is sought in the configuration and chemical nature of sites which can adsorb or in some way complex individual metal ions. These sites in and around the cell wall are largely in the younger tissues of the root since exclusion appears to follow secondary anatomical developments in older regions.

Recent evidence suggests that the carbohydrates concerned with adsorption are of less importance than amino acids and proteinaceous materials in the development of tolerance mechanisms. It is possible to suggest complexes (1) which could account for specific metal tolerance in plants. The main problem is to devise ways of extracting and identifying such metal complexes without denaturing them, so strongly are they bound in the plant (71).
It is important to remember that, although mechanisms may be specific, the evolution of new systems can be rapid (2). Ideally, a tolerant species may be considered as a dynamic system in which the rate of production of complexes keeps pace with the input of potential toxins.

Evidence of mechanisms is still fragmentary and advances in several areas will be made only if experimental techniques are improved. The response of plants varies not only between species but also among individuals of different age and development. It is the experience of most investigators that the younger the seedling the more sensitive it is to adverse conditions.

Further understanding of tolerance mechanisms may well come from new knowledge of ion transport, enzyme location and activity, and of cell wall and membrane composition and function.

It seems most unlikely that higher plants will grow in unaltered soil materials of pH < 3.0 but micro-organisms may. Very little is known of their activities except in the case of chemosynthetic bacteria (2). The absence of nitrifying bacteria has been mentioned and although Ericaceous plants are known to have active mycorrhizal associations at pHs down to 3.0+) there is little information about other groups of species.

All these considerations may appear academic since amelioration of the conditions by controlled draining, liming and fertilizing are possible and economic in the case of many cat clays. But for the recolonisation of uneconomic areas such as waste heaps of high pyritic content, the selection of tolerant species or the introduction of organisms which would form a chain reaction of reclamation is of prime importance. Further research into mechanisms of tolerance in a wide range of organisms thus presents a very worthwile challenge.

ACKNOWLEDGMENTS

I thank Drs. D.T. Clarkson, J.G. Hodgson, G.Norton and D.J. Read for valuable discussion on various aspects of this work, and the Natural Environment Research Council for financial support.

+) D.J. Read, personal communication

Rumex acetosa

pH	4.2	5.8	7.2
NH_4	239	390	655
NO_3	922	887	996

Deschampsia flexuosa

pH	4.2	5.8	7.2
NH_4	94	78	117
NO_3	80	73	13

Scabiosa columbaria Zurich

pH	4.2	5.8	7.2
NH_4	-	63	160
NO_3	226	598	484

Scabiosa columbaria Lathkilldale

pH	4.2	5.8	7.2
NH_4	-	-	123
NO_3	145	153	198

Plant *Dry wt.* in *mg* at six weeks

Table 1. The dry weights in mg of plants grown for six weeks in nutrient solutions containing nitrogen in either the ammonium or nitrate form (21)

Pretreatment	Al_0	Al_{20}
Fraction %		
Nucleotide	35.7 ± 0.9	12.3 ± 2.2
Hexose phosphate	13.8 ± 0.5	7.5 ± 3.1
Inorganic phosphate	50.5 ± 1.3	80.2 ± 1.4
Esterification	49.5 ± 1.3	19.8 ± 1.4
Extraction	87.0 ± 3.6	91.3 ± 2.3

Table 2. Percentage of total readily soluble ^{32}P incorporated after 10 minutes by excised roots of sainfoin into different fractions, with and without pretreatment in aluminium sulphate solution ± S.D. (51)

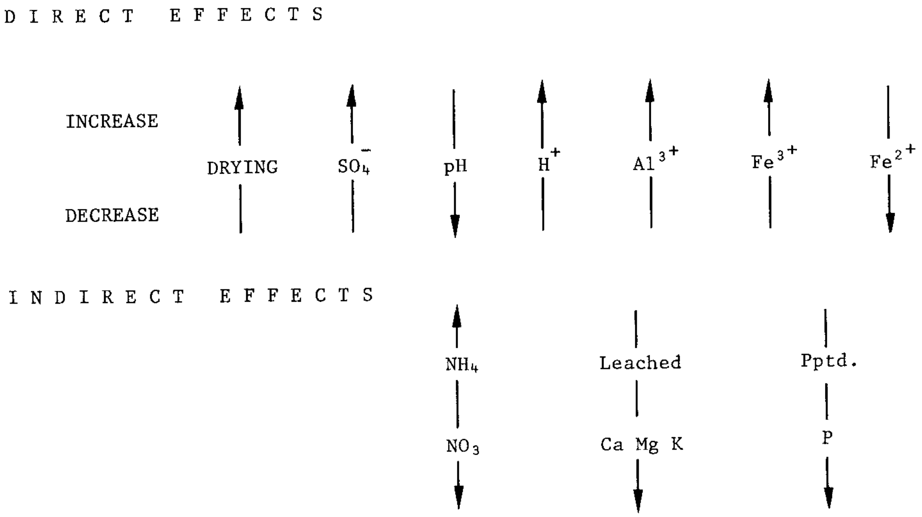


Fig.1. Some effects on the chemical composition of acid sulphate soils which dry out

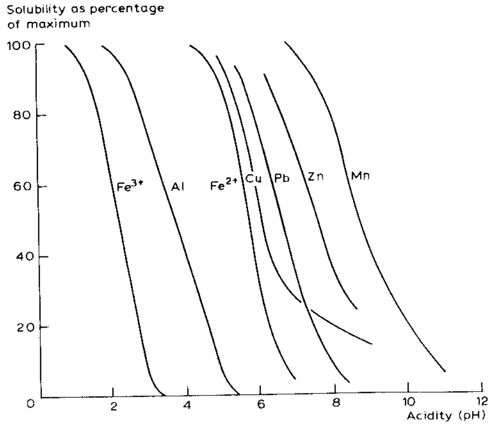


Fig.2. Solubilities of some metallic cations at various pH levels. *See also ref. (59)*

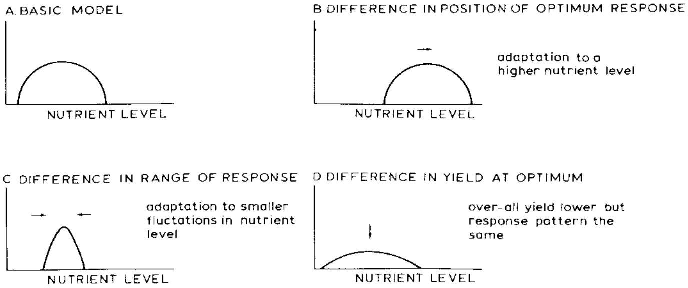


Fig.3. The evolutionary significance of different types of response curves. *See also ref. (3)*

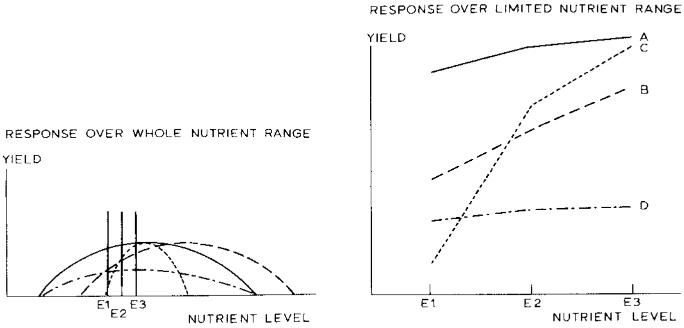


Fig.4. Response curves over different ranges of nutrient levels. *For explanation, see ref. (3)*

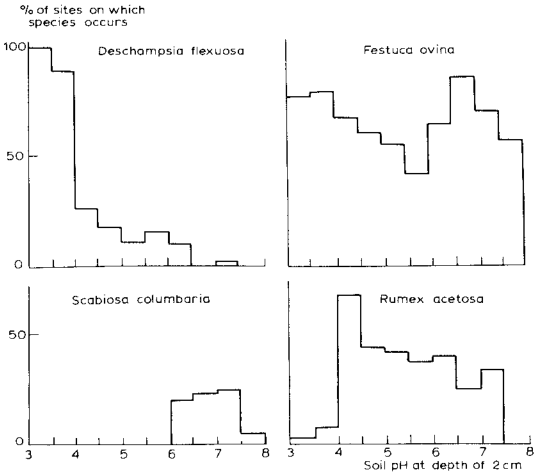


Fig.5. Histograms showing the frequency of occurrence of 4 species over a range of soil surface pH's. Data provided from 340 random m^2 quadrats in established grassland from 41 sites in the Sheffield area. *See (53)*

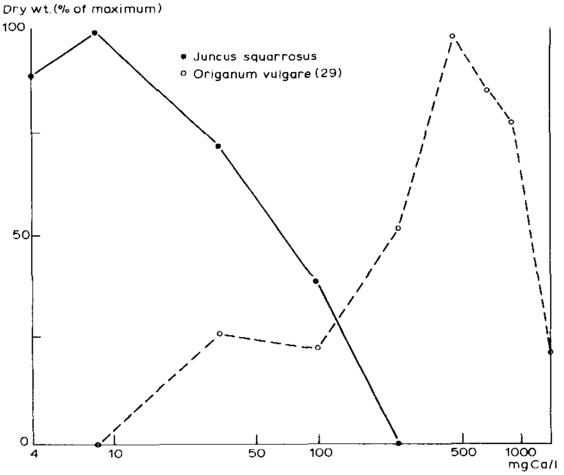


Fig.6. The growth of roots in cultures of calcium supplied as nitrate. *See (29)*

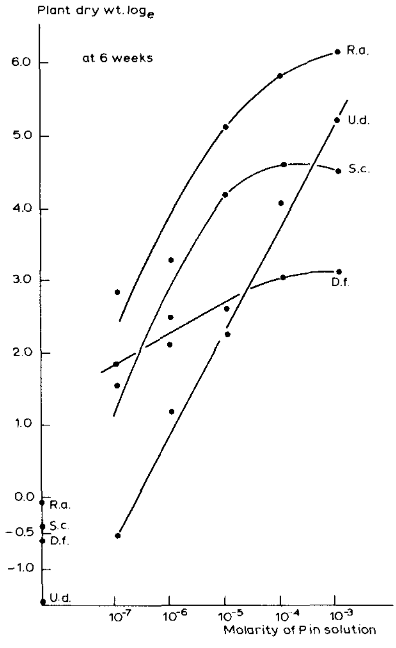


Fig.7. Dry weight achieved in 6 weeks by Rumex acetosa (R.a.), Urtica dioica (U.d.), Scabiosa columbaria (S.c.) and Deschampsia flexuosa (D.f.). Data transformed to natural logarithms and plotted against external phosphorus concentration. Seed weights are indicated on the Y axis. *See ref.(51)*

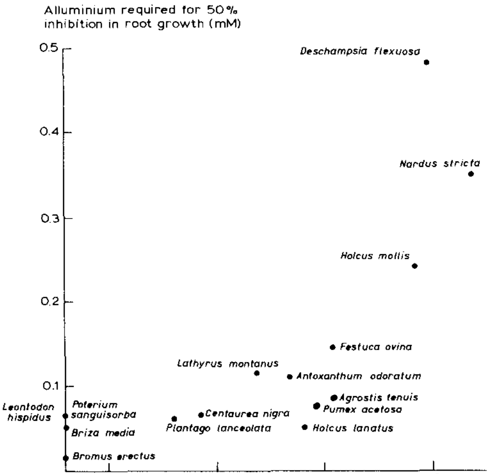


Fig.8. The relationship between relative frequency of occurrence below pH 4.5 and resistance of the seedling root to aluminium toxicity. *See ref.(22)*

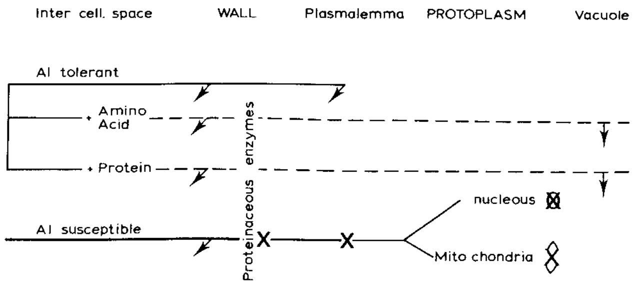


Fig.9. Possible sites of reaction in and around the cortical cells of roots of tolerant and non-tolerant plants

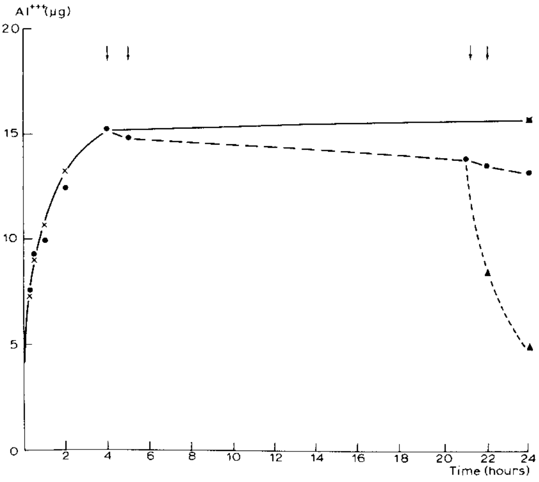


Fig.10. Uptake of aluminium in μg, by sainfoin root tips shaken in 3.7 × 10^{-5} M $Al_2(SO_4)_3$ 18 H_2O at 25 °C *(solid line)*. Aluminium leached during aqueous washing *(broken line)*.

● *Uptake determined, by difference, from solution analysis*

× *Uptake determined by analysis of roots*

▲ *Washing in buffer solution (dotted line)*

↓ *Solution changes. See also ref. (51)*

REFERENCES

(1) ALBERT, A. 1968. "Selective Toxicity", 4th ed. Methuen, London.

(2) ANTONOVICS, J., BRADSHAW, A.D. and TURNER, R.G. 1971 Heavy metal tolerance in plants. Adv. in Ecol. Res.7: 1-85.

(3) ANTONOVICS, J., LOVETT, J. and BRADSHAW, A.D. 1967. The evolution of adaptation to nutritional factors in populations of herbage plants. Isotopes in plant nutrition and physiology. International Atomic Agency, Vienna.

(4) ARMSTRONG, W. and BOATMAN, D.J. 1967. Some field observations relating the growth of bog plants to conditions of soil aeration. J. Ecol. 55: 101-110.

(5) ARNON, D.I. and JOHNSON, C.M. 1942. Influence of hydrogen ion concentration on the growth of higher plants under controlled conditions. Plant Physiol. 17: 525-539.

(6) BOGNER, W. 1968. Experimentelle Prüfung von Waldbodenpflanzen auf ihre Ansprüche an die Form der Stickstoff-Ernährung. Mitt.Ver.forstl.Standortskunde u. Forstpflanzenzüchtung. 18: 3-45.

(7) BRIGGS, G.E., HOPE, A.B. and ROBERTSON, R.N. 1961. "Electrolytes and Plant cells". *Blackwell, Oxford.*

(8) BRITTON, H.T.S. 1955. "Hydron Ions". Vol.2. Chapman and Hall, London.

(9) BURSTROM, H.G. 1968. Calcium and plant growth. Biol. Rev. 43: 287-316.

(10) CLARKSON, D.T. 1965. The effect of aluminium and some other trivalent metal cations on cell division in the root apices of *Allium cepa*. Anns.Bot. 29: 309-315.

(11) CLARKSON, D.T. 1966. Aluminium tolerance in species within the genus *Agrostis*. J. Ecol. 54:167-178.

(12) CLARKSON, D.T. 1969. Metabolic aspects of aluminium toxicity and some possible mechanisms for resistance. (*In* "Ecological Aspects of the Mineral Nutrition of Plants". Ed. I.H. Rorison, pp.381-397. Blackwell, Oxford).

(13) CLARKSON, D.T. and SANDERSON, J. 1969. The uptake of a polyvalent cation and its distribution in the root apices of *Allium cepa*: tracer and autoradiographic studies. Planta (Berl.) 89: 136-154.

