

NN31545.1821

ICW note 1821

november 1987



nota

— instituut voor cultuurtechniek en waterhuishouding, wageningen. —

MODELLING PHYSICAL AND CHEMICAL
PROCESSES IN ACID SULFATE SOILS

Analysis of important parameters and
first outline of simulation model

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JSN 264700 *

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1. INTRODUCTION

Reclamation and drainage of potential acid sulphate soils leads to aeration, oxidation of pyrite and acidification. High acidity and corresponding Al toxicity restricts or inhibits crop growth on these soils. Flooding eventually stops acidification but other problems, for instance Fe toxicity, occur.

From the start of reclamation, the water regime is a dominant factor in the chemical processes that occur in (potential) acid sulphate soils. At first the net water extraction determines the rate of ripening of a potential acid sulphate soil, and therefore the entry of oxygen into the soil matrix. When an actual acid sulphate soil has developed, water supply (precipitation, flooding) eventually stops acidification and leads to rising of pH. Upon subsequent water extraction (evapotranspiration, drainage), oxidation of pyrite and corresponding acidification starts anew. In all the stages of development, supply of fresh water, leaching and drainage determine the removal of acidity and toxicity from the soil profile.

Water management of acid sulphate soils can either be aimed at total reclamation, i.e. complete oxidation and leaching to remove all acid quickly, or at minimum disturbance, i.e. avoidance of oxidation, in order to produce as little acid as possible. In the second case, leaching may also be indispensable. An important issue during the whole reclamation of acid sulphate soils is the rate with which the several physical and chemical processes take place. For instance, when it is not possible, even with optimum water management, to oxidize all pyrite and remove all acidity within a few years, total reclamation should not be considered.

The integration of all the mentioned physical and chemical processes into a simulation model offers the opportunity to predict the effects of different water management strategies on production of acidity and toxic compounds. Such a model should predict concentrations of all

major elements over long time periods. In this paper a first outline of such a model is presented. In chapter 2 the elementary chemical processes are described. In chapters 3, 4 and 5, the time dependency of the important physical and chemical processes in acid sulphate soils is analyzed. In chapter 6, a first outline of a simulation model is presented. Finally, in chapter 7, experiments are suggested, both for developing and calibration of a simulation model.

2. CHEMICAL PROCESSES

2.1. Occurrence of pyrite

The ionic composition of soil solutions can vary largely both in time and space. Firstly this is caused by the enormous variety of minerals found in soils, each with its own resistance against physical and chemical weathering processes. Secondly the continuous release of ions into the soil solution as a result of these weathering processes does not guarantee a definite ionic composition because for instance also adsorption, precipitation, complexation and transport processes do take place. However, the ionic composition of most soil solutions can be explained by the behaviour of one or a couple of minerals which are present in relatively large amounts. Sometimes a mineral which is present only in minor amounts, such as pyrite in acid sulfate soils, can influence soil chemical behaviour in particular.

Pyrite is stable only under submerged conditions. Oxidation of this mineral can cause a seriously decrease in soil pH (RITSEMA, 1986) so knowledge of the stability of pyrite is essential in understanding the occurrence of such processes. In figure 1 a stability diagram is shown from which it can be concluded that pyrite is stable under a wide range of pH but only under low p_e conditions. The parameter p_e expresses the negative logarithm of the electron activity. A high value of p_e corresponds with strongly oxidised conditions, a low one with reduced. The relations and assumptions used in constructing figure 1 are summarized and worked out in appendix 1. Further it can be seen from figure 1 that jarosite, which is commonly found in association with decomposing pyrite, can only be formed under strongly acid, oxidised circumstances. Goetite is produced by the oxidation of iron-bearing minerals such as pyrite or magnetite. Goetite has a wide distribution, ranging from the tropics to the arctic and is one of the main colouring substances in soils: Hematite has a widespread occurrence in sedimentary rocks in which it may be of primary origin or as a secondary mineral, precipitated from iron-bearing percolating waters and replacing other minerals such as pyrite. Transformation of goetite to hematite is a very slow process (LANGMUIR, 1971). Hematite varies in colour between steel-grey to bright red and occurs chiefly in soils of tropical and subtropical areas in old geological formations.

Ferrichydroxide, an amorphous yellowish-brown substance, occurs in many non-acid soils in the initial stages of formation.

Field values of redoxpotential and pH can be added to figure 1 in order to investigate which mineral(s) are stable under the measured conditions.

BAAS BECKING et al (1960) have reported numerous redox measurements made in natural environments. Those most frequently measured for soils are shown by the enclosed region on figure 2.