(14) CLARKSON, D.T. and SANDERSON, J. 1971. Inhibition of the uptake and long-distance transport of calcium by aluminium and other polyvalent cations. J. exp.Bot. 2: 837-751.

(15) DIJKSHOORN, W. 1969. The relation of growth to the chief ionic constituents of the plant. (In "Ecological Aspects of the Mineral Nutrition of Plants". Ed. I.H.Rorison, pp.201-213. Blackwell, Oxford.)

(16) ELLENBERG, H. 1958. Mineralstoffe für die pflanzliche Besiedlung des Bodens. A. Bodenreaktion (einschliesslich Kalkfrage). Hdb.PflPhysiol.IV: 638-709.

(17) EVERS, F.H. 1964. Die Bedeutung der Stickstoff-Form für Wachstum und Ernährung der Pflanzen, insbesondere der Waldbäume. Mitt.Ver.forstl. Standortskunde u.Forstpflanzenzüchtung 14: 19-37.

(18) FOSTER, W.N.M. and SCOTT RUSSELL, R. 1958. Factors affecting the ability of plants to absorb phosphate from soils. III. Plant-physiological effects of iron. J.Soil Sci. 9: 280-288.

(19) FOY, C.D. and BROWN, J.C. 1964. Toxic factors in acid soils. II. Differential aluminium tolerance of plant species. Soil Sci. Soc. Am. Proc.28:27-32.

(20) FOY, C.D., BURNS, G.R., BROWN, J.C., and FLEMING, A.L. 1965. Differential aluminium tolerance of two wheat varieties associated with plant-induced pH changes around their roots. Soil Sci. Soc. Amer. Proc. 29: 64-67.

(21) GIGON, A. and RORISON, I.H. 1972. The response of some ecologically distinct plant species to nitrate- and to ammonium-nitrogen. J.Ecol.60:93-102.

(22) GRIME, J.P. and HODGSON, J.G. 1969. An investigation of the ecological significance of lime-chlorosis by means of large-scale comparative experiments. (In "Ecological Aspects of the Mineral Nutrition of Plants". Ed. I.H.Rorison, pp.67-99. Blackwell, Oxford).

(23) HARLEY, J.L. 1971. Fungi in ecosystems. J.Ecol. 59: 653-668.

(24) HARTWELL, B.L. and PEMBER, F.R. 1918. The presence of aluminium as a reason for the difference in the effect of so-called acid soil on Barley and Rye. Soil Sci. 6: 259-279.

(25) HEWITT, E.J. 1952. A biological approach to the problems of soil acidity. Trans. Int. Soc. Soil Sci. Jt. Meet. Dublin 1:107-118.

(26) HEWITT, E.J. 1966. Sand and water culture methods used in the study of plant nutrition. 2nd ed. Commonwealth Agric. Bureaux. Tech.Comm. No.22.

(27) HODGSON, J.G. 1972. A comparative study of seedling root growth with respect to aluminium and iron supply. Ph.D. thesis, University of Sheffield.

(28) JACKSON, W.A. 1967. Physiological effects of soil acidity. (In "Soil acidity and Liming", ed. R.W.Pearson and F. Adams, pp.43-124. Agronomy 12, Am. Soc. Agronomy, Madison, U.S.A.)

(29) JEFFERIES, R.L. and WILLIS, A.J. 1964. Studies on the calcicole-calcifuge habit. II. The influence of calcium on the growth and establishment of four species in soil and sand cultures. J.Ecol. 52: 691-707.

(30) JONES, H.E. 1971. Comparative studies of plant growth and distribution in relation to waterlogging. II. An experimental study of the relationships between transpiration and the uptake of iron by Erica cinerea L. and E. tetralix L. J. Ecol. 59: 167-178.

(31) JONES, R.G.W., SUTCLIFFE, M. and MARSHALL, C. 1971. Physiological and biochemical basis for heavy metal tolerance in clones of Agrostis tenuis. (In "Recent Advances in Plant Nutrition", ed.R.M.Samish, Gordon & Breach Sci. Pub.Inc.New York, Vol.2, pp.575-581).

(32) KELLER, P. and DEUEL, H. 1957. Kationenaustauschkapazität und Pektingehalt von Pflanzenwurzeln. Verlag Chemie. 79: 119-131.

(33) KELLER, P. and DEUEL, H. 1958. Kationenaustauschgleichgewichte an abgetöteten Pflanzenwurzeln. Ver.II and IV Komm.Inter.Boden. Gesell.Hamburg 1958. II: 164-168.

(34) KLIMAN, S. 1937. The importance of ferrous iron in plants and soils. Soil Sci. Soc. Amer. Proc. 2: 385-392.

(35) KURAEV, V.N. 1966. (Effect of various concentrations of Fe^{2+} in solution culture on the growth and development of crop plants.) In Russian. Agrokhimiya 12: 110-117.

(36) LAUCHLI, A. 1968. Investigations on the distribution and transport of ions in plant tissues with the Electron Probe X-ray Microanalyser. Planta (Berl.) 83: 137-149.

(37) LEE, J.A. and WOOLHOUSE, H.W. 1971. The relationship of compartmentation of organic acid metabolism to bicarbonate-ion sensitivity of root growth in calcicoles and calcifuges. New Phytol. 70: 103-111.

(38) LEVAN, A. 1945. Cytological reactions induced by inorganic salt solutions. Nature 156: 751-752.

(39) LIGON, W.S. and PIERRE, W.H. 1932. Soluble Al studies: II.Minimum concentrations of Al found to be toxic to corn, sorghum and barley in culture solutions. Soil Sci. 34: 307-332.

(40) McLEAN, F.T. and GILBERT, B.E. 1927. The relative Al tolerance of crop plants. Soil Sci. 24: 163-175.

(41) MARTIN, M.H. 1968. Conditions affecting the distribution of *Mercurialis perennis L.* in certain Cambridgeshire woodlands. J. Ecol. 56: 777-793.

(42) MEVIUS, W. 1927. "Reaktion des Bodens und Pflanzenwachstum". Freising u. München, Datterer 1927.

(43) MUNNS, D.N. 1965. Soil acidity and growth of a legume. II. Reactions of aluminium and phosphate in solution and effects of aluminium, phosphate, calcium and pH on *Medicago sativa L.* and *Trifolium subterraneum L.* in solution culture. Aust. J. Agric. Res. 16: 743-755.

(44) OLSEN, C. 1958. Iron uptake in different plant species as a function of the pH value of the nutrient solution. Physiol. Pl. II: 889-905.

(45) PAUL, H. 1906. Zur Kalkfeindlichkeitsfrage der Torfmoose. Ber. der Dtsch. Bot. Ges. 24: 148-154.

(46) PEASLEE, D.E. and FRINK, C.R. 1969. Influence of silicic acid on uptake of Mn, Al, Zn and Cu by tomatoes (*Lycopersicum esculentum*) grown on an acid soil. Proc. Soil Sci. Soc. Amer. 33: 569-571.

(47) PETERSON, P.J. 1971. Unusual accumulations of elements by plants and animals. Sci. Prog. Oxf. 59: 505-526.

(48) RASMUSSEN, H.P. 1968. Entry and distribution of aluminium in *Zea mays*. The mode of entry and distribution of aluminium in *Zea mays*: Electron Microprobe X-ray analysis. Planta (Berl.) 81: 28-37.

(49) RORISON, I.H. 1958. The effect of aluminium on legume nutrition. (*In* "Nutrition of the legumes". Ed. E.G.Hallsworth. pp.43-61. Butterworth, London.)

(50) RORISON, I.H. 1960. The calciole-calcifuge problem. II. The effects of mineral nutrition on seedling growth in solution culture. J.Ecol.48:679-688.

(51) RORISON, I.H. 1965. The effect of aluminium on the uptake and incorporation of phosphate by excised Sainfoin roots. New Phytol. 64: 23-27.

(52) RORISON, I.H. 1968. The response to phosphorus of some ecologically distinct plant species. I. Growth rates and phosphorus absorption. New Phytol. 67: 913-923.

(53) RORISON, I.H. 1969. Ecological inferences from laboratory experiments on mineral nutrition. (In "Ecological Aspects of the Mineral Nutrition of Plants". Ed. I.H. Rorison, pp.155-175. Blackwell, London.)

(54) RORISON, I.H. 1971. The use of nutrients in the control of the floristic composition of grassland. (In "The Scientific Management of Animal and Plant Communities for Conservation". Ed. E. Duffey and A.S.Watt. pp.65-77. Blackwell, Oxford..)

(55) RORISON, I.H., SUTTON, C.D. and HALLSWORTH, E.G. 1958. The effects of climatic conditions on aluminium and manganese toxicities. (In "Nutrition of the Legumes". Ed. E.G.Hallsworth, pp.62-68. Butterworth, London.)

(56) RUSSELL, E.W. 1961. "Soil conditions and plant growth", 9th ed. Longmans, London.

(57) SALISBURY, E.J. 1920. The significance of the calcicolous habit. J.Ecol. VIII: 202-215.

(58) SMALL, J. 1954. "Modern aspects of pH with special reference to plants and soils." Tindall and Cox, London.

(59) SPARLING, J.H. 1967. The occurrence of Schoenus nigricans L. in blanket bogs. II. Experiments on the growth of S. nigricans under controlled conditions. J. Ecol. 55: 15-31.

(60) SUTTON, C.D. and HALLSWORTH, E.G. 1958. Studies on the nutrition of Forage Legumes. I. The toxicity of low pH and high manganese supply to Lucerne, as affected by climatic factors and calcium supply. Pl. Soil 9: 305-317.

(61) TANSLEY, A.G. and ADAMSON, R.S. 1925. Studies in the vegetation of the English Chalk. III. The chalk grasslands of the Hampshire Sussex border. J. Ecol. 13: 177-223.

(62) TURNER, R.G. 1969. Heavy metal tolerance in plants. (In "Ecological Aspects of the Mineral Nutrition of Plants. Ed. I.H.Rorison, pp.399-410. Blackwell, Oxford).

(63) UNGER, F. 1836. Über den Einfluss des Bodens auf die Verteilung der Gewwächse, nachgewiesen in der Vegetation des nordöstlichen Tirols. Wien.

(64) VLAMIS, J. and WILLIAMS, D.E. 1967. Manganese and silicon interaction in the Gramineae. Pl. Soil 27: 131-140.

(65) VOSE, P.B. and RANDALL, P.J. 1962. Resistance to aluminium and manganese toxicities in plants related to variety and cation-exchange capacity.

Nature 196: 85-86.

(66) WAISEL,Y., HOFFEN,A. and ESHEL,A.1970. The localization of Al in the cortex cells of bean and barley roots by X-ray microanalysis. Physiol. Pl. 23:75-79.

(67) WALLACE, A., FROLICH, E. and LUNT, O.R. 1967. Calcium requirements of higher plants. Nature 209: 634.

(68) WILKINS, D.A. 1957. A technique for the measurement of lead tolerance in plants. Nature 180: 37-38.

(69) WOOLHOUSE, H.W. 1966. The effect of bicarbonate on the uptake of iron in four related grasses. New Phytol. 65: 372-375.

(70) WOOLHOUSE, H.W. 1969. Differences in the properties of the acid phosphatases of plant roots and their significance in the evolution of edaphic ecotypes.(In "Ecological Aspects of the Mineral Nutrition of Plants. Ed. I.H. Rorison, pp.357-380. Blackwell, Oxford).

(71) WOOLHOUSE, H.W. 1970. Environment and enzyme evolution in plants. (In "Phytochemical Phylogeny". Ed. J.B. Harborne. pp.207-231. AP, London and New York).

Summary

The main adverse physiological effect of acid soil conditions on plant growth is the inhibition by polyvalent cations of nutrient uptake and of cell division especially in younger roots. Best known are the inhibitory effects of Al^{3+}, Fe^{3+}, Fe^{2+} *and* Mn^{2+}*. Plants differ in their response to these toxins from very tolerant to highly susceptible. The response varies between species, varieties and also among stages of development of the same individual. Some Ericaceous plants are known to grow at soil pH's down to 3.0. The tolerance to polyvalent cations is a function of the plant's inherent physiological mechanisms and also of the interaction between its roots, possible micro-organisms and the totality of the soil components in the rhizosphere. These processes are thought to inactivate the potential toxins by selective adsorbtion and complexing in the rhizosphere and at non-vulnerable sites in and around the cell walls of younger root tissues, before the toxins can reach the cell nucleus and bring about inhibition of cell division and general toxicity symptoms. The maximum concentration of polyvalent cations in an acid soil that can be tolerated by a specific plant is higher as more of those cations are inactivated in the rhizosphere, e.g. by organic matter and microorganisms, and in the non-vital younger root tissues, e.g. by fast growth of the root system.*

Résumé

Dans les sols très acides les plantes sont gênées surtout par les cations polyvalents Al^{3+}, Fe^{3+}, Fe^{2+} *et* Mn^{2+} *que inhibitent l'absorption des substances nutritives ainsi que la division cellulaire dans les racines jeunes. La tolérance des plantes à l'acidité du sol varie énormement selon espèces, variétés et phases de dévéloppement individuel. Il y a des Ericacés tolérant des pH du sol jusqu'à 3.0. La tolérance est déterminée par le mécanisme physiologique inhérent des plantes et par l'interaction dans la rhizosphère entre racines, micro-organismes et les components du sol. Ces procédés inactivent sélectivement les cations polyvalents par moyen d'adsorption et de formation de complexes dans la rhizosphère et dans les parois cellulaires des tissus racinaires avant que ces cations pénètrent dans les cellules même en endommageant les noyaux et provocant les symptômes de toxicité. La concentration maximale des cations polyvalents dans un sol acide que peut tolérer une plante spécifique, sera plus haute à mésure que ces cations sont inactivés en plus grande quantité dans la rhizosphère (entre autres par matière organique, micro-organismes) et dans les parois cellulaires des tissus racinaires (entre autres par croissance rapide des racines).*

Resumen

En los suelos muy ácidos son sobre todo los cationes polivalientes de Al, Fe y Mn que perjudican al crecimiento de las plantas en provocando trastornos tróficos en los raíces jóvenes y en molestando la absorpción de substancias alimentícios. La tolerancia de las plantas frente al acidez de suelo varía largamente según especie, variedad y fase de desarrollo individual. Hay plantas de la familia de las Ericáceas que aguantan suelos con pH bajo hasta 3.0. La tolerancia es inherente a los mecanismos fisiológicos en la planta y a la interferencia en el esfera raigal entre raíces, micro-organismos y componentes del suelo. Estos procesos immoviliscan los cationes tóxicos a través del adsorbarlos y del ligarlos en complejos orgánicos sobre todo en los paredes celulares de los tejidos raigales, de tal modo que los cationes tóxicos no logren perjudicar a los nucleos celulares. La concentración maximal en cationes tóxicos que aguanta una planta en su ambiente puede ser más alto según sea más larga la cantidad de estos cationes immovilizada en el esfera raigal (a través de micro-organismos, materia orgánica etc.) y en las paredes celulares de los raíces jóvenes (tal como por crecimiento rapido del sistema raigal).

Zusammenfassung

In extrem sauren Böden sind es vor Allem die polyvalenten Katione Al, Fe und Mn, die durch ihre hemmende Wirkung auf die Zellteilung in den jungen Wurzeln und auf die Nährstoffaufnahme für die Pflanze sehr schädlich sind. Die Toleranz bezüglich Bodensäure ist stark verschieden zwischen Pflanzenarten, Varietäten und individuellen Entwicklungsstufen. Unter den höheren Pflanzen gibt es einige Ericaceen, die die pH-Werte bis 3.0 aushalten. Die Toleranz wird bestimmt durch inhärenten physiologischen Mechanismus der Pflanze und durch Wechselwirkung zwischen Wurzeln, Mikroorganismen und Bodenbestandteilen in der Rhizosphäre. Es handelt sich dabei um Inaktivierung der potentiell schädlichen Katione mittels selektiver Adsorbtion und Komplexformung in der Rhizosphäre, sowie in den Zellwändern des jüngeren Wurzelgewebes, bevor diese Katione die Zellkerne erreichen und beschädigen. Die Maximalkonzentration der polyvalenten Katione, die eine bestimmte, in Sauerböden wachsende Pflanze verträgt, ist grösser je nachdem mehr diese Katione inaktiviert werden in der Rhizosphäre (z.B. mittels Mikroorganisme) und in den Zellwändern jünger Wurzel (z.B. mittels schneller Wurzelentwicklung).