The parameter pe can be converted to Eh according to:

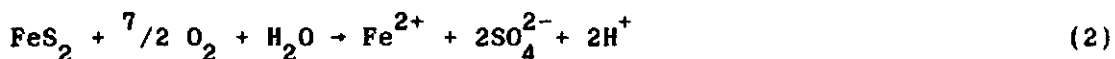
$$59.2 * pe = Eh \quad (1)$$

Most soils fall in the pH range of 3.0 to 9 and in the pe range of -6 to +12. The pe + pH range of most soils lies between 2 and 18.

2.2. Pyrite oxidation

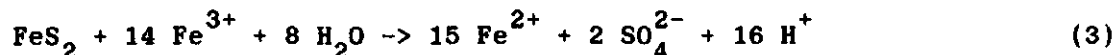
Potential acid sulfate soils become acid as a result of drainage. Pyrite is stable only under anaerobic conditions. Drainage allows oxygen to enter the soil and pyrite is then oxidized, generating sulphuric acid (see figure 3).

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



The above reaction produces H^+ which of course lowers the pH. Some Fe^{2+} may be lost from the soil in drainage waters, and will precipitate under more oxidizing conditions in drains and ditches as Fe^{3+} (hydro)oxides.

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

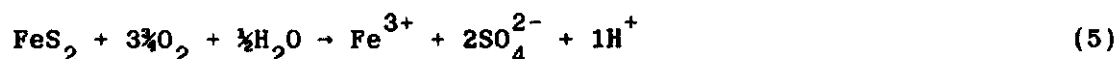


In the presence of oxygen, the Fe^{2+} produced by these reactions is oxidized to Fe^{3+} . At pH values lower than 3.5, chemical oxidation is a slow process with a half time of the order of 1000 days (SINGER and STUMM, 1970). However, autotrophic bacteria, which seem to be ubiquitous in sulphidic and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



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

Combining equations 3 and 4 results in:



If oxidation processes proceeds ultimately jarosite or goetite can be formed, according to reactions 6 and 7:



The different stages of oxidation do not necessarily occur at exactly the same locations in soil. Field and micromorphological examination of acid sulphate soils shows distinct separation of pyrite and its oxidation products: jarosite, iron oxides, and gypsum. In horizons where there is a reserve of pyrite to be oxidized, this is confined to the cores of peds, whereas jarosite and iron oxides and gypsum are closely associated with pores and ped faces.

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

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

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

2.3. Kinetic aspects of pyrite oxidation

Pyrite oxidation is a time dependent process. Factors that influence the rate of pyrite oxidation are the supply of oxygen and ferric iron, the temperature and the total surface area of pyrite per unit of soil. Several authors tried to define rate laws in order to calculate and predict the decrease in pyrite (and the consequently increase in sulfuric acid) as a result of the oxidation of pyrite by dissolved oxygen or by ferric iron in soils.

2.3.1. Pyrite oxidation by ferric iron

WIERSMA en RIMSTIDT (1984) measured rates of reduction of ferric iron by pyrite and marcasite in chloride solutions. Preparation of grain surfaces to avoid anomalous rapid initial rates was not reported. The pyrite was suspended in solution by stirring, so any rate effects due to abrasion of colliding grains are unknown in their experiments. Wiersma and Rimstidt assumed a first-order rate law (see table 1), and determined rate constants by integrating the rate over time according to the assumed law. However, they noted that the derived rate constants decreased with decreasing initial ferric iron concentration. In nearly identical series of experiments, SINGER AND STUMM (1969) noted the same behaviour when they calculated rate constants from an assumed first-order rate law. They consequently rejected a first-order rate law as invalid. For these reasons it is not acceptable to assume a first-order rate law and rate constants calculated from such a law as valid.

Table 1. Rate laws for oxidation of pyrite by ferric iron in low temperature (30°C) acidic solutions.

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

*Rate dependence on ferric ion assumed rather than derived

MATHEWS and ROBINS (1972) studied the oxidation of pyrite-marcasite mixtures by ferric sulfate solutions. They also assumed a first order dependence on ferric iron to derive their rate constant. They concluded that the rate was proportional to the ratio of ferric to total iron, but gave no supporting data. According to their rate law, oxidation in solutions containing no ferrous iron should be independent of

ferric iron concentration. Such behaviour does not agree with the data given by McKIBBEN and BARNES (1986). MATHEWS and ROBINS (1972) rate dependence on pH is nearly identical to that determined in the study of McKIBBEN and BARNES (1986), although the ionic strength may also have been varied with pH in the experiments carried out by MATHEWS and ROBINS (1972).

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

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

2.3.2. Pyrite oxidation by dissolved oxygen

In table 2 different rate laws describing the oxidation of pyrite by dissolved oxygen are shown.

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

SMITH and SHUMATE (1970) did not specifically determine a rate law, but presented enough data for McKibben and Barnes to derive the one shown in table 2.

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

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

*Rate law calculated from their data for $PO_2 < 1$ atm.

To determine rates of oxidation, they measured oxygen consumption rates and assumed that the stoichiometry of this reaction can be applied at all pH values. Recently MOSES (1982) and GOLDBABER (1983) show this assumption to be invalid, because of the persistence of metastable sulfur oxyanions at pH values above about 4. Consequently, some of the rate data of SMITH and SHUMATE (1970) are subject to question. McKIBBEN and BARNES (1986) suggest that a complete reinvestigation of the rate of pyrite oxidation by oxygen is warranted above pH 4. The fact that elemental sulfur or metastable sulfur oxyanions are

not observed as products of pyrite oxidation below pH 4 suggests that the sequential electron transfer reactions forming sulfate from pyrite sulfide are rapid at low pH. However, according to McKIBBEN and BARNES (1986), elucidation of the exact pyrite oxidation mechanisms will probably require high-resolution spectroscopic studies of adsorbed complexes formed on pyrite surfaces. Nevertheless, experimental determined relations describing the rate of pyrite oxidation as a function of dissolved oxygen, ferric iron and/or H^+ concentrations can be a useful tool in modelling the chemical processes taking place in (potential) acid sulfate soils.

3. EFFECT OF WATER REGIME ON OXIDATION AND REDUCTION

Chemical processes that occur in acid sulphate soils depend strongly on the water regime of the soil. First, the water regime plays a dominant role in the genesis of actual acid sulphate soils. Without a change in the water regime, either natural or man-made, a potential acid sulphate soil will not turn into an actual acid sulphate soil. Second, when after some period of oxidation, an actual acid sulphate soil has developed, the water regime determines whether oxidation and thus pH lowering, or reduction and pH rising takes place. In these situations, the water regime also determines the supply of fresh water to the soil and the removal of acid and toxic Al^{3+} and Fe^{2+} concentrations.

Initially an unripened potential acid sulphate soil may have pH values between 5 to 7 (VAN BREEMEN, 1976). Only on natural or artificial drainage the water table lowers, the soil ripenes and air enters the soil through shrinkage cracks or already present root holes and other biopores. On the walls of this macropores, oxygen diffuses into the soil matrix, whereby pyrite is oxidized and acidity produced. In fresh unripe acid sulphate soils, this process leads to rapid acidity production. When, after a period of aeration, the soil is flooded again, pyrite oxidation and acid production may continue for some time, as a result of stored ferric iron during the dry season (VAN BREEMEN, 1976). Eventually, however, oxidation of pyrite and acid production stops in reduced environment. Because of subsequent reduction of organic matter, hydrogen ions are consumed and the pH rises. However, the pH may stay well below 5, even after prolonged flooding (DENT, 1986). Because of pH rising, Al^{3+} activity is reduced. Therefore Al-toxicity decreases some time after flooding. On the contrary, as a second result of flooding different iron oxides and hydroxides get reduced whereby toxic concentrations of ferrous iron can occur.

It is because of these processes that once a potential acid sulphate soil has been aerated for some period, it is quite difficult to maintain pH and both Al^{3+} and Fe^{2+} at acceptable levels. Sufficient leaching is necessary, but leaching also introduces fresh oxygen-rich water into the soil system, which causes further oxidation. So, aeration of a potential acid sulphate can be an irreversible process.

Therefore, when possible, at an early stage a choice should be made between the two principal methods of reclaiming potential acid sulphate soils:

- 1) Minimum disturbance. Limit pyrite oxidation and acid production by maintaining a constant high water table
- 2) Total reclamation. Aerate and drain intensively, causing maximum pyrite oxidation and acid production. Leach to remove all the acid.