DISCUSSION

COULTER: Al toxicity is minimal at pH values larger than 5,0 and Mn toxicity is seldom a problem; why is liming to pH 6,5 so often recommended?

RORISON: May be to be on the safe side. Certainly many species which fail to grow in soils of pH 4,5 will do so if pH is raised by liming to c. 5,5.

COULTER: Varieties of certain crops, e.g. wheat, differ considerably in their tolerance of Al-toxicity. Is there a possibility of using this property in cropping systems for acid sulphate soils?

RORISON: Evolution of tolerant races can be rapid and a breeding program should be possible. Productivity, even with fertilizer additions, would need careful testing.

MOBERG: Is Al-toxicity also dependent on Al-saturation percentage?

RORISON: I have no quantitative evidence. There are other factors involved than just concentration, e.g. a 10^{-5} molar Al solution may be toxic or not to plant roots dependent on whether one uses a static solution or a constant flow.

DRIESSEN: In Southern Kalimantan (Borneo) the Bandjarese farmers obtain a yield increase of up to 50% by adding 70 kg/ha of NaCl to their wet rice fields. Antagonistic processes seem not to be involved as no nutrient deficiencies were found. Trace elements are not likely to be involved either. What could be the explanation for this yield increase?

RORISON: I only can refer you to Evans, H. and R.B.Cate Jr. - Studies in the improvement of problem soils in British Guiana. World Crops, November 1962, which describe leaching toxic materials from pegassay soils with sea water.

VAN DIEST: In a very young stage rice plants are very susceptible to Al toxicity. AFter a few weeks they build up tolerance. Do you have any physiological explanation?

RORISON: I can offer no adequate physiological explanation. It is an frequently reported occurrence. If seedlings survive the initial "sensitive" period they may subsequently "grow away" from toxicity (Rorison et al., 1958). Also, healthy seedlings which are transplanted into potentially toxic soils often survive where direct seeding has failed.

VAN DIEST: In experiments with rice, we noticed that this plant is more susceptible to Al given in EDTA form than to Al applied as $Al(NO_3)_3$. This seems contrary to general experience with heavy metals.

RORISON: In my experience Al-EDTA is not toxic to plants susceptible to Al in the inorganic form. It could be that the EDTA is complexing some other micronutrient, e.g. Mn at high pH, thus causing indirectly a deficiency.

THE MANAGEMENT OF ACID SULPHATE AND PSEUDO-ACID SULPHATE SOILS FOR AGRICULTURE AND OTHER USES

J. K. Coulter
Rothamsted Experimental Station, Harpenden, United Kingdom

Introduction

Conditions for the accumulation of sulphides in sediments and soils have been widely investigated and have been discussed in detail in other sessions of this symposium. The basic problems for agriculture are toxicities and/or deficiencies when such soils are used in the waterlogged state or when drained; this paper discusses these problems and the attempts to solve them.

On oxidation, sulphidic soils show pale yellow streaks or mottles along root channels and on ped faces. These have given rise to the name "cat clay" although the term "acid sulphate soil" is now more widely used. pH values in the range 2.5 to 3.0 are frequent, though occasionally values as low as 1.3 have been noted (10). The term "pseudo-acid sulphate soil" has been applied by Pons (41) to less acid soils formed by oxidation of sulphidic muds in the presence of sea-water salts. However, Pons and van der Kevie (42) state that in Thailand salinity does not prevent a sulphidic clay developing very high acidity on oxidation.

The formation of acid sulphate soils results from the presence of sulphides, the introduction of aerobic conditions, and the absence of bases, usually calcium carbonate, to neutralize the acidity. Most anaerobic soils contain some sulphides, a recent definition of a sulphidic material being a waterlogged soil having 0.75 per cent or more S on a dry weight basis (44). There is evidence in literature that smaller amounts should be used to differentiate between soils with and without potentially serious acidity.

Aerobic conditions are introduced when the soils are drained for agriculture but areas with seasonally aerobic conditions, due to natural changes in the drainage pattern, are described in the Gambia (22), Senegal (48) and Surinam (3); these occur behind belts of Avicennia mangrove on land flooded only by occasional high tides. Evaporation leaves surface salts, giving the typical "fluffy" appearance of saline soils, devoid of vegetation, whilst the subsoils dry out sufficiently to give yellow mottles and streaks of jarosite.

Sulphidic materials are exposed to oxidation by mining (33) and the high acidity prevents the growth of vegetation, desirable for both amenity and stabilization purposes. Fish ponds constructed in sulphidic soils give poor yields (49) and sub-soil drains may be blocked by ferrous iron (7, 59).

Though many sediments contain much sulphide, the formation of acid sulphate soils is prevented by carbonates neutralizing the acidity. Van Beers (5) states that most marine sediments in Holland contain 10 to 20 per cent $CaCO_3$, whilst river sediments have 6 to 15 per cent. Edelman and van Staveren (16) contrast the marsh soils of the United States, which contain little or no $CaCO_3$, with those in The Netherlands, which nearly always do so, or did when reclaimed. Most tropical marsh soils resemble those of the United States in having little or no reserves of $CaCO_3$. This is due to the base-poor nature of their river catchments though there are certain rivers with catchments in base-rich areas carrying sufficient bases to neutralize some or all of the acids (42) thus giving soils with large quantities of gypsum crystals; beds of shells supply the $CaCO_3$ in some areas. Other minerals in the soil can supply bases to neutralize the acidity and the development of high acidity involves not only the loss of exchangeable bases but some destruction of the clay lattice, producing aluminum as the major exchangeable ion (11).

Geographical distribution

Van Beers (5) records acid sulphate soils in all continents except Australia; West Africa, South and Southeast Asia, and Northeast South America have the largest extent. Moormann (36) has reported about 2 million ha in South Vietnam, Watts (49) 200,000 ha in Malaya, Pons and van der Kevie 1.5 million ha in Thailand; Jordan (31) notes that there are about 100,000 ha of mangrove in Sierra Leone which could be regarded as potential rice land; considerable areas have been reported in Finland, Sweden, Holland, and the United States. Though their serious agricultural problems have long been recognized, their irregular distribution and frequent occurrence within or adjacent to areas of good land carrying heavy population accounts for the many attempts to develop them. Broadly they are distributed in:

1. Coastal areas with marine or brackish water influence

These are marsh areas, now or until very recently under halophytic vegetation, of which mangrove (Rhizophora, Avicennia sp.) and nipa palm (Nipa fructescens) are the most important. In West Africa (22, 29, 31, 48) Rhizophora racemosa grows on the silty soils along the major tidal creeks, and the landward extension is controlled by the daily limit of tidal flooding. In Sierra Leone and Guinea this tidal water is saline during the dry season but in the wet season, with about 2,500 mm of rain in 6-8 months, it is virtually salt-free. Many of these areas have been cleared by hand for rice, relatively good yields of 2,000 to 3,000 kg/ha being reported. The success of this system depends on the intrusion of very large quantities of fresh water during the rainy season. Where this is insufficient, as in the smaller creeks with limited catchments (46) or along the coast, empoldering to prevent access of saline water and improve drainage has caused high acidity where the soils have grown *Rhizophora* mangrove.

The large-scale rice industry in the tidal zone in West Africa is a comparatively recent development; perhaps rice cultivation in the deltaic areas of West Pakistan started under rather similar conditions, but there is relatively little rice cultivation in the tidal zones in Asia. Agriculture on the youngest marine clays has followed clearing of mangrove or nipa palm in Sarawak, but coconut rather than rice is the usual crop.

2. Fresh water backswamps, formerly brackish

These represent much the largest areas used for agriculture. Under natuural conditions they support a limited range of species of grasses, sedges, shrubs, and trees. Sedges (*Phragmites vulgaris*) and Cyperus sp. have been reported from Gambia and pure stands of *Melaleuca leucadendrum* from Malaya (14). Although the specialized vegetation can be indicative of sulphidic soils, it grows on non-sulphidic ones also, whilst non-specialized forest vegetation occurs in areas with buried horizons of sulphidic material.

Vegetation influences not only the amount but also the way in which sulphides accumulate. *Rhizophora* mangrove flourishes just below mean sea level; thus sulphates and strong reducing conditions are present due to the large amount of organic matter from the root system and continuous water-logging. The fibrous muds, with 10-50 per cent organic matter, may contain 2 to 3 per cent sulphur (25) with pH levels as low as 2.0 on drying (46). Some of these muds may be at least 100 cm deep (45) thus holding much sulphides. Pyrite formation takes place as the muds are depositing, and will continue as long as these fibrous materials are flooded with sea or brackish water. Thus an important feature is the sulphidic nature of the surface layers, so giving very acid conditions with even a slight lowering of the water table.

Backswamps on the other hand may have a layer of non-sulphidic soil overlying sulphidic material. This forms when *Avicennia* mangrove follows *Rhizophora*, and in the Gambia such soils have a 30 to 45 cm horizon overlying sulphidic material of *Rhizophora* origin (45). Muds can also build up under non-mangrove vegetation and so bury horizons of sulphidic soil. Peaty material will continue to accumulate under fresh water anaerobic conditions and, if periodically flooded with brackish water, sulphides will form. The so-called "pegassy" soils of Guyana are peaty soils with sulphides, whereas the peats of Malaysia are fresh-water deposits with no pyrite. The pyrite formed by salt-water flooding of peaty deposits has been termed "tertiary" pyrite by Pons (41). It appears that this can form quite rapidly, for neglect of the dykes in empoldered areas in Surinam and the United States has led to brackish-water flooding and formation of pyrite within a few years. Reclamation of backswamps may thus involve soils with exposed or buried sulphidic horizons.

3. Fossil acid sulphate soils

In Thailand (42), Vietnam (36) and Guyana (Coulter & Robinson, unpublished FAO report) soils with very intensive purple, red, and brownish blotches and mottles on a gray matrix are reported. Such soils are usually very acid, with the exchange complex dominated by Al and Mg, are very compact, and are thought to have formed in Pleistocene times.

4. Inland peat swamps

Chenery (10) describes papyrus swamps at 2,000 meters elevation in Uganda with sulphides from sodium sulphate in pre-Cambian schists and phyllites. When drained, these swamps develop sterile patches with pH values of 2.4 to 2.7 at the surface and 1.3 in the air-dried sub-soils. Rost (43) describes peats in Minnesota which have a large amount of pyrite.

Factors responsible for poor yields

Sulphidic soils occur under a wide range of rainfall regimes and some may dry out only very infrequently under natural conditions. Dunn (15) reports an unusual drought in Southeast Malaya in which the swamps under natural forest dried out and large quantities of acid sulphates were then leached into the rivers, killing the fish and flocculating the suspended mud. Other areas have dry periods extending over several months, e.g. Vietnam, Thailand, and soils there dry out quite deeply, giving an annual regeneration of sulphates.

Agriculture on acid sulphate soils has consisted of keeping them waterlogged as long as possible and growing rice, or draining them for dryland crops; so the factors influencing yield are different.

When waterlogged, sulphidic soils have pH levels of 6 to 8; H_2S, Fe^{++} and Mn^{++} ions can be toxic under these conditions. Hart (23) treated mangrove soils with 0.2M KCl and extracted 500 ppm Fe^{++} at 65 per cent moisture and a pH of 6.5, and

900 ppm at 50 per cent moisture and a pH of 5.5; at a moisture level below 40 per cent, less than 100 ppm was extracted. The pH of flooded acid sulphate soils appears to vary, depending on the soil and whether measured in pots or in the field. In pot experiments with soils from Vietnam, the pH rose only from 3.6 to 4.7 in 16 weeks of flooding (35) whereas Tomlinson (47) reported a rise from 2.7 to 6.2 when mangrove soils in Sierra Leone were flooded with rain water; he regarded this as due to the leaching of sulphates. In the Vietnam soils Fe^{++} reached 800 ppm after 6 weeks' submergence, 500 ppm Fe^{++} being regarded as toxic; treating the soils with 1 per cent MnO_2 (equivalent to 20,000 kg/ha) kept the Fe^{++} below this limit. In continuously flooded unlimed soils, the plants died soon after transplanting. In contrast to this Cate and Sukhai (8) found that early and continuous flooding improved rice growth in pots and they suggested that, when the soils are flooded well before transplanting, Fe^{++} will neutralize aluminum and allow good crops to be grown, provided the fertility has been improved.

H_2S is known to be toxic to rice at levels below 1 ppm (39) and Japanese workers have reported a disease (akiochi) arising from this. Sulphide production is strongly pH dependent, little forming outside the pH range of 6.5 to 8.5 (12) but forming very rapidly within this range on submergence (13). It is usually suggested that H_2S is inactivated by precipitation as FeS by Fe^{++}, so that toxity would occur only in the absence of adequate amounts of the latter. On the other hand measurements in Louisiana rice soils have shown that Fe^{++} concentration had no appreciable effect on H_2S accumulation and that it was sorbed on the clay fraction (2). Other work on these soils has suggested that a flexibacterium capable of detoxifying H_2S exists in rice soils.

Varying levels of aluminum have been reported as toxic to rice (8); Hart (29), using solution culture, found 270 ppm toxic and 27 ppm root inhibiting. Aluminum solubility is strongly pH dependent, being 76.4 ppm at pH 3.11, 5.8 ppm at 3.95, and 0.3 ppm at 4.50 (34). Hart (29) found that the extractable Al of soils rose steeply as soon as the pH fell below 4.00. However, it seems doubtful whether simple relationships between aluminum and plant growth exist in acid sulphate soils, for Hesse (26), using a fresh mud at pH 6.2 from the 0-10 cm horizon of a mangrove swamp, found that leaves of the stunted rice plants from unfertilized pots had 900 ppm Al, whereas those from pots with lime and fertilizer had about 500 ppm. An important observation in Thailand (42) and Vietnam (36) is the damage to rice by the extremely acid flood water (pH 2.5 to 3.5) from acid sulphate soils within the area or flowing from adjacent areas.

No clear picture of the factors affecting rice growth in acid sulphate soils emerges from the pot experiments, the results of which sometimes conflict with those from field experiments. Pham-Hui-Anh et al. (38) report greatly improved yields in field experiments with lime and NPK fertilizer, but Jeffery (28) found no response to 10 tons/ha dolomitic limestone and 600 kg/ha superphosphate on undrained mangrove mud soils in Sierra Leone; so water control obviously affects responses greatly.

With dry land crops the upper part of the profile will be aerobic, so oxidation of sulphides continues as long as any remain. pH values may drop to about 2.5, at which levels large amounts of Fe^{++} enter the soil solution. More commonly, values in top soils range between 3.0 and 4.0, a modal value of 3.8 from 0 to 30 cm samples from 208 profiles in Malaya being reported (6). At these pH levels both hydrogen and aluminum ions are active. pH per se is not considered toxic to plant growth in acid soils, but work with nutrient solutions has shown depression of root growth of certain crops as pH dropped from 5.00 to 4.0. However, it is highly likely that, in soils, the detrimental effect of Al or Mn in solution would far outweigh that of H ion concentration (1). Although acid sulphate soils lose exchangeable cations when the acids form, H clays break down rapidly to release Al and Mg from the lattice, and such soils have large amounts of exchangeable Al whilst exchangeable Mg often exceeds exchangeable Ca.

On oxidation, sulphidic horizons provide large quantities of soluble sulphates, mostly aluminum salts; when formed in the deep sub-soil, they rise with the water table after the rains start or, if the water table is shallow, they concentrate at the surface by evaporation. Auriol and Lam-van-Vang (4) found that a sample of the efflorescence contained 24.12 per cent SO_3, 9.93 per cent Al_2O_3, and 10.36 per cent Na_2O.