For already developed actual acid sulphate soils, that have been aerated for some time, the first method is difficult to apply because of persisting low pH and Al^{3+} and Fe^{2+} toxicity, as mentioned earlier. To overcome this problems, some leaching or at least refreshing of the surface water in paddy rice must be carried out. Complete leaching could be also considered, but will probably take much time and investments (Drainage systems). The choice which method for reclamation should be applied also depends strongly on environmental factors, which determine the availability of water. Examples of these factors are a.o. precipitation, natural drainage, and flooding by river or sea water. Evidently, another important parameter which relates to the water regime of the soil is the type of crop that is grown. Paddy rice is especially suitable on acid sulphate soils, because it is the only major crop that benefits from a constant water layer on the field. When there is no dry season, limitation of pyrite oxidation is relatively easy in paddy rice. During a dry period, however, pyrite oxidation, pH lowering and Al^{3+} toxicity occurs, causing low yields. For other crops, such as coconut, oil palm, rubber, ananas, etc., the watertable must be lowered and oxygen must enter the rootzone. When pyrite containing material occurs not close to the soil surface but at some depth in the profile, it can be possible to maintain the ground water at a level above this layer, and still give roots enough space. However, when pyrite containing material is close to the surface, partial or total oxidation, leaching and liming are the only possibilities for growing dryland crops.

An important aspect of the presence of crops is their role in the process of soil ripening. Extraction of water by roots promotes ripening and structure improvement. Structure improvement leads to increased aeration, oxidation and acidification (Chapter 5). So when a strategy of total oxidation and leaching is considered, the presence of roots

will strongly reduce the required time. However, as acidification restricts root growth, in many cases it will be difficult to benefit from deep water extraction by roots.

4. EFFECT OF PARTICLE SIZE AND ION ACTIVITIES ON THE RATE OF PYRITE OXIDATION

4.1. Oxidation by dissolved oxygen

In order to calculate the oxidation rate of pyrite by dissolved oxygen use has been made of a relation recently formulated by McKIBBEN & BARNES (1986):

$$K = -10^{-6.77} \cdot (O_2)^{0.5} \quad (8)$$

where: K = oxidation rate of pyrite by dissolved oxygen (mole pyrite.cm⁻².min⁻¹)

(O_2) = concentration of dissolved oxygen (mole.l⁻¹)

As can be seen from this relation the rate of pyrite oxidation is a function of the concentration of dissolved oxygen. The concentration of dissolved oxygen in soil solutions in equilibrium with the air atmosphere at a temperature of 20°C equals more or the less 3.0E-04 mole.l⁻¹. Soil solutions which are not in equilibrium with the atmosphere possess concentrations of oxygen in the soil air and consequently in the soil solution which are much lower. The concentration of soil air oxygen and the concentration of dissolved oxygen in soil solutions are linearly related to each other. As can be seen from figure 2 the concentration of soil air oxygen under normal field circumstances is very low and consequently the concentration of dissolved oxygen also. Only in fresh water, e.g. used for irrigation practises, the dissolved oxygen concentration can be high enough to oxidate pyrite significantly.

So in calculating the rate of pyrite oxidation by dissolved oxygen it has been assumed that the oxygen concentration equals 4.6E-04 mole.l⁻¹ (under the conditions of a temperature of 30°C and a 5‰ salinity). According to relation 8 this results in an oxidation rate of 6.2E-04 g pyrite.cm⁻².day⁻¹, undependently of pH or grain size.

Of course the size of the pyrite particles ultimately stipulates how long the complete oxidation process will take up. Using the "equal-diameter reduction model" summarized by SWARTZENDRUBER & BARBER (1965) it is possible to calculate the fractional mass loss of pyrite due to oxidation. The "equal-diameter reduction model" is based on the assumptions that:

- particles are spheres;
- particles are of uniform diameter;
- rate of loss is directly proportional to surface area.

The "equal-diameter reduction model" can mathematically be written as:

$$\frac{m}{m_0} = 1 - \left(1 - \frac{2 \cdot K \cdot t}{\rho \cdot d_0}\right) \quad (9)$$

where: $\frac{m}{m_0}$ = fractional mass loss of pyrite due to oxidation
 K^0 = oxidation rate of pyrite ($\text{g} \cdot \text{cm}^{-2} \cdot \text{day}^{-1}$)
 t = time (days)
 ρ = density of pyrite ($\text{g} \cdot \text{cm}^{-3}$)
 d_0 = initial particle diameter (cm)

In fact K and ρ (circa $5 \text{ g} \cdot \text{cm}^{-3}$) are known. So with this relation it is simple to calculate the fractional mass loss of pyrite as a function of an initial particle diameter and time. For several particle diameters ranging from $1000 \mu\text{m}$ to $2 \mu\text{m}$ the fractional losses of pyrite have been calculated. Graphical representations of the results are shown in figures 4a to 4f. It can be seen from these figures that the particle size of pyrite in soil influences the time necessary for the complete oxidation process significantly.