There are wide variations in the tolerance of various species and of varieties within species to aluminum toxicity. Foy and Brown (21) found that oats yielded 75 per cent of the maximum yield with 6 ppm Al in solution, whereas mustard yielde only 7 per cent. No such comparative studies have been reported for tropical crops; observations suggest that rubber, oil palms, and coconuts can tolerate pH levels around 4 in the surface soil (6). Bananas and cassava are also tolerant of high acidity, and pineapples grow at pH values well below 4. Sugarcane is susceptible to Al toxicity and produces a coralloid root system unter these conditions, with a marked reduction in yields (18).

Deficiency of phosphate has been attributed to strong fixation by high levels of aluminum in the soil solution. Moormann (36) states that an application of 800 kg/ha rock phosphate failed to give a residual response with rice in the second year in Vietnam. Fresh mangrove muds have been shown to retain large quantities of P, values of 3,000 lb P/acre being quoted (26, 49); in Senegal, on the other hand, 1200 kg/ha phosphate still gave a residual response 5 years after application (27). Another example of P response in acid sulphate soils is recorded by Watts (49), who found greatly improved production of fish by treating ponds with phosphate and lime. Field and pot experiments do not give a consistent picture of phosphate responses on acid sulphate soils, probably due to the many different soils to which the fertilizer has been applied, but in some places heavy dressings are obviously needed for good yields.

Copper deficiency in pineapples has been reported by Moormann (36), but this is probably associated with the high level of organic matter, for pineapples show copper deficiency on non-sulphidic peat soils in Malaya. Other deficiencies specific to acid sulphate soils have not been confirmed; some sediments are low in Zn and Mn, and highly acid conditions give molybdenum deficiency. Nitrogen responses would be expected where other limiting factors have been removed; lime is obviously needed for many crops, but the need for Ca per se has not been elucidated. Response to K and Mg have not been specifically noted.

Development of improved agriculture

Sulphidic and acid sulphate soils occur in many different climatic situations over a wide range of landscapes and in very different economic and social settings. The soils themselves may have greatly varying degrees of sulphide or acid sulphate levels. Thus no single technique or agricultural system will be applicable in all areas and it is possible to consider their reclamation only in terms of a few major concepts.

In some areas farmers have cultivated these soils for some time and in other areas they probably tried to develop them but abandoned the attempt. They have been used for rice production in Sierra Leone, sugar cane and rice in Guyana, rubber, oil palm, coconuts, rice and fruit trees in Thailand, grass in The Netherlands, and fodder crops in Finland. Low yields have been reported of 700 kg/ha rice in Vietnam (36), 6,000 kg/ha oil palm bunches and 150-400 kg/ha copra in Malaya (6), 2,000 kg/ha rice in Sierra Leone but negligible yields where the soils have dried out and oxidized (24), and 1,000 kg/ha fodder crops in Finland (32). Farmers themselves have attempted to improve the soils by drainage, by ridging, or by maintaining flooded conditions and growing rice (36).

The depth at which pyrite occurs is important, Zuur (50) stating that, where the toxic horizon is buried to a depth of 40 cm, yields of crops like sugar beet are not affected but fruit trees are. Bloomfield et al. (6) concluded that 75 cm of top soil free of pyrite or acid sulphate gave good growth of oil palms. Thus in soils with toxic layers at some depth shallow rooting crops can be grown if the water table is controlled to minimize oxidation of the sulphidic horizon. Table I records the results of water table control on oil palms in Malaya

Where there is a layer rich in calcium carbonate within ploughing depth, it can be mixed into the acid sulphate horizon, Pons (40) suggesting a level of about 8 per cent carbonate for the success of this technique.

Oxidation of the sulphides and the removal of the soluble sulphates by leaching and drainage could eventually improve these soils and many laboratory measurements have been made on the rate of pyrite oxidation. Hart et al. (24) found that one quarter of the pyrite oxidized in 8 hours, one half in 36 hours, and all in about 1000 hours, and from this they estimated that drying during one field season would oxidize about half the pyrite. Unfortunately, no reports could be found in literature where the oxidation of sulphides and removal of sulphates have been followed under actual field conditions. Zuur (50) records 6 years for the sulphates in the soils of the Zuider Zee to fall below 0.7 g/liter. In the United States Fleming and Alexander (20) reported that the top 30 cm or so in an empoldered area had 0.34 to 0.4 per cent S, whilst that outside the polder had 2.0 to 3.0 per cent S; they suggested that this difference was due to oxidation and leaching over a 10 year period. Bloomfield et al. (6) in Malaya measured the sulphur levels at different depths in soils which had been drained for 5 years by 1 meter deep drains placed at distances varying from 10 meters to 60 meters. At depths below 50 cm in the area with the 60 meter drains the S content was 2.0 per cent whilst that in the intensely drained area was 0.36 per cent. Although these observations suggest that good drainage removes a large proportion of the sulphur in 5 to 10 years, the well known variability of pyrite levels in these soils makes such conclusions very tentative.

However, even if an optimistic figure of 10 years is taken as the time for removal of most of the pyrite by efficient leaching and drainage, there is the problem of using these soils over that period, since intense acidity develops during leaching. Alternatives are leaving the soil uncropped, which means expensive investments in drainage with a long delay on returns, growing crops which can tolerate the high acidity thus limiting severely the agricultural choice, or liming at regular intervals to keep the acidity within tolerable limits. Several experiments with liming have been reported in literature, but most lack information on long term residual effects and do not define the levels of sulphates, the amounts of pyrite, or the degree of drainage of the soils used. Calculations of the amounts required to neutralize the potential acidity show as much as 150 tons/ha, which is completely uneconomic especially in countries without indigenous supplies.

Attempts to increase the rate of leaching have been made; in Sierra Leone, Hart et al. (24) flooded, drained and oxidized soils with saline water and reported improved growth of rice. Evans and Cate (19) leached sugarcane land in Guyana with brackish water pumped for several miles through the canals and reported enhanced yields. Neither experiment records whether the yields were improved permanently or whether the leaching was done annually and, if so, the long term consequences of treating the soils with large amounts of saline water. Various field trials are summarized in Table II.

Conclusions

It is not yet possible to suggest generally applicable techniques for improved agriculture on acid sulphate soils. Experiments in pots and in the field record improved yields but these usually give the results of one or two years' experiments. Few of the experiments define adequately the characteristics of the soils being used and probably some experiments have shown no improvement in yield and have not been reported. Even more striking is the lack of reports on adoption by farmers of any of the proposed practices.

It is suggested, therefore, that a more intensive research program is needed on (1) the factors which are responsible for the low yields to such soil factors as pyrite level,m pH, and exchangeable Al and (3) the investigation of techniques for improving yields which are scientifically sound and yet practicable in the agricultural context of the countries involved.

Such a research effort is justified, particularly in the tropics, because these soils cover large areas of flat land which are, or could be, supplied with irrigation. They are often adjacent to, or admixed with, good soils carrying dense populations and the drainage waters from acid sulphate areas are detrimental to crops on the good soils.

Acknowledgements

I would like to thank Dr. Frans Moormann of I.I.T.A. and Mr. Poon Yew Chin of Harrisons & Crosfield (Malaysia) for supplying me with unpublished material.

TABLE 1. YIELD OF OIL PALM ON ACID SULPHATE SOILS IN WEST MALAYSIA 1961-1971
(1,000 kg/ha fresh fruit bunches)
Water table controlled at shallow depth from 1966-1967

FIELD No.	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971
SG 2	19.8	17.6	13.3	16.6	11.8	13.8	19.3	21.8	21.8	19.3	19.8
SG 4	18.6	20.9	13.8	18.8	12.8	17.1	22.6	24.9	24.9	21.8	24.1
ROP 61	-	-	-	-	5.0	8.3	9.8	16.3	16.8	20.9	22.3
ROP 64	-	-	-	-	-	-	8.3	19.6	24.6	25.1	23.9
N 4	14.1	15.1	12.3	8.8	6.0	8.3	9.0	13.8	19.3	17.3	19.3
N 5	17.6	19.1	16.1	14.3	10.8	13.1	14.6	16.1	19.3	18.8	20.8

TABLE 2. YIELDS FROM SOME FIELD EXPERIMENTS

REF.	COUNTRY	CROP	TREATMENTS	YIELDS (kg/ha)
(32)	Finland	Fodder[+]	0	1150
			PK	1400
			NPK	1700
			NPK + 7 tons lime/ha	2600
			NPK +14 tons lime/ha	2700
			NPK +21 tons lime/ha	2700
(24)	Sierra Leone	Rice[++]	0	0
			2½ tons lime/ha	620
			5 tons lime/ha	1880
			7½ tons lime/ha	1680
			10 tons lime/ha	2020
			0 lime leached with sea water	1980
			2½ tons lime leached with sea water	2420
			5 tons lime leached with sea water	2480
			7½ tons lime leached with sea water	2420
			10 tons lime leached with sea water	2500

[+] Averaged over 10 year period

[++] Yields for one year

REFERENCES

(1) ADAMS, F. and PEARSON, R.W. 1967. Crop responses to lime in the Southern United States and Puerto Rico. In Soil Acidity and Liming. Amer. Soc.Agron. Monograph 12. ed. R.W.Pearson and F.Adams.

(2) ALLAM, ABDEL-WAHAB. 1971. Soluble sulphides in rice fields and their in vitro effects on rice seedlings. PhD thesis. Louisiana State University.

(3) AUGUSTINUS, P.G.E.F. and SLAGER, S. 1971. Soil formation in swamp soils of the coastal fringe of Surinam. Geoderma 6. 203-211.

(4) AURIOL, P.F. and LAM-VAN-VANG.1934.Etudes sur les terres et les eaux alunées. Bull. Econ. de l'Indochina. Hanoi. 221-266.

(5) BEERS, W.F.J. van. 1962. Acid sulphate soils. Bull. Int. Inst. Land Reclamation and Improvement 3. pp.31.

(6) BLOOMFIELD, C., COULTER, J.K. and KANARIS-SOTIRIOU, R. 1968. Oil Palms on acid sulphate soils in Malaya. Trop. Agric. (Trin) 45. 289-300.

(7) BLOOMFIELD, C. 1972. The oxidation of iron sulphides in soils in relation to the formation of acid sulphate soils and of ochre deposits in field drains. J. Soil Sci. 23, 1-16.

(8) CATE, R.B. and SUKHAI, A.P. 1964. A study of aluminum in rice soils. Soil Sci. 98, 85-93.

(9) CHENERY, E.M. 1953. A digest of the chemistry of dead swamps in Kigezi district, S.W.Uganda. Government Printer, Uganda Protectorate. pp.6.

(10) CHENERY, E.M. 1954. Acid sulphate soils in Central Africa. Trans. 5th Int. Cong. Soil Sci. 4. 195-198.

(11) COLEMAN, N.T. and CRAIG, D. 1961. The spontaneous alteration of hydrogen clay. Soil Sci. 91, 14-18.

(12) CONNELL, W.E. and PATRICK, W.H. 1968. Sulphate reduction in soil. Effects of redox potential and pH. Science 159, 86-87.

(13) CONNELL, W.E. and PATRICK, W.H. 1969. Reduction of sulphate to sulphide in waterlogged soil. Soil Sci. Soc. Amer. Proc. 33, 711-715.

(14) COULTER, J.K. 1952. "Gelam" soils. A study of their sulphur content. Malay. Agric. J. 35, 22-35.

(15) DUNN, I.G. 1965. Notes on mass fish death following drought in South Malaya. Malay. Agric. J. 45, 204-211.

(16) EDELMAN, C.H. and STAVEREN, J.M.van. 1958. Marsh soils in the United States and in The Netherlands. J. Soil and Water Conserv. 13, 5-17.

(17) EL BARADI, T.A. 1967. Acid sulphate soils in the tropics. Tropical Abstr. 22, 137-142.

(18) EVANS, H. 1955. Studies in the mineral nutrition of sugar cane in British Guiana. Trop. Agric. (Trin) 32, 124-133.

(19) EVANS, H. and CATE, R.B. 1962. Studies in the improvement of problem soils in British Guiana. World Crops 14, 370-373.

(20) FLEMING, J.F. and ALEXANDER, L.T. 1961. Sulphur acidity in South Carolina tidal marsh soils. Soil Sci. Soc. Amer. 25, 94-95.

(21) FOY, C.D. and BROWN, J.C. 1964. Toxic factors in acid soils. II. Differential aluminum tolerance of plant species. Soil Sci. Soc. Amer. Proc. 28, 27-32.

(22) GIGLIOLI, M.E.C. and THORNTON, I. 1965. The mangrove swamps of Keneba, Lower Gambia river basin. I. Descriptive notes on the climate, the mangrove swamps and the physical composition of their soils. J. appl.Ecol.2, 81-103.

(23) HART, M.G.R. 1959. Sulphur oxidation in tidal mangrove soils of Sierra Leone. Plant and Soil 11, 215-236.

(24) HART, M.G.R., CARPENTER, A.J. and JEFFERY, J.W.O. 1963. Problems in reclaiming saline mangrove soils in Sierra Leone. Agron. Trop. 18, 800-802.

(25) HESSE, P.R. 1969. Some differences between the soils of *Rhizophora* and *Avicennia* mangrove swamps in Sierra Leone. Plant and Soil 14, 335-346.

(26) HESSE, P.R. 1963. Phosphorus relationships in a mangrove-swamp mud with particular reference to aluminum toxicity. Plant and Soil 19, 205-218.

(27) IRAT. 1971. Rapport d'activités 1970. Service d'Agropédologie. Secteur IRAT/Casamance, Station de Djibélor.

(28) JEFFERY, J.W.O. 1963. Fertilizer trials on Sierra Leone swamp rice soils Agron. Trop. 18, 806-810.

(29) JORDAN, H.D. 1963. The vegetation of mangrove swamps in Sierra Leone. Agron. Trop. 18, 796-797.

(30) JORDAN, H.D. 1963. Development of mangrove swamp areas in Sierra Leone. Agron. Trop. 18, 798-799.

(31) JORDAN, H.D. 1964. The relation of vegetation and soil to development of mangrove swamps for rice growing in Sierra Leone. J. appl. Ecol. 1, 209-212.

(32) KIVENEN, E. 1950. Sulphate soils and their management in Finland. Trans. 4th Int.Cong.Soil Sci.2, 259-262.

(33) KOHNKE, H. 1950. The reclamation of coal mine spoils. Adv. Agron.2, 318-349.

(34) MAGISTAD, C.C. 1925. The Al content of the soil solution and its relation to soil reaction and plant growth. Soil Sci. 20, 181-225.

(35) MAI-THI MY NHUNG and PONNAMPERUMA, F.N. 1966. Effects of calcium carbonate, manganese dioxide, ferric hydroxide and prolonged flooding on chemical and electrochemical changes and growth of rice in a flooded acid sulphate soil. Soil Sci. 102, 29-41.

(36) MOORMANN, F.R. 1961. Acid sulphate soils (cat clays) of the tropics. In Researches on acid sulphate soils and their amelioration by liming. Agronomic Library. Ministry of Rural Affairs, Saigon.

(37) MOORMANN, F.R. 1963. Acid sulphate soils (cat-clays) of the tropics. Soil Sci. 95, 271-275.

(38) PHAM-HUU-ANH, MOORMANN, F.R. and GOLDEN, J.D. 1961. Liming experiments on acid sulphate soils. In Researches on acid sulphate soils and their amelioration by liming. Agronomic Library, Ministry of Rural Affairs, Saigon.

(39) PITTS, R.G. 1971. Explorations in the chemistry and microbiology of Louisiana rice plant-soil relationship. PhD thesis. Louisiana State University.

(40) PONS, L.J. 1956. Some aspects of the improvement of pyrite containing old marine soils in The Netherlands. Trans. 6th Int. Cong. Soil Sci. B, 727-734.

(41) PONS, L. J. 1964. Pyrites as a factor controlling chemical "ripening" and formation of "cat clay" with special reference to the coastal plain of Surinam. Agric. Exp. Sta. Panamaribo Bull. 82, 141-161.