In these figures complete oxidation occurs after several hours up to one year.

4.2 Oxidation by ferric iron

In calculating the oxidation rate of pyrite by dissolved ferric iron use has been made of the rate law formulated by McKIBBEN & BARNES (1986):

$$K = -10^{-9.74} \cdot (\text{Fe}^{3+})^{0.5} \cdot (\text{H}^+)^{-0.5} \quad (10)$$

where: (Fe^{3+}) = ferric iron concentration (mole.l^{-1})

According to LINDSAY (1979) ferric and ferrous iron are related to each other following:

$$(\text{Fe}^{3+}) = \frac{(\text{Fe}^{2+})}{(e^-) \cdot (10^{13.04})} \quad (11)$$

In laboratory measurements normally Fe^{2+} is analysed. According to SATAWATHANANONT (1986) concentrations of Fe^{2+} in acid sulfate soils can vary between negligible up to $1.0\text{E}+04 \text{ mg.l}^{-1}$. Under field circumstances pe can vary between -6 up to +14. Taking these values in mind it is possible to carry out some calculations. Use has been made of the following assumptions:

- pe equals +14 or +8
- Fe^{2+} concentrations equals $1.0\text{E}+04$, $1.0\text{E}+03$, $1.0\text{E}+02$, $1.0\text{E}+01$ and $1.0\text{E}+00 \text{ mg.l}^{-1}$

With use of relation 11 the corresponding Fe^{3+} concentrations have been calculated. With use of relation 10 the corresponding rates of oxidation have been calculated for pH values of 2, 3 and 4. Further calculations with help of the "equal-diameter reduction model" of SWARTZENDRUBER & BARBER (1965) resulted in fractional pyrite losses versus time. In these calculations it has been assumed that the size of pyrite particles equals $2\text{E}-04 \text{ cm}$.

The results are shown graphically in the figures 5a up to 5o for the condition $pe=14$ and in the figures 6a up to 6j for $pe=8$. The resulting time in which pyrite is fully oxidated vary between a several hours up to more than a hundred days for $pe=14$. For $pe=8$ the time vary between a hundred days up to more than three hundred years. For still lower pe 's the oxidation process will go on even longer.

5. INFLUENCE OF SOIL STRUCTURE ON OXIDATION OF PYRITE

Oxidation of pyrite starts when oxygen enters the unripened water saturated soil. Two parameters determine the speed with which the available pyrite is oxidized:

- 1) The rate of diffusion of oxidizing compounds (O_2, Fe^{3+}) into the soil matrix
- 2) The rate with which the reaction of O_2 and Fe^{3+} with pyrite takes place.

In this part, the speed of oxygen diffusion into a initially unripe water saturated soil is analyzed. Special attention is paid to the role of soil structure.

In figure 7 the development of soil structure in an initially unripened clay soil is pictured schematically. Figure 7a pictures an unripened saturated soil matrix with no macroporosity. Hydraulic conductivity is very slow. Pyrite is present in the whole soil matrix. In this situation oxygen diffusion occurs from the soil surface downwards.

In figure 7b, the same soil is pictured after a period of ripening. Cracks have developed and rootholes may be present. Biological activity may also have caused some macroporosity. The soil matrix is saturated. Pyrite is present in the soil matrix in between the macropores. The macropores contain oxygen. Diffusion of oxygen takes place from the walls of the macropores into the soil matrix. In the field this situation also occurs when a bore hole in unripe acid sulphate soil is augered. The results of these processes are visible as jarosite accumulations along rootholes and cracks.

In figure 7c, the soil is pictured after prolonged structure development. The soil can now be pictured as a configuration of aggregates. Pyrite is present within these aggregates. In most clay soils, these aggregates are still saturated. Oxygen diffusion into the soil matrix takes place on the walls of the aggregates. In the field this process becomes visible in the form of jarosite accumulations at the walls of aggregates, while pyrite is still present in the centre. In field circumstances, the development of this kind of structure would take tens of years. However, the pictured situation also occurs when digging up fresh, unripe acid sulphate soil and spreading it over the field, or

in situations of soil mixing. In this third case, the contact area of soil matrix with oxygen is much higher than in the first two situations.

From this general picture it is clear that oxygen diffusion into the soil matrix and corresponding pyrite oxidation and acidity production, depends strongly on the structure of the soil. In the next part the influence of soil structure on pyrite oxidation will be illustrated with some quantitative examples.