(42) PONS, L.J. and KEVIE, W. van der. 1969. Acid sulphate soils in Thailand.

Studies on the morphology, genesis and agricultural potential of soils with cat clay. Soil Survey Division. SSR-81-1969. Land Development Department. Ministry of National Development. Bangkok.

(43) ROST C.O. 1922. Occurrence of sulphides in Minnesota peat soils. Soil Sci. 14, 167-176.

(44) Soil Taxonomy. 1970. Soil Survey, Soil Conservation Service. U.S.Dep. Agric. Washington D.C.

(45) THORNTON, I. and GIGLIOLI, M.E.C. 1965. The mangrove swamps of Keneba, Lower Gambia river basin. II. Sulphur and pH in the profiles of swamp soils. J.appl. Ecol. 2, 257-269.

(46) Tomlinson, T.E. 1957. Relationship between mangrove vegetation, soil texture and reaction of surface soil after empoldering saline swamps in Sierra Leone. Trop. Agric. (Trin.) 34, 41-50.

(47) TOMLINSON, T.E. 1957. Seasonal variation of the surface pH value of some rice soils of Sierra Leone. Trop. Agric.(Trin.)34,287-294.

(48) VIEILLEFON, J. 1969. La pédogénèse dans les mangroves tropicales. Un example de chronosequence. Sci.du Sol.2,115-148.

(49) WATTS,J.C.D. 1969. Phosphate retention in acid sulphate pond muds from the Malacca area. Malay.Agric.J.47,187-202.

(50) ZUUR,A.J. 1952. Drainage and reclamation of lakes and of the Zuiderzee. Soil Sci. 74, 75-89.

Summary

Acid sulphate soils are characterized by the presence in the profile of excessively acid horizons, resulting from aeration and oxidation of non-calcareous sulphidic muds, mainly of marine or fluvio-marine origin. Both aerated acid sulphate and reduced sulphidic soil layers present serious toxicity and deficiency problems for most agricultural crops. Nevertheless acid sulphate soils have often been reclaimed, because of their geographical association with fertile non-acid soils in densely populated coastal plains and deltas. Such reclamations were tried in a wide range of climates and economic settings, mainly on a trial-and-error basis. Complete case histories are not available. The results are mainly poor or were complete failures. A common practice in wet tropical climates is trying to keep the soil in flooded conditions, thus preventing possible superficial sulphidic layers from oxidizing and acidifying. Crops are restricted to rice and yields are generally poor due to inadequate water control and to physiological problems arising from soil deficiencies or toxicities. Rather successful have been reclamations of acid sulphate soils with buried acid horizons (deeper than 75 cm), with subsoils containing lime, or with acid layers that were partly neutralized by percolating sea water (pseudo-acid sulphate soils). In all these cases potential acidity or salinity in the subsoil is kept under control by strict water management. Depending on depths of the drained non-acid toplayer these soils are used for pasture, cultivated dry crops or tree crops. Systematic trials with draining, oxidizing and leaching of sulphidic soils, combined with liming and fertilizing remain until now restricted to laboratory measurements over short periods. Field trials on this subject have never been completed. It is not yet possible to recommend generally applicable techniques for improved agriculture on acid sulphate soils. It is suggested that this problem be studied more systematically and over longer periods especially in the agricultural part of the densely populated tropical coastal plains and deltas.

Résumé

Les sols sulfatés acides se distinguent par la présence dans leur profils des horizons extrèmement acides, provenant de l'aération et de l'oxidation des vases sulphidiques non-calcaires surtout d'origine marine. Ces horizons, dans l'état reducé ainsi que oxidé, présentent des problèmes de toxicité et de carence pour la plupart des plantes. Tout de même les sols sulfatés acides ont été récupérés souvent, à cause de leur association géographique avec des sols fertils et non-acides dans des plaines côtières et des deltas densement peuplés. On trouve de *telles récupérations dans des conditions climatologiques et économiques très diverses, mais très peu des cas ont été documenté. En général les résultats étaient pauvres ou on a eu des échecs complets. Dans les tropiques humides la pratique courante c'est l'inondation permanente prévenant l'oxidation et l'acidification des couches sulphidiques superficielles. Cette méthode restreint l'utilisation des sols à la riziculture. Dû aux insuffisances du contrôle d'eau et du milieu racinaire, les récoltes restent assez basses. Un succès relative ont été les récupérations des sols sulfatés acides avec les horizons acides à profondeur (plus profond que 75 cm), de ceux avec sous-sols calcaires et de ceux dont les horizons acides étaient neutralisés partiellement par la percolation des eaux salines (dits "pseudo acid sulphate soils"). Dans ces cas il faut maintenir une régime d'eau très stricte pour éviter l'ascension des acides ou les sels du sous-sol. A mesure que la couche superficielle qu'on peut maintenir libre d'acides soit plus profonde la choix des plantes cultivables devient plus large. Des essais systématiques sur le drainage, l'oxidation et la lixiviation des sols sulphidiques, en combinaison avec le chaulage et l'apport d'engrais, ont été restreints au laboratoire et aux périodes assez courtes. Les essais dans le terrain restaient incomplets. Pour le moment ce n'est pas encore possible de recommender pour l'agriculture sur les sols sulfatés acides des techniques appropriées. Il est sugéré que cette problème soit étudiée systématiquement à la longue durée, surtout dans les conditions de l'agriculture dans les plaines côtières et les deltas densement peuplées des régions tropicales.*

Resumen

Los suelos de sulfatos ácidos se caracteriscan por la presencia en sus perfiles de capas muy ácidas provenientes de la aeración y la oxidación inicial de barros sulfidicos non-calcareos de origen marino. Estas capas o sea en estado reducido o oxidado, presentan problemas de toxicidad y de carencia a la mayoría de las plantas. Sin embargo han sido recuperados estos suelos sobre todo donde se encuentran en pleno suelos fertiles non-ácidos de llanuras costaneras y deltas densamente poblados. Existen experiencias con suelos de śulfatos ácidos en un gran variedad de ambientes climatológicas y económicas, pero muy pocos de los casos han sido documentados. En general han salido muy pobres o fueron fracasos completos. En las regiones tropicales humedas una práctica común es la inundación permanente, impediendo la oxidación y la acidificación de las capas sulfidicas en la superficie. Esta práctica limite el uso de los suelos hasta el cultivo de arroz. Las cosechas suelen quedar bajas a consecuencia de deficiencias en el manejar del agua y de carencias en el ambiente raigal. Un éxito relativo tienen recuperaciones de

suelos de sulfatos ácidos con capas ácidas más profundas que 75 cm, o con subsuelos calcáreos y también de éstos con capas ácidas neutralisadas en parte por el percolar de aguas salinas (dichos "pseudo acid sulphate soils"). En todos estos casos se tiene que mantener un régimen de agua estricto para impedir el ascender de los ácidos y los sales del sub-suelo. Según las capas superficiales nonácidas se extienden más profundo, esté más amplio el escoger de cultivos. Ensayos sistemáticos con drenaje, oxidación y lixiviar los ácidos en suelos de sulfatos ácidos se han limitado hasta modeles de laboratorio. Ensayos en el campo quedaban de muy corto plazo. Hasta ahora falta la base para el recomendar métodos de aplicación general para la agricultura mejorada en suelos de sulfatos ácidos. Por eso se sugiere el estudio sistemático de este problema, de antemano en conexión con las condiciones agricolas en las llanuras costaneras y los deltas densamente pobladas de las regiones tropicales.

Zusammenfassung

Die schwefelsauren Böden sind gekennzeichnet durch die stark sauren Profilhorizonte, die durch Oxidation kalkloser Sulphidschlämme, meistens ozeanischer Herkunft, entstanden sind. Der reduzierte Sulphidschlamm sowie die oxidierten schwefelsauren Horizonte bringen für die meisten Pflanzenwurzeln Giftigkeits- und Nährstoffmangelprobleme mit. Trotzdem hat man versucht diese Böden urbar zu machen, vor Allem im Zusammenhang mit fruchtbaren Ablagerungen, in dicht bevölkerten Küstenebenen und Deltas. Mit diesen Böden gibt es also praktische Erfahrungen bei mannigfaltigen klimatologischen und ökonomischen Verhältnissen. Diese Erfahrungen sind jedoch fast niemals beschrieben worden. Es handelt sich um Fälle mit ungünstigem Verlauf und geringem Erfolg. In den Feuchttropen hat man öfters versucht untiefe Sulphidhorizonte bleibend reduziert zu halten mittels Hochwasserstand. Unter diesen Umständen kann man nur Reis anbauen; die Ernte bleibt niedrig infolge des mangelhaften Wasserhaushaltes und ungünstiger Bodenbedingungen. Beziehungsweise mehr Erfolg hat die Nutzbarmachung schwefelsaurer Böden, in denen entweder Sauerschichten tiefer als 75 cm, oder kalkhaltiger Untergrund vorkommen, oder Böden, in denen die schwefelsauren Horizonte bereits durch perkolierendes Seewasser teilweise neutralisiert sind (sogenannte "pseudo acid sulphate soils"). In allen diesen Fällen ist das Aufsteigen der Säuren und Salze aus dem Unterboden vorzubeugen mittels zielbewusster Wasserbeherrschung. Wenn der nicht-saure Boden tiefer reicht, können diese Böden benutzt werden als Wiesen, für Ackerbau oder Baumpflanzungen. Systematische Versuche mit Entwässerung, Oxidation und Auswaschung, kombiniert mit Bekalkung und Düngung hat es nur noch im Bodenprüflabor

gegeben. Diesbezügliche Feldversuche sind entweder vorzeitig beendet oder mangelhaft dokumentiert worden. Bisher fehlen also Grundlagen für Empfehlungen hinsichtlich einer Meliorationstechnik für schwefelsaure Böden. Es wird daher ein systematisches und langfristiges Studium dieser Frage befürwortet, vornehmlich im Zusammenhang mit der Agrarlage der dicht bevölkerten tropischen Küstenebenen und Deltas.

DISCUSSION

ZONNEVELD: Could leaching with sea water also cause new formation of pyrites?

VAN BREEMEN: Sea water contains 28 m mole SO_4 which is less than in most groundwater of acid sulphate soils. Hence the sulphate concentration itself is not raised by leaching with sea water. Important is that the rise of pH facilitates microbial sulphate reduction and possible pyrite formation.

PONNAMPERUMA: Let the sea water in just before the rains come.

GORA BEYE: Leaching with sea water will induce serious additional salinity problems in areas with insufficient rainfall. One should be careful in recommending it.

HEW: Can liming cause antagonism and differential nutrient uptake in acid sulphate soils, e.g. potassium antagonism with oil palm?

COULTER: There has not been paid much attention to possible antagonism after applying lime as the elimination of toxicity was the overruling problem.

PONNAMPERUMA: In rice we are careful with liming mainly because raised pH induces accelerated sulphate reduction and, if not enough iron is available, hydrogen sulphide toxicity may occur.

KANAPATHY: In Malaysia we have good results with limited lime dressings (1-2 ton/ha, pH 4,2) on cassave and rice. On increasing liming yields drop again and there are indications of deficiences of potassium.

GORA BEYE: In Senegal experiments with liming of acid sulphate soils in rice gave only positive results where iron toxicity was involved.

VAN DIEST: Iron toxicity would be expected to decrease with increasing pH upon flooding, provided enough organic matter is available for the microbial iron reduction.

PONNAMPERUMA: Soils that contain less than 1,5% organic matter show only slight increase in soluble iron on flooding.

GORA BEYE: In Senegal iron toxicity occurs in flooded soils with 2-3% organic matter, but the material is very rich in iron due to flooding water coming from ferruginous upland areas.

BIBLIOGRAPHY ON ACID SULPHATE SOILS 1863-1973

This bibliography was compiled from reference lists assembled by A.Kawalec (FAO, Rome), S.Sombatpanit (Land Development Dept., Bangkok) and N.van Breemen (University of Agriculture, Wageningen).

The emphasis is on publications providing first-hand or secondary information on actual and potential acid sulphate soils. References to publications on related topics (formation and oxidation of pyrite; soil acidity; soil acidity and plant growth; sedimentation in tidal areas, etc.) and on soils affected by acid mine spoils or sulphuric acid from industrial pollution are not given.

(1) AALTONEN, V.T. et al. 1949. Maaperäsanaston ja maalajien luok ituksen Tarkistus.

(2) AARNIO, B. 1922. Über Salzböden (Alaunböden) des humiden Klimas in Finnland. Int.Mitt.Bodenk.12:180-185.

(3) AARNIO, B. 1930. Salt Soils in Finland. Maataloustieteelinen Aikakauskirja 2:39-47.

(4) AARNIO, B. 1936. Über Gyttjaböden. Bodenk.u.Pfl.Ernähr.2:186-192.

(5) AARNIO, B. 1938. Die Mineralböden Finnlands. Agrog.Julk.47. Helsinki.

(6) AHMAD, N. 1960. Aluminium toxicity of certain soils on the coast of British Guiana. Trans. 7th Int.Congr.Soil Sci.II:161-170.

(7) ALLBROOK, R.F. 1973. The identification of acid sulphate soils in North-west Malaysia. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(8) AMSON, F.W.van. 1966. Some aspects of clay soils in the Demerara formation of Surinam. Landb. Proefst. Suriname. Bull.84:1-68.

(9) ANDRIESSE, J.P., BREEMEN, N.van, BLOKHUIS, W.A. 1973. The influence of mud-lobsters (Thalassina anomala) on the development of acid sulphate soils in mangrove swamps in Sarawak (East Malaysia). Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(10) ANONYME. 1954. Report on Sierra-Leone. 2nd Interafr.Soils Conf. Léopoldville, pp.1095-1097.

(11) APPLEWHITE, C. 1964. Semi-detailed Soil Survey of the Mahaica Mahaicony Abary Area. Report FAO, Rome.

(12) AUGUSTINUS, P.G.E.F., SLAGER, S. 1971. Soil formation in swamp soils of the coastal fringe of Surinam. Geoderma 6:203-211.

(13) AURIOL, P.F., LAM-VAN-VANG. 1934. Etudes sur les terres et les eaux alunées. Bull.Econ.de l'Indoch. Hanoi.

(14) BARADI, T.A.el. 1967. Acid Sulphate Soils in the Tropics. Tropical Abstr. Vol.22:137-141.

(15) BEERS, W.F.J.van. 1949. Reconnaissance soil survey of the Sorong Area, New Guinea. Unpubl.Report. Soil Survey Inst.,Bogor.

(16) BEERS, W.F.J.van. 1955. Reconnaissance Soil Survey of the Khulna Area, Ganges Delta, East Pakistan. Unpubl.Report. FAO, Rome.

(17) BEERS, W.F.J.van. 1962. Acid Sulphate Soils. I.L.R.I., Bull.3:1-31. Wageningen.

(18) BEMMELEN, J.M.van. 1863. Bouwstoffen tot de kennis van de kleigronden der provincie Groningen. G.J.Mulder, Scheik.Verh.en Onderz. Deel III, stuk 2.

(19) BEMMELEN, J.M.van. 1866. Landw. Versuchsstationen. III:271-276, 302-306.

(20) BEMMELEN, J.M.van. 1886. Bijdragen tot de kennis van den alluvialen bodem in Nederland. Verhandelingen Academie Wetenschappen. Amsterdam 25-B:33-105.

(21) BENNEMA, J. 1953. De ontkalking tijdens de opslibbing bij Nederlandse alluviale gronden. Boor en Spade VI:30-41.

(22) BENNEMA, J. 1953. Pyrite and calcium carbonate in the soil of the reclaimed lake "Groot Mijdrecht". Boor en Spade VI:134-149. (In Dutch)

(23) BENZLER, J.H. 1973. Probleme bei der Kartierung von "Maibolt" und "Pulvererde" - besonderen Formen der sulfatsauren Böden - in den Marschengebieten Niedersachsen (BRD). Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(24) BERNER, R.A. 1967. Diagenesis of iron sulfide in recent marine sediments. Am.Ass.Advanc.Sci.Publ.83:268-272.