5.1. Calculation of pyrite oxidation in soils with different structure

In this part the diffusion of oxygen into the soil and the corresponding oxidation of pyrite will be compared for different types of soil structure. Three cases will be compared:

- 1) The soil has no structure. Oxygen diffusion takes place from the soil surface downward
- 2) The soil has large vertical continuous cracks. Oxygen diffusion takes place into the walls of the cracks
- 3) The soil is well structured and consists of rounded aggregates. Oxygen diffusion takes place into the walls of the aggregates.

These cases more or less represent the three types of soil structure in figure 7.

In the presented calculations, we consider 1 m³ of saturated soil. The soil contains 6.6% by mass of pyrite. If we assume a water filled porosity of 0.77 then we have the following quantities:

- . Volume of solids: 0.23 m³
- . Volume of water : 0.77 m³
- . Mass of solids : 0.23*2700 = 621 kg
- . Mass of water : 0.77*1000 = 770 kg
- . Mass of pyrite : 0.066*621 = 41.3 kg = 344 moles

According to DENT AND RAISWELL (1982) the diffusion coefficient of dissolved oxygen in the case of diffusion and reaction is given by:

$$\frac{D}{R + D} \quad (12)$$

where R is defined as:

$$\begin{aligned} \text{Concentration of oxidisable material,} &= R \times \text{Concentration of } O_2 \quad (13) \\ \text{expressed as the number of moles of } O_2 &\text{ in water, expressed} \\ \text{required for its oxidation} &\text{ in moles} \end{aligned}$$

The expression on the left side of this equation can be calculated from the amount of pyrite and the water content of the soil:

Quantity of pyrite = 344 moles

This quantity of pyrite consumes $344 \times 15/4$ (Eq. 5) moles O_2
= 1290 moles O_2

The total volume of water equals 0.770 m^3 . Therefore:

Pyrite consumption: $1675 \text{ moles } O_2/\text{m}^3 \text{ water}$

The solubility of oxygen in water at 30°C and a salinity of 0.5% equals $0.46 \text{ moles}/\text{m}^3$ (DENT AND RAISWELL, 1982).

According to equation 13:

$$1648 = R \times 0.46$$

$$R = 3.6 \times 10^3$$

At 30°C , the diffusion coefficient D, for O_2 in water = $0.0000262 \text{ cm}^2 \cdot \text{s}^{-1}$ (DENT AND RAISWELL, 1982) so the corrected diffusion coefficient of O_2 for diffusion in water and reaction with pyrite equals:

$$\frac{D}{R + 1} = 7.2 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$$

In the following lines we will present diffusion equations for three different soil structures.

- 1) The soil has no structure and is completely saturated. Oxygen diffusion takes place from the soil surface downward (fig. 7a).

This case can be calculated applying the equation for diffusion into a semi infinite medium. CRANK (1975) gives the following solution:

$$\frac{m}{m_o} = \frac{2C_o}{m_o} \left(\frac{Dt}{\pi} \right)^{\frac{1}{2}} \quad (14)$$

in which: $\frac{m}{m_o}$: fraction of pyrite oxidized (-)
 C_o : concentration of oxygen in water (mol.m^{-3})
 D : Diffusion coefficient ($\text{m}^2.\text{s}^{-1}$)
 t : time (s)

2) The soil has large vertical continuous cracks. Oxygen diffusion takes place into the walls of the cracks (fig 7b.)

We will approximate this situation by considering a soil sytem of cilindrical colums in between of the cracks.

CRANK (1975) and RAISWELL AND DENT (1982) give the solution for diffusion into a cylinder:

$$\frac{m}{m_o} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} \exp (-D\alpha_n^2 t) \quad (15)$$

in which: $\frac{m}{m_o}$: fraction of pyrite oxidized (-)
 D : Diffusion coefficient ($\text{m}^2.\text{s}^{-1}$)
 t : time (s)
 a : radius of cylinder (m)
 α_n : the root of $J_0(\alpha_n)=0$, J_0 is the Bessel function.

3) The soil is well structured and consists of rounded aggregates. Oxygen diffusion takes place into the walls of the aggregates. (Fig 7c.)

This situation is approximated by considering a soil system of spheres and macropores in between of these spheres.

CRANK (1975) gives the solution for diffusion into a sphere:

$$\frac{m}{m_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-Dn^2\pi^2 t/a^2} \quad (16)$$

in which: $\frac{m}{m_0}$: fraction of pyrite oxidized (-)

D : Diffusion coefficient ($m^2.s^{-1}$)

t : time (s)

a : radius of cylinder (m)

With equations 14, 15 and 16, the oxidation rate of pyrite was calculated for 6 different soil structures, ranging from completely unripe to extremely well structured. Results are presented in figure 8 and table 3.

It is clear that soil structure strongly influences the rate of oxidation of pyrite. In a completely unripened soil, with constant supply of fresh aerated water, oxygen diffusion into the soil matrix through the soil surface is so slow that after 50 years only 5% of the available pyrite is oxidized. In partially ripe soils where some cracks have developed, oxygen diffusion into the soil matrix and corresponding pyrite oxidation proceeds much faster. The half time of the pyrite oxidation, however is still 30 years or more. Only when a good soil structure is established, with a large surface area through which oxygen can enter the soil matrix, pyrite oxidation is a quick process, with a half time of about 5 years or less. In the extreme case of very small aggregates, which resembles a situation of digging up unripe soil, soil mixing or tillage, pyrite oxidation is complete within a few years (fig 9.)

5.2. Production of acidity

For the three presented cases, the production of acidity can be compared. When doing this, however, two major questions arise :

- 1) What are the reaction products of pyrite?
- 2) What is the fate of the produced acidity?

With respect to question 1, the type of reaction products of pyrite determines the amount of H^+ that is produced per mol pyrite. From the paragraph on chemical reactions, we can conclude that the conversion of pyrite into $Fe(OH)_3$ release 4 H^+ per mol pyrite. However, in acid environment pyrite is converted into Jarosite (VAN BREEMEN, 1976). This reaction release 3 H^+ per mole pyrite. In the presented calculations, we will assume that pyrite is converted rapidly into Jarosite. In the long run Jarosite will turn into goethite, releasing a further mole H^+ . However, this conversion takes many years (VAN BREEMEN, 1976). Therefore, in appendix 1 the oxidized amount of pyrite is converted into acid production, assuming both 3 H^+ per mol pyrite (Jarosite formation) and 4 H^+ per mol pyrite (Goethite formation).

With respect to question 2, the following is important: When oxygen diffuses for instance into a saturated soil clod, pyrite is converted into jarosite, releasing 3 moles H^+ per mole pyrite. When this happens at the edge of the clod, H^+ is easily leached, when water is flushed through the soil. However, when pyrite reacts in the centre of the clod, H^+ will be released at this spot. Leaching of this H^+ is only possible after transportation to the edge of the clod. In a completely saturated soil, this transport takes place through diffusion, and will be very slow. In the case of evaporation from clod walls or water extraction by plant roots, mass transport of water will take place, resulting in much more rapid transport of H^+ to the walls of the clods.

5.3. Diffusion of Fe^{3+}

According to VAN BREEMEN (1976), oxidation of pyrite in ripened acid sulphate soils takes place through oxidation of pyrite by Fe^{3+} . Therefore, it may well be that not oxygen diffusion but Fe^{3+} diffusion into the soil matrix is the rate limiting factor in the process of pyrite oxidation. In that case the presented calculations should be repeated with Fe^{3+} .

6. OUTLINE OF SIMULATION MODEL

From the foregoing it is clear that many physical and chemical processes interact with each other in acid sulfate soils. The major physical processes include structure development of the soil, oxidation of O_2 and Fe^{3+} into the soil matrix, water transport through the soil profile and water transport through the boundaries of the soil system. Major chemical processes are oxidation and reduction, dissolution and precipitation, and adsorption and desorption.

Some of these processes are slow while others proceed very quickly. Especially in well structured soil, oxidation of pyrite may occur very rapidly. Another example of a rapid proceeding process is the acidification of fresh surface water in paddy rice. In addition to this accurate simulation of water balance and water transport requires simulation with small timesteps. In figure 10, a first outline of a one dimensional simulation model for physical and chemical processes in acid sulphate soil is presented. It is suggested that calculations are carried out over one-day periods, giving for each day physical and chemical simulation results.