(25) BERRIT, G.R. 1964. Les eaux salées du Golfe de Guinée. Actes du Colloque de Dacca. UNESCO, pp.13-22.

(26) BLACKBURN, G., BAKER, R.M. 1958. A soil survey of part of Brunei, British Borneo. CSIRO, Div.Soils. Soils and Land Use Ser. No.25. 84 p.

(27) BLOOMFIELD, C., COULTER, J.K., KANARIS-SOTIRIOU, R. 1968. Oil palms on acid sulphate soils in Malaya. Trop.Agric.(Trin.) 45:289-300.

(28) BLOOMFIELD, C. 1972. The oxidation of iron sulphides in soils in relation to the formation of acid sulphate soils, and of ochre deposits in field drains. J.Soil Sci. 23:1-6.

(29) BLOOMFIELD, C. 1973. Acidification and ochre formation in pyritic soils. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(30) BONFILS, P. 1950. Etudes morphologiques des sols rizicoles de la basse côte de Guinée. ORSTOM, Paris. Mimeo.

(31) BOYE, M. 1962. Les palétuviers du littoral de la Guyane française. Ressources et problèmes d'exploitation. Les cahiers d'Outre-mer 15:271-290.

(32) BREEMEN, N.van. 1968. Formation and conversion of sulphides and sulphates in marine sediments and acid sulphate soils. Unpublished literature study (in Dutch). Univ. of Agriculture, Wageningen.

(33) BREEMEN, N.van. 1973. Calculation of ionic activities in natural waters. Geochim.Cosmochim.Acta 37:101-107.

(34) BREEMEN, N.van. 1973. Soil forming processes in acid sulphate soils. Proc. Int.Symp.on Acid Sulphate Soils. Vol.I. Wageningen.

(35) BREEMEN, N.van, MANOP TANDATEMIYA, SOPON CHANCHAREONSOOK. 1973. A detailed survey on the actual and potential soil acidity at the Bang Pakong land development centre, Thailand. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(36) BRINKMAN, R. 1964. Semi-detailed soil survey of the Canje Area. Report FAO, Rome.

(37) BRINKMAN, R., PONS, L.J. 1968. A pedo-geomorphological classification and map of the Holocene sediments in the coastal plain of the three Guianas. Soil Survey Paper 4:1-44. Inst. of Soil Survey, Wageningen.

(38) BRINKMAN, R.,PONS, L.J. 1973. Recognition and prediction of acid sulphate soil conditions. Proc.Int.Symp.on Acid Sulphate Soils. Vol.I. Wageningen.

(39) BRUGIERE, J.M., SOURDAT, M. 1963. Mission pédologique au Surinam en mai 1963. Rapport ORSTOM.

(40) BRÜMMER, G. 1968. Untersuchungen zur Genese der Marschen. Inaug.Diss.Hohenheim. Landw.Fak.Christian-Albrechts Universität. Kiel, pp.1-350.

(41) BRÜMMER, G., GRUNWALDT, H.S., SCHROEDER, D. 1971. Beitrage zur Genese und Klassifizierung der Marschen. II. Zur Schwefelmetabolik in Schlicken und Salzmarschen. Z.Pflanzenernährung & Bodenkde. 128:208-220.

(42) BRÜMMER, G., GRUNWALDT, H.S., SCHROEDER, D. 1971. Beitrage zur Genese und Klassifizierung der Marschen. III. Gehalte, Oxydationsstufen und Bindungsformen des Schwefels in Koogmarschen. Z.Pflanzenernährung & Bodenkde.129:92-108.

(43) BRUNT, M. 1959. The Gambia Land-Use and Vegetation Survey. Proc.2nd Interafr. Soils Conf. Dalaba. Vol.I:389-394.

(44) BUURMAN, P., BREEMEN, N.van, JONGMANS, A.G. 1973. A fossil acid sulphate soil in ice-pushed Tertiary deposits near Uelsen. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(45) CATE, R.B., SUKHAI, A.P. 1964. Study of aluminium in rice soils. Soil Sci. 98:85-93.

(46) CATE, R.B., SUKHAI, A.P. 1965. Salt, acidity and base status in the coastal clays of British Guiana. Landb.Proefst.Suriname. Bull.82:133-139.

(47) CHAPMAN, V.J. 1964. Some factors involved in mangrove establishment. Actes du Colloque de Dacca. UNESCO, pp.219-225.

(48) CHENERY, E.M. 1952. The soils of central Trinidad. Dept.Agric., Trinidad.

(49) CHENERY, E.M. 1954. Acid sulphate soils in Central Africa. Trans.5th Int. Congres Soil Sci., Léopoldville, 4:195-198,

(50) CLARK, J.S., GOBIN, C.A., SPROUT, P.N. 1961. Yellow Mottles in some poorly drained soils of the Lower Frazer Valley, British Columbia. Can.J.Soil Sci. 41:218-227.

(51) COULTER, J.K. 1952. Gelam Soils. Malayan Agr. 35:22-35.

(52) COULTER, J.K. 1968. Acid sulphate soils in Malaya. Report of the Pedology Department, Rothamsted.

(53) COULTER, J.K. 1973. The management of acid sulphate soils and pseudo-acid sulphate soils for agriculture and other uses. Proc.Int.Symp.on Acid Sulpate Soils. Vol.I. Wageningen.

(54) COUTINET, S., DURAND, J.H. 1966. Les sols de mangroves de la côte nord-ouest de Madagascar, Région d'Ambanja. Agron.Trop.21:347-360.

(55) DAM, D.van, PONS, L.J. 1973. Micromorphological observations on pyrite and its pedological reaction products. Proc.Int.Symp.on Acid Sulphate Soils. Vol. II. Wageningen.

(56) DENNET, J.H. 1932. A preliminary note on the reaction of paddy soils. Mal. Agr.J. 20:518.

(57) DENNET, J.H. 1933. The Western Coastal Alluvial Soils. Malayan Agric.J. 21: 345-361.

(58) DENT, J.M. 1947. Some soil problems of empoldered rice lands in Sierra Leone. Emp.J. Exp.Agric. 15:206-212.

(59) DENT, F.J. 1968. Reconnaissance soil survey of rubber growing areas in Thailand. Land Dev.Dep.Soil Survey Rep.63:1-35. Bangkok.

(60) DIJKERMAN, J.C. 1969. Soil resources of Sierra Leone, West Africa. Sols Afr. XIV:185-206.

(61) DOEMEL, W.N., BROCK, T.D. 1971. pH of very acid soils. Nature 229:574.

(62) DOST, H., HORN, M.E. 1969. Etudes d'un aménagement hydro-agricole des terres rizicultivables de la Basse Guinée. Vol.II. Rapport FAO, Rome.

(63) DOYNE, H.C., GLANVILLE, R.R. 1933. Some swamp rice growing soils of Sierra Leone. Trop.Agric. (Trin.) 10:132-138.

(64) DOYNE, H.C. 1937. A Note on the acidity of mangrove swamp soils. Trop.Agric. (Trin.) 14:286-287.

(65) DRIESSEN, P.M. 1973. Pyrite-containing sediments of Southern Kalimantan, Indonesia. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(66) DUDAL, R., MOORMANN, F.R. 1964. Major soils of South East Asia. Trop.Geography 18:54-80.

(67) DURAND, J.H. 1967. Les sols des bassins paraliques de la côte ouest de Madagascar. Agr.Trop.XXII:1176-1186.

(68) EDELMAN, C.H. 1948. Katteklei. Boor en Spade I:172-176.

(69) EDELMAN, C.H. 1950. Soils of The Netherlands. Amsterdam. 176 p.

(70) EDELMAN, C.H., STAVEREN, J.M.van. 1958. Marsh soils in the United States and in The Netherlands. J.Soil Water Conserv.13:5-17.

(71) ESWARAN, H. 1967. Micromorphological study of a cat-clay soil. Pedologie (Gent) 17:259-265.

(72) EVANS, H., CATE, R.B. 1962. Studies in the improvement of problem soils in British Guiana. World Crops 14:370-373.

(73) EYK, J.J.van der. 1957. Reconnaissance soil survey in Northern Surinam. Wageningen.

(74) FLEMING, J.F., ALEXANDER, L.T. 1961. Sulfur acidity in South Caroline tidal marsh soils. Soil Sci.Soc.Amer.Proc.25:94-95.

(75) FORD, H.W., CALVERD, D.V. 1970. A method for estimating the acid sulphate potential of Florida soils. Soil Sci.Soc.Florida Proc.30:304-307.

(76) GASSER, J.K.R. 1961. Investigations on rice growing in British Guiana. I. Characteristics of some rice soils of the coastland. J.Soil Sci.12:234-241.

(77) GAUCHER, G. 1967. Les conditions de pédogenèse dans la partie septentrionale du littoral Sénégalais. Pedologie (Gent) 17:153-186.

(78) GEBHARDT, W. 1973. Cation exchange and anion adsorption properties of some acid soils in the Central German Mountain range. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(79) GIBBS, H.S., COWIE, J.D., PULLAR, W.A. Soils of North Island. Regional Soil Descr. of New Yealand to accompany Soil Maps of North and South Islands on 1:1 000 000 scale.

(80) GIGLIOLI, M.E.,THORNTON, I. 1965. The mangrove swamps of Keneba, Lower Gambia river basin I. Descriptive notes on the climate, the mangrove swamps and the physical composition of their soils. J.Appl.Ecol. 2:81-103.

(81) GORA BEYE. 1973. Acidification of mangrove soils after empoldering in Lower Casamance. Effects of the type of reclamation system used. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(82) GRANT, C.J. 1973. Acid sulphate soils in Hong Kong. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(83) GRASS, L.B., ARONOVICI, V.S., MUCKEL, D.C. 1962. Some chemical characteristics of submerged and reclaimed sediments of the San Francisco Bay system. Soil Sci.Soc. Amer.Proc. 26:453-455.

(84) GRUNWALDT, H.S. 1969. Untersuchungen zum Schwefelhaushalt Schlewig-Holsteiner Böden. Inaug.Diss.Hoh.Landw.Fak.Christian-Albrechts Univ.Kiel, pp.1-184.

(85) HADDAD, G. 1969. Proposition d'une classification des rizières aquatiques de la Casamance. Agr.Trop.XXIV:392-402.

(86) HANNERZ, E. 1932. Om så kallade alunjordar. Ber.verksamheten vid Kemisk-Växtbiologiska Anst.och Frönkontrollanst. i Lülea. 1929-1932, pp.114-138.

(87) HARMSEN, G.W. 1938. Biologische ijzeromzettingen in de grond. Chem.Weekbl. 35:495-500.

(88) HARMSEN, G.W. 1954. Observations on the formation and oxidation of pyrite in the soil. Plant & Soil 5:324-348.

(89) HART, M.G.R. 1959. Sulphur Oxydation in tidal mangrove soils in Sierra Leone. Plant & Soil 11:215-236.

(90) HART, M.G.R. 1962. Observations on the source on acid in empoldered mangrove soils. I. Formation of Elementar Sulphur. Plant & Soil 17:87-98.

(91) HART, M.G.R. 1963. Observations on the source of acid in empoldered mangrove soils. II. Oxidation of Soil Polysulphides. Plant & Soil 19:106-114.

(92) HART, M.G.R. ÇARPENTER A.J., JEFFERY, J.W.O. 1963: Problems in reclaiming saline mangrove soils in Sierra Leone. Agron.Trop.18:800-802.

(93) HERBILLON, A.J., PECROT, A., VIELVOYE, L. 1966. Aperçu sur la minéralogie des fractions fines de quelques grands groupes de sols du Vietnam. Pedologie (Gent) 16:5-16.

(93a)HERVIEU, J. 1968. Contributions à l'étude de l'alluvionnement en milieu tropical. Mém.ORSTOM 24:1-465.

(94) HESSE, P.R. 1961. The decomposition of organic matter in a mangrove-swamp soil. Plant & Soil 14:249-263.

(95) HESSE, P.R. 1961. Some differences between the soils of Rhizophora and Avicennia mangrove swamps in Sierra Leone. Plant & Soil 14:335-346.

(96) HESSE, P.R. 1962. Phosphorus fixation in mangrove swamp muds. Nature 193: 295-296.

(97) HESSE, P.R. 1963. Phosphorus relationships in a mangrove-swamp mud with particular reference to aluminium toxicity. Plant & Soil 19:205-218.

(98) HESSE, P.R., JEFFERY, J.W.O. 1963. Some properties of Sierra Leone mangrove soils. Agr.Trop.18:803-805.

(99) HISSINK, D.L. 1935. De bodemkundige gesteldheid van de achtereenvolgens ingedíjkte Dollarpolders. Bijdrage tot de kennis van het verouderingsproces van de zware zeekleigronden. Versl.Landbouwk.Onderz. No.41-B:47-172.

(100) HOLST, A.F.van, WESTERVELD, C.J.W. 1973. Corrosion of concrete foundations in potential acid sulphate soils and subsoils in The Netherlands. Proc.Int. Symp.on acid Sulphate Soils. Vol.II. Wageningen.

(101) HORN, M.E., HALL, V.L., CHAPMAN, S.L., WIGGINS, M.M. 1967. Chemical Properties of the Coastal Alluvial Soils of the Republic of Guinea. Soil Sci.Soc.Amer.Proc.31:108-114.

(102) HORN, M.E., CHAPMAN, S.L. 1968. Clay mineralogy of some acid sulphate soils on the Guinea coast. Trans. 9th Int.Congr.Soil Sci.Adelaide III:31-40.

(103) HUBERMAN, M.A. 1959. Sylviculture de la mangrove. Unasylva 13:188-197.

(104) JACQ, V.A. 1971. Recherches préliminaires concernant la sulfato-réduction rhizosphérique et la sulfatoréduction spermosphérique. Thèse Doc.Spéc.Nancy ORSTOM.

(105) JACQ, V.A. 1973. Biological sulphate reduction in the spermosphere and the rhizosphere of rice in some acid sulphate soils of Senegal. Proc.Int.symp. on Acid Sulphate Soils. Vol.II. Wageningen.

(106) JACQUES FELIX, H., CHEZEAU, R. 1960. Sols et groupements végétaux de la zone littorale de Guinée dans leur rapport avec la riziculture 1. L'Ile du Kabak. Agr.Trop.XV:325-341.

(107) JACQUES FELIX, H., CHEZEAU, R. 1960. Sols et groupements végétaux de la zone littorale de Guinée dans leur rapport avec la riziculture 2. La région du Koba. Agr.Trop.XV:609-623.

(107a) JAKOBSEN, B., JENSEN, K.L.M. 1956. Undersögelser verdrörende landvindingsmetoder i det Danske Vadehav. Geogr.Tidsskr.55:21-61.

(107b) JANSSEN, B.H., KAMERLING, G.E. 1964. Een onderzoek naar de consistentie, de de stabiliteit en de rijping van enkele kleigronden in de kustvlakte van Suriname. Landb.Proefstation Paramaribo. Intern.rapport No.18.

(108) JEFFERY, J.W.O. 1963. Fertilizer trials on Sierra Leone swamp rice soils. Agr.Trop.18:806-810.

(109) JORDAN, H.D. 1957. Crabs as pests of rice on tidal swamps. The Emp.J. of Exp.Agric. 25:197-206.

(110) JORDAN, H.D. 1959. The utilization of saline mangrove soil for rice growing. Proc.2nd Interafr.Soils Conf., pp.327-331.

(111) JORDAN, H.D. 1963. Development of mangrove swamp areas in Sierra Leone. Agr.Trop.18:798-799.

(112) JORDAN, H.D. 1963. The vegetation of mangrove swamp in West Africa. Agr. Trop.18:796-797.

(113) JORDAN, H.D. 1964. The Relation of vegetation and soil to development of mangrove swamps for rice growing in Sierra Leone. J.Appl.Ecol.1:209-212.

(114) KANAPATHY, K. 1966. Acid swamp soils and problems in their utilization. Proc.2nd Malaysian Soils Conf., pp.209-213.

(115) KANAPATHY, K. 1973. Reclamation and improvement of acid sulphate soils in West Malaysia. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(116) KAWAGUCHI, K., KYUMA, K. 1969. Lowland rice soils in Thailand. Natural Sc Ser. N-4. Centre for S.E.Asian Studies, Kyoto Univ. pp.1-270.

(117) KAWALEC, A. 1973. World distribution of acid sulphate soils. References and Map. Proc.Int.Symp.on Acid Sulphate Soils. Vol.I. Wageningen.

(118) KEVIE, W.van der. Morphology, genesis, occurrence and agricultural potential of acid sulphate soils in Central Thailand. Thai J.Agric.Sci.5:165-182.

(119) KEVIE, W.van der. 1973. Physiography, classification, and mapping of acid sulphate soils. Proc.Int.Symp.on Acid Sulphate Soils. Vol.I. Wageningen.

(120) KIVINEN, E. 1938. Über die Eigenschaften der Gyttjaböden. Bodenk.Pflanzenernährung 9/10:122-134.

(121) KIVINEN, E. 1939. Soil Maps No.12. Expl.text. 73 p. Helsinki. (In Finnish)

(122) KIVINEN, E. 1944. Sulfat-eller alunjordar, deras egenskaper och synpunkter pa deras odling. Sv.Vall och Mosskultur fören. Tidskr.6:152-164.

(123) KIVINEN, E. 1949. Über Sulfatböden in Finnland. Z.Pflanzenernährung & Düngung 45:38-40.

(124) KIVINEN, E. 1950. Sulphate soils and their management in Finland. Fourth Int. Congress Soil Sci. Amsterdam. II:259-262.

(125) KIVINEN, E. 1960. Über die Moore Finnlands und ihre Nützung. Wasser&Boden 1:2-6.

(126) KOBAYASHI, T. 1939. Reclamation of barren polder soil in Ibaragi Prefecture Special Rept. Ibaragi Agric.Exp.Sta. 3 (in Jap.)

(127) KOBAYASHI, T. 1952. Studies on the law productive soils in reclaimed lands. 5. The soils in the Hane-Ko polder in Shimane prefecture. J.Sci.Soil Manure. 293-296. (In Jap.)

(128) KOUTLER-ANDERSSON, E., TOMLINSON, T.E., VAHTRAS, K., WIKLANDER, L. 1956. Studies on Gyttja Soils. V. Description of a hydrologic profile series. Ann. R.Agric.Coll.22:279-295.

(128a) KOVDA, V.A. 1965. Alkaline Soda-Saline soils. Proc.Symp.on Sodic Soils. Budapest 1964. Agrokémia és Talajtan 14:15-48.

(129) LAFOND, L.R. 1957. Aperçu sur la sédimentologie de l'estuaire de la Betsiboka. Rev.de l'Ind.fr.du Pétrole. XII. 4:425-431.

(130) LAW WEI MIN. 1971. The Generalized Soil Map of West Malaysia. Dept. of Agric. West Malaysia, unpubl.

(131) LEVEQUE, A. 1961. Mémoire explicatif de la carte des sols de terres basses de Guyane Française. Mém.ORSTOM 3:1-88.

(132) LEVEQUE, A. 1964. Facteurs de la stabilité structurale des sols dévelopés sur alluvions marines en Guyane Française. Cah.Pédol.ORSTOM 2:13-21.

(133) LYNN, W.C., WHITTIG, L.D. 1966. Alteration and formation of clay minerals during cat clay development. Clays & Clay Min.Proc.14th Nat.Conf.26:241-248.

(134) MARILLONET, L. 1953. Problème de mise en valeur des polders aux Pays-Bas. Agr.Trop.VIII:5-71.

(135) MARIUS, C. 1965. Etude pédologique de la feuille au 1:50 000 Cayenne. Centre ORSTOM de Cayenne. Rapport p.82. Mimeo. Map.

(136) McLUSKIE, H. 1952. The reclamation of the mangrove swamp areas for rice cultivation. World Crops. 4:129-132.

(137) MOHR, E.C.J., BAREN, F.A.van, SCHUYLENBORGH, J.van. 1972. Tropical Soils. Part II. Cahpter 4.2 (Acid sulphate soils), pp.374-396. Mouton-Ichtiar Baru - van Hoeve.

(138) MOHR, W. Estudo critico do valor pH e das suas causas determinaentes para a avaliacao da productividade dos solos do Rio Grande do Sul. Anais de Associacao Brasileira de Quimica.

(139) MONTAGNE, D.G. 1964. New facts on the geology of the young, unconsolidated sediments of Northern Surinam. Geol.Mijnb. 43:499-515.

(140) MOORMANN, F.R. 1959. Le problème des sols alluviaux acides au Vietnam. Causeries sur le développement des Res.Nat. au Vietnam.

(141) MOORMANN, F.R. 1959. Notes sur les conditions pédologiques de la genèse de la plaine des Joncs. Agr.Library. Saigon, pp.1-34.

(142) MOORMANN, F.R. 1961. Les sols de la République du Viet-Nam. Min.of Agric., Saigon.

(143) MOORMANN, F.R. 1961. Researches on Acid Sulphate Soils and their amelioration by liming. Min. of Kural Affairs, Agronomic Library, Saigon.

(144) MOORMANN, F.R. 1961. Note explicative de la carte génerale des sols du Vietnam. Rép.du Vietnam.

(145) MOORMANN, F.R. 1963. Acid Sulphate Soils of the Tropics. Soil Sci.95:271-275.

(146) MOORMANN, F.R. 1964. Morphology, genesis and occurrence of acid sulphate soils (Cat clays) in deltas of the Humid Tropics. Act.Col.Dacca.UNESCO,pp. 103-106.

(147) MULLER, H.J. 1950. On the occurrence of Katteklei (Cat clay) in Surinam. Caribbean Soils Conference, Puerto Rico.

(148) MURAKAMI, H. 1967-1968. Characteristics and improvement of acid sulphate soils. I.-V. J.Sci.Soil Manure Japan 38:112-120;39:116-120,194-198,514-519.

(148a) ORLOVSKII, N.V. 1965. Genesis and utilization of salt-affected soils in Siberia (in Russian). Proc.Symp.on Sodic Soils, Budapest, 1964. Agrokémia és Talajtan 14:155-174.

(149) PENDLETON, R.L. 1947. The formation, development and utilization of the soils of the Bangkok Plain. Siam.Soc.Nat.Hist.Bull. 14:1-41.

(150) PENDLETON, R.L. 1949. Soil map of the Kingdom of Thailand. Min.Agric.Bangkok.

(151) PHAM-HUU-ANH, MOORMANN, F.R., GOLDEN, J.D. 1961. Liming experiments on acid sulphate soils. Agron.Library, Saigon, pp.19-52.

(152) POELMAN, J.N.B. 1973. Soil material rich in pyrite in non-coastal areas. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(153) PONNAMPERUMA, F.N., TIANCO, E.M., LOY, T. 1967. Redox equilibria in flooded soils. I. The iron hydroxides systems. Soil Sci. 103:374-382.

(154) PONNAMPERUMA, F.N., TASNEE ATTANANDANA, GORA BEYE. 1973. Amelioration of three acid sulphate soils for lowland rice. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(155) PONS, L.J. 1956. Some aspects of the improvement of pyrite-containing old marine soils in The Netherlands. Transact.6ème Int.Congr.de la Science du Sol. B:727-734.

(156) PONS, L.J., WIGGERS, A.J. 1959. The Holocene genesis of the Province of North Holland and the former Zuider Sea Region. Tijdschr.Kon.Ned.Aardr.Genootsch.74:104-152.

(157) PONS, L.J. 1960. Soil genesis and classification of reclaimed peat soils in connection with initial soil formation. Transact.7th Int.Congr.of Soil Sci.4:205-211.

(158) PONS, L.J. 1964. A quantitative microscopical method of pyrite determination in soils. In: Soil Micromorphology. Ed.A.Jongerius. Elsevier Publ.Co.,Amsterdam, pp.401-409.

(159) PONS, L.J. 1965. Pyrites as a factor controlling chemical "ripening" and formation of "Cat Clay" with special reference to the Coastal Plain of Suriname. Landb.Proefst.Suriname Bull.82:141-162.

(160) PONS, L.J., ZONNEVELD, I.S. 1965. Soil ripening and soil classification. Initial soil formation in alluvial deposits and a classification of the resulting soils. ILRI Bull.13:1-128. Wageningen.

(161) PONS, L.J. 1966. Geogenese en pedogenese in de jong-holocene kustvlakte van de drie Guyanas. Tijdschr.Kon.Ned.Aardr.Genootsch.83:153-172.

(162) PONS, L.J., KEVIE, W. van der. 1969. Acid sulphate soils in Thailand. Soil Survey Rept. Land Dev.Dept. SSR-81:1-65. Bangkok.

(163) PONS, L.J. 1973. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils. Proc.Int.Symp.on Acid Sulphate Soils. Vol.I. Wageningen.

(164) PUROKOSKI, P. 1956. Förekomst och föreningar av svavel i gyttjalera. Nordisk Jordbruksforskning 38:263-266.

(165) PUROKOSKI, P. 1958. Die schwefelhaltigen Tonsedimenten in dem Flachlandgebiet von Liminka im Lichte chemischer Forschung. Agrogeol.Publ.70:1-88.

(166) PUROKOSKI, P. 1959. The effect of liming on the sulphate soils of the Finnish coast. Agrogeol.Publ.72:1-21. (Finnish, German summary)

(167) PUROKOSKI, P. 1959. The sulphate soils of the Finnish coast. Agrogeol.Publ. 74:1-27.

(168) PUROKOSKI, P. 1959. "Pikileerin" levinneisyydestä rannikkoalueella. Eripainos Maasendun Tulevaisuuden lütteestä Koetoiminta ja Käytäntö No.3.

(169) QUADIR, A. 1951. The Kosh soils of the Chittagong Coastal Area, East Pakistan. Unpublished Report.

(170) QUISPEL, A., HARMSEN, G.W., OTZEN, D. 1952. Contribution to the chemical and bacteriological oxidation of pyrite in soil. Plant & Soil 4:43-55.

(171) RASMUSSEN, K. 1961. Transformation of inorganic sulphur compounds in soil. Diss.Veterinaer- og landbohöjskole, Köbenhavn.

(172) RIEDEL, C.E. 1959. Les sols alluviaux maritimes. Mer du Nord-Manche-Océan Atlantique. Ann.Agron.Paris. 10:543-598.

(173) REIJNDERS, J.J. 1961. The landscape in the Maro- and Koembe-river district. Boor en Spade XI:104-119.

(174) ROBINSON, G.H. 1963. Soils Survey of the Bartica Area. Report FAO, Rome.

(175) ROCHE, P., RIQUIER, J., HERVIEU, J., MOUREAUX, C., AMAND, R.D.de S. 1959. Les osols à riz et leur problèmes à Madagascar. Mém.de l'Inst.Sci.de Mad., D:75-90.

(176) ROQUERO DE LABURU, C., GARCIA-CASAL, J. 1973. Acid sulphate soils of Banhado do Taim. Rio Grande do Sul, Brazil. (In Spanish.) Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(177) SCHLICHTING, E., WIKLANDER, L. 1956. Studies on gyttja soils. IV. Kurze Mitteilung über die Bindung des Kupfers in einigen Profilen. Ann.R.Agric. Coll. 22:93-99.

(178) SCHMID, M. 1964. Aperçu sur la végétation occupant les alluvions récentes de la partie méridionale de l'Indochine. Act.Col.Dacca.UNESCO, pp.235-241.

(179) SCHWERTMANN, U. 1961. Über das Vorkommen und die Entstehung von Jarosit in Marschböden (Maibolt). Naturwissenschaften 48:159-160.

(180) SCHROEDTER, E. 1930. Das Vorkommen freier Schwefelsäure in einem Grundwasserboden. Chem.Erde 4:70-75.

(181) SEGEBERG, H. 1937. Die Azidität der Moorböden insbesondere die durch Ferrodisulfid hervorgerufene, und ihre analytische Bestimmung. Bodenkde & Pflanzenernährung 4:50-64.

(182) SILVA TEIXEIRA, A.J.da 1959. The Soils of Portuguese Guinea. Proc.3rd Interafr.Soils Conf. I:467-477.

(183) SLAGER, S., SCHUYLENBORGH, J.van. 1970. Morphology and geochemistry of three clay soils of a tropical coastal plain (Surinam). Versl.Landbk.Onderz. 734:1-34. Wageningen.

(184) SOMBATPANIT, S. 1970. Acid sulphate soils - Their nature and properties. Unpubl.Thesis. Royal Agric.Col.Uppsala, pp.1-135.

(185) SPEK, J.van der. 1934. Bijdrage tot de kennis van zure gronden van het Nederlands alluvium. Versl.Landbouwk.Onderz.40 B:409-503. Groningen.

(186) SPEK, J. van der. 1950. Katteklei. Verslagen Landbouw.Onderz.56.2, pp.1-40.

(187) SPEK, J. van der. 1952. The loss of $CaCO_3$ from sea clay deposits by oxidation of sulphides. Landbouwk.Tijdschr.64:473-478. (In Dutch)

(187a) STEPHENS, C.G. 1961. The soil landscapes of Australia. CSIRO Melbourne. Soil Publ. No.18:1-43.

(188) SUBRAMANYAN, V. 1952. Kari Soils, their problems and reclamation. Travancore, Cochin, India. Unpubl. Report.

(188a) TANAKA, A., NAVASERO, S.A. 1966. Growth of the rice plant on acid sulphate soils. Soil Sci.& Plant Nutr. 12:107-114.

(189) TEAKLE, L.J.H., SOUTHERN, B.L. 1937. The peat soils and related soils of Western Australia. II. A Soil Survey of Herdsman Lake. J.Dept.Agric.W. Austr.14:404-424.

(190) THORNTON, I., GIGLIOLI, M.E.C. 1965. The mangrove swamps of Keneba, Lower Gambia river basin. II. Sulphur and pH in the profiles of swamp soils. J.Appl.Ecol.2:257-269.

(190a) THORP, J. 1935. Geographic distribution of the important soils of China. Bull. of the Geol.Soc.of China. Vol.XIV, No.2.

(191) TOMLINSON, T.E. 1957. Relationship between mangrove vegetation, soil texture and reaction of surface soil after empoldering saline swamps in Sierra Leone. Trop.Agric. (Trin.) 34:41-50.

(192) TOMLINSON, T.E. 1957. Seasonal variations of the surface pH values of some rice soils of Sierra Leone. Trop.Agric.(Trin.) 34:287-294.

(193) TOMLINSON, T.E. 1957. Changes in sulphide containing mangrove soil and their effect upon suitability of the soil for the growth of rice. Emp.J. Exp.Agric. 25:108-118.

(194) TORSTENSSON, G., ERIKSSON, S. 1938. Studien über die Festlegung der Phosphorsäure in Gyttjaböden. Ann.R.Agric.Coll.5:377-403.

(195) TURENNE, J.F. 1967. Rapport explicatif de la carte pédologique au 1:50 000 du littoral guyanais entre Sinnamary et Iracoubo. Rapport Centre ORSTOM de Cayenne. Mimeo. Map.

(196) VERHOEVEN, B. 1973. Acid sulphate soils in the Wieringermeerpolder, a good 40 years after reclamation. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(197) VIEILLEFON, J. 1968. Etude des variations du pH et du RH dans les sols de mangroves de Basse Casamance. Comm.6e Congrès West Afr.Sc.Ass.,Abidjan.

(198) VIELLEIFON, J. 1969. La pédogenèse dans les mangroves tropicales, un exemple de chronoséquence. Science du Sol 2:115-148.

(199) VIEILLEFON, J. 1971. Rôle du soufre dans la pédogenèse et l'évolution des caractères physio-chimiques dans les sols hydromorphes littoraux des régions tropicales. Comm.Réun.Conf.AISS. Stuttgart.

(200) VIEILLEFON, J. 1971. Contribution à l'étude du cycle du soufre dans les sols de mangroves. Cahier ORSTOM, Série Pédol.IX:3-24.

(201) VIEILLEFON, J. 1973. Sur quelques transformations sédimentologiques et minéralogiques dans les sols sulphatés acides du Sénégal. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(202) VIRCHOW, K. 1880. Das Kehdinger Moor. Landw. Jahrbücher 9.

(203) VIRCHOW, K. 1883. Das Kehdinger Moor. Landw. Jahrbücher 12:83-128.

(204) VLEK, P. 1971. Some morphological, physical and chemical aspects of acid sulphate soils in Thailand. Land Dev.Dept.Report SSR 84:1-37. Bangkok.

(205) VUORINEN, J. 1959. Soil Maps No.16. Explanatory Text. Helsinki.

(206) WALKER, P.H. 1960. Soil investigations in the Alumy Creek - Great Marlow Area Grafton, N.S.W. CSIRO Div.Soils Techn.Memo No.6/60.

(207) WALKER, P.H. 1961. Groundwater characteristics of the Kempsey district, N.S.W. CSIRO Div.Soils Devel. Report No.1/61.

(208) WALKER, P.H. 1963. A reconnaissance of soils in the Kempsey district, N.S.W. CSIRO Austr.Soils and Land Use Ser. No.44.

(209) WALLENBURG, C. 1973. Cat clay and potential cat clay in inland polders. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(210) WATTS, J.C.D. 1960. Sea Water as the primary source of sulphate in tidal swamp soils from Sierra Leone. Nature 186:308-309.

(211) WATTS, J.C.D. 1965. Liming the local acid sulphate soils. Invest.Tpt. Trop.Fish Cult.Res.Inst.1:1-4.

(212) WATTS, J.C.D. 1965. The chemical analysis of muds from the pond system of the Tropical Fish Culture Research Institute. Invest.Tpt.Trop.Fish Cult. Res.Inst.3:1-9.

(213) WATTS, J.C.D. 1968. A comparison of some conventional methods for estimating available phosphate in acid sulphate type pond muds. Malayan Agric.J. 46:244-251.

(214) WATTS, J.C.D. 1968. Phosphate relationships in acid sulphate soils from the Malacca area. Malayan Agric.J.46:252-269.

(215) WATTS, J.C.D. 1968. Changes in the available phosphate (Olson's) in acid sulphate pond muds from the Malacca area. Malayan Agric.J.46:476-484.

(216) WESTERVELD, C.J.W., HOLST, A.F.van. 1973. Detailed soil survey and its application in areas with actual and potential acid sulphate soils in The Netherlands. Proc.Int.Symp.on Acid Sulphate Soils. Vol.II. Wageningen.

(217) WIJK, C.L.van. 1951. Soil Survey of the Tidal Swamps of South Borneo. Contr. Gen.Agric.Res.St.Bogor, Indonesia. No.123:1-49.

(218) WIKLANDER, L., HALLGREN, G. 1949. Studies on gyttja soils. I. Distribution of different sulphur and phosphorus forms and of iron, manganese, and calcium carbonate in a profile from Kungsängen. Ann.R.Agric.Coll.16:811-827.

(219) WIKLANDER, L., HALLGREN, G., BRINK, N., JONSSON, E. 1950. Studies on Gyttja Soils II. Some characteristics of two profils from Northern Sweden. Ann.R.Agric.Coll.17:24-36.

(220) WIKLANDER, L., HALLGREN, G., BRINK, N., JONSSON, E. 1950. Studies on Gyttja Soils III. Rate of sulfur oxidation. Ann.R.Agric.Coll.17:425-440.

(221) WILSHAW, R.G.H. 1940. Note on the development of high acidity in certain coastal clay soils of Malaya. Malayan Agric.J.28:352-357.

(222) WIND, G.P., STEEGHS, B.H. 1964. Kattezand. Landbouwk.Tijdschr.76:150-157.

(223) YONEDA, S., KAWADA, N. 1954. A study on polder soils in Japan. (5) A note on the forming process of the strong acid found in halogenetic polders. J.Sci.Soil Manure 25:36-40. (In Jap.)

(224) YONEDA, S. 1964. Genetic and edaphologic studies of the polder soils in Japan. Rept.Fac.Agric.Okayama Univ.No.8:1-183. (In Jap.)

(225) YONEDA, S. 1966. Oxidizable Sulphur contents and acid sulphate soils in improvement of saline lands in Japan. Int.Comm.on Irrig.Drain. Trans.2, 6th Congress, New Delhi.

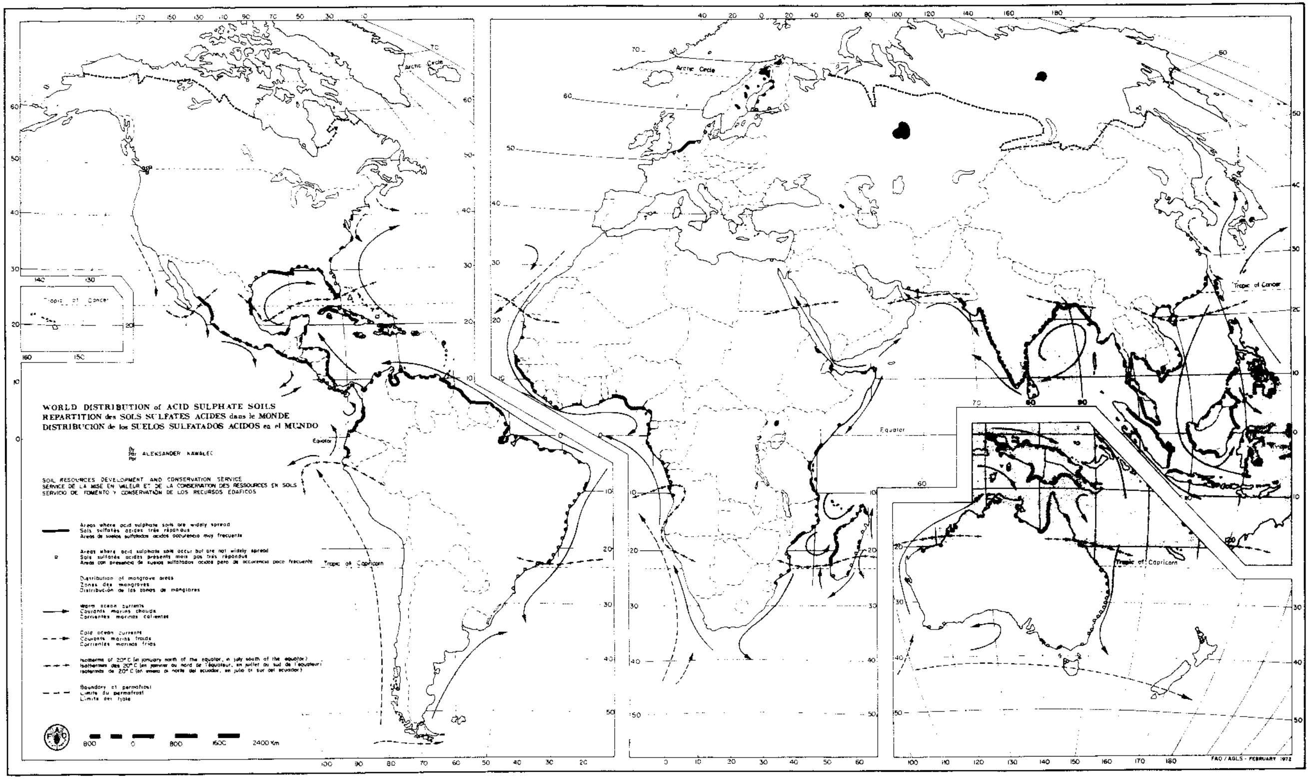
(226) ZONNEVELD, I.S. 1961. De minerale alluviale gronden. In: Bodemkunde. Voordrachten gehouden op de B-cursus Bodemkunde, pp.194-218. Min.van Landbouw en Visserij. Den Haag. (In Dutch).

(227) ZONNEVELD, I.S. 1963. Soil Formation in deltaic Areas. App.I of the Proceedings, Reg.Symposium Flood Control, etc. of Deltaic Areas. ECAFE. Water Resources Series 25:106-128.

(228) ZUUR, A.J. 1952. Drainage and reclamation of lakes and of the Zuiderzee. Soil Sci.74:75-89.

(229) ZUUR, A.J. 1954. Bodemkunde der Nederlandse bedijkingen en droogmakerijen. (Soil Science of the Dutch endykements and polders. Transl. by F.Tijsen and V.S.Aranovici. Oct.1958.)

(230) ZUUR, A.J. 1961. Initiële bodemvorming bij mariene gronden. (Initial Soil Formation in Marine Soils.) Meded.van de Landbouwhogeschool en de Opzoekingsstations van de Staat te Gent, 26:7-33.



WORLD DISTRIBUTION of ACID SULPHATE SOILS
REPARTITION des SOLS SULFATES ACIDES dans le MONDE
DISTRIBUCION de los SUELOS SULFATADOS ACIDOS en el MUNDO

By
Par ALEKSANDER KAWALEC
Por

SOIL RESOURCES DEVELOPMENT AND CONSERVATION SERVICE
SERVICE DE LA MISE EN VALEUR ET DE LA CONSERVATION DES RESSOURCES EN SOLS
SERVICIO DE FOMENTO Y CONSERVATION DE LOS RECURSOS EDAFICOS

WORLD DISTRIBUTION OF ACID SULPHATE SOILS. REFERENCES AND MAP

Presented by
A.Kawalec
FAO, Rome

Note of the editor

On behalf of FAO, A.Kawalec presented the World Map of Acid Sulphate Soils prepared by himself on the basis of an intensive study of the relevant literature. The study resulted moreover, in a treatise on acid sulphate soil phenomena roughly along the line of the symposium's program, and was completed with a list of 224 references to the literature consulted.

Due to its volume, the complete documentation to the map cannot be incorporated in these proceedings. The map has been printed on page 292. The bibliography was combined with other overlapping literature compilations into the "Bibliography on Acid Sulphate Soils 1863-1973", pp.275-291 of this volume. For cross reference between this latter mentioned bibliography and the World Map of Acid Sulphate Soils the following list was prepared also largely with data from Kawalec's treatise.

GEOGRAPHICAL REFERENCES PERTAINING TO THE WORLD MAP OF ACID SULPHATE SOILS PREPARED FOR FAO BY A.KAWALEC

The numbers enter parenthesis behind author's names refer to the Bibliography on page 275.

AFRIKA

GAMBIA: Giglioli c.s. 1965 (80); Thornton c.s. 1965 (190)

GUINEA: Bonfils 1950 (30); Dost c.s. 1969 (62); Horn c.s. 1967, 1968 (101, 102); Jacques Félix c.s. 1960 (106, 107)

GUINEA BISSAU: Silva Teixeira 1959 (182)

MADAGASCAR: Coutinet c.s. 1966 (54); Durand 1967 (67); Hervieu 1966 (93a); Lafond 1957 (129); Roche c.s. 1959 (175)

SENEGAL: Gaucher 1967 (77); Gora Beye 1973 (81); Hadad 1969 (85); Jacq 1973 (105); Vieillefon 1968, 1969, 1971, 1973 (197/201)

SIERRA LEONE: Anonyme 1954 (10); Dent 1947 (57); Dijkerman 1969 (60); Doyne c.s. 1933, 1937 (63, 64); Hart c.s. 1959, 1962, 1963, 1965 (89/92); Hesse c.s. 1961, 1962, 1963 (94/98); Jeffery 1963 (108); Jordan 1957, 1959, 1963, 1964 (109/113); Tomlinson 1957 (191/193); Watts 1965 (210)

UGANDA: Chenery 1954 (40)

ASIA

BANGLADESH: Beers 1955 (16); Quadir 1951 (169)

BRUNEI: Blackburn c.s. 1958 (26)

CHINA: Thorp 1935 (190a)

HONG KONG: Grant 1973 (82)

INDONESIA: Beers 1949 (15); Driessen c.s. 1973 (65); Reijnders 1961 (173); Wijk 1951 (217)

JAPAN: Kobayashi c.s. 1939, 1952 (126, 127); Murakami 1967/68 (148); Tanaka c.s. 1966 (188a); Yoneda c.s. 1954, 1964, 1966 (223/225)

MALAYSIA: Allbrook 1973 (7); Andriesse c.s. 1973 (9); Bloomfield c.s. 1968 (27); Coulter 1952, 1968 (51, 52); Dennet 1932, 1933 (56, 57); Kanapathy 1966, 1973 (114, 115); Law Wei Min 1971 (130); Watts 1965, 1968 (211/215); Wilshaw 1940 (221)

THAILAND: Breemen c.s. 1973 (36); Dent 1968 (54); Kawaguchi c.s. 1969 (116); v.d.Kevie 1973 (118, 119); Pendleton 1947, 1949 (149, 150); Pham Huu Anh c.s. 1961 (151); Pons c.s. 1969 (162); Sombatpanit 1970 (184); Vlek 1971 (204)

U.S.S.R.: Orlovskij 1965 (148a)

VIETNAM: Auriol 1934 (13); Herbillon c.s. 1966 (93); Moormann 1959, 1964 (140/146); Subramanyan 1952 (188)

EUROPE

DANMARK: Rasmussen 1961 (171)

FINLAND: Aaltonen 1949 (1); Aarnio 1938, 1939, 1944, 1949, 1950, 1960 (120/125)

GERMANY: Benzler 1973 (23); Brümmer c.s. 1968, 1971 (40/42); Buurman c.s. 1973 (44); Grunwaldt 1969 (84); Schwertmann 1961 (179); Schroedter 1930 (180); Segeberg 1937 (181); Virchow 1880, 1883 (202, 203)

NETHERLANDS: van Bemmelen 1863, 1866, 1886 (18/20); Bennema 1953 (21, 22); Edelman 1948, 1950 (68, 69); Harmsen c.s. 1938, 1954 (86, 87); Hissink 1935 (99); Holst c.s. 1973 (100); Marillonet 1953 (134); Poelman 1973 (152); Pons c.s. 1956, 1959, 1960 (155/157); Quispel c.s. 1952 (170); van der Spek 1934, 1950, 1952 (186/188); Wallenburg 1973 (209); Westerveld c.s. 1973 (216); Wind c.s. 1964 (222); Zonneveld 1961, 1963 (226, 227); Zuur 1952, 1954, 1961 (228/230)

SWEDEN: Hannerz 1932 (86); Schlichting c.s. 1956 (177); Torstensson c.s. 1938 (194); Wiklander c.s. 1949, 1950 (218/220)

U.S.S.R.: Kovda 1965 (128a)

AUSTRALIA

AUSTRALIA: Stephens 1961 (187a); Teakle c.s. 1937 (189); Walker 1960, 1961, 1963 (206/208)

NEW ZEALAND: Gibbs c.s. (79)

NORTH AMERICA

CANADA: Clark c.s. 1961 (50)

U.S.A.: Edelman c.s. 1958 (70); Flemming c.s. 1961 (74); Ford c.s. 1970 (75); Grass c.s. 1962 (83)

SOUTH AMERICA

BRAZIL: Mohr (138); Roquero de Laburu c.s. 1973 (176)

GUIANA: Ahmad 1960 (6); Applewhite 1964 (11); Brinkman c.s. 1964, 1968 (36, 37); Cate c.s. 1964, 1965 (45, 46); Evans c.s. 1962 (72); Gasser 1961 (76); Pons 1966 (161); Robinson 1963 (174)

FRENCH GUIANA: Boyé 1962 (31); Brinkman c.s. 1968 (37); Lévêque 1961, 1964 (131, 132); Marius 1965 (135); Pons 1966 (161); Turenne 1967 (195)

SURINAM: Amson 1966 (8); Augustinus c.s. 1971 (12); Brinkman c.s. 1968 (37); Brugière c.s. 1963 (39); Eijck 1957 (73); Muller 1950 (147); Pons c.s. 1965, 1966 (159/161)