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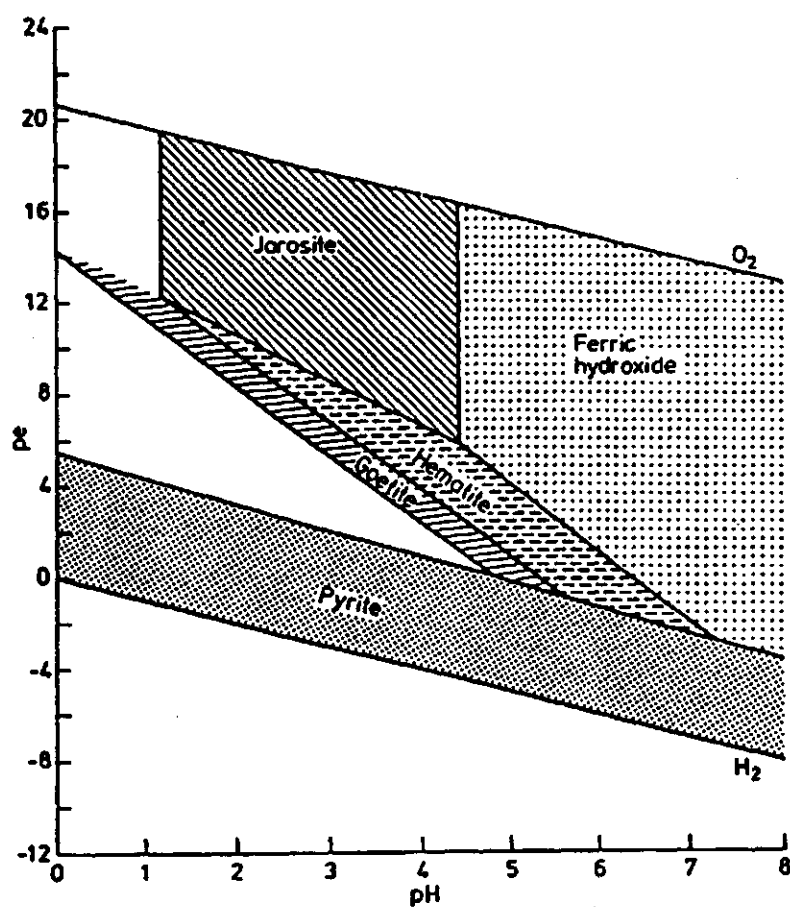


Fig. 1. Stability diagram of pyrite, goetite, hematite, ferric hydroxide and jarosite at 25°C

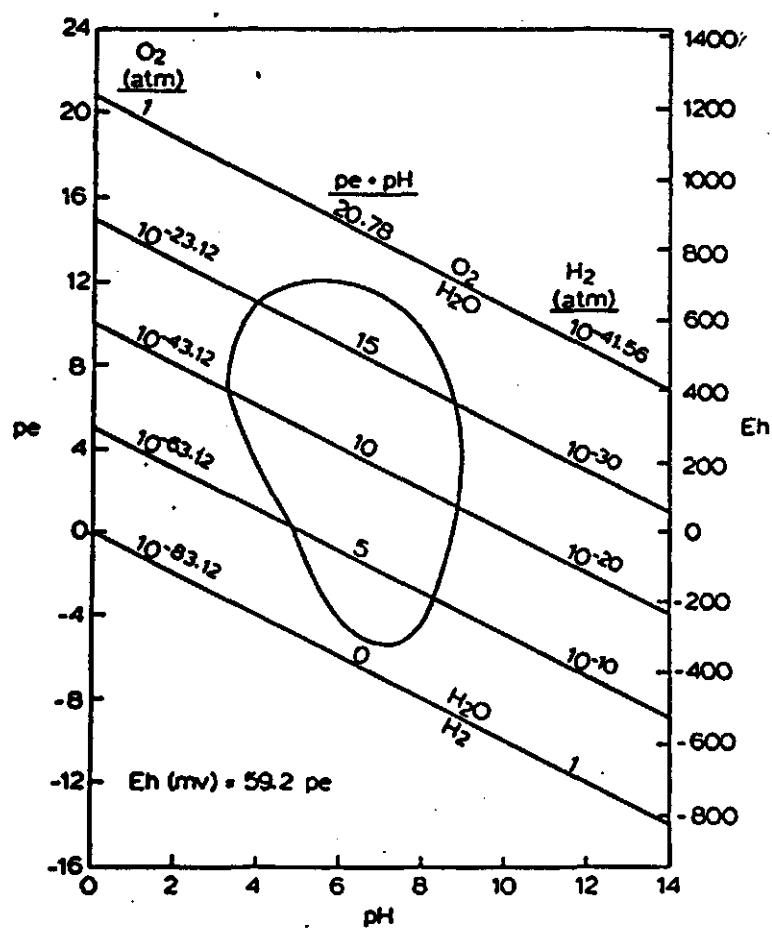


Fig. 2. Equilibrium redox relationships of aqueous systems. The inscribed area was adopted from BAAS BECKING et al (1960) and is representative of most soils (after LINDSAY, 1979)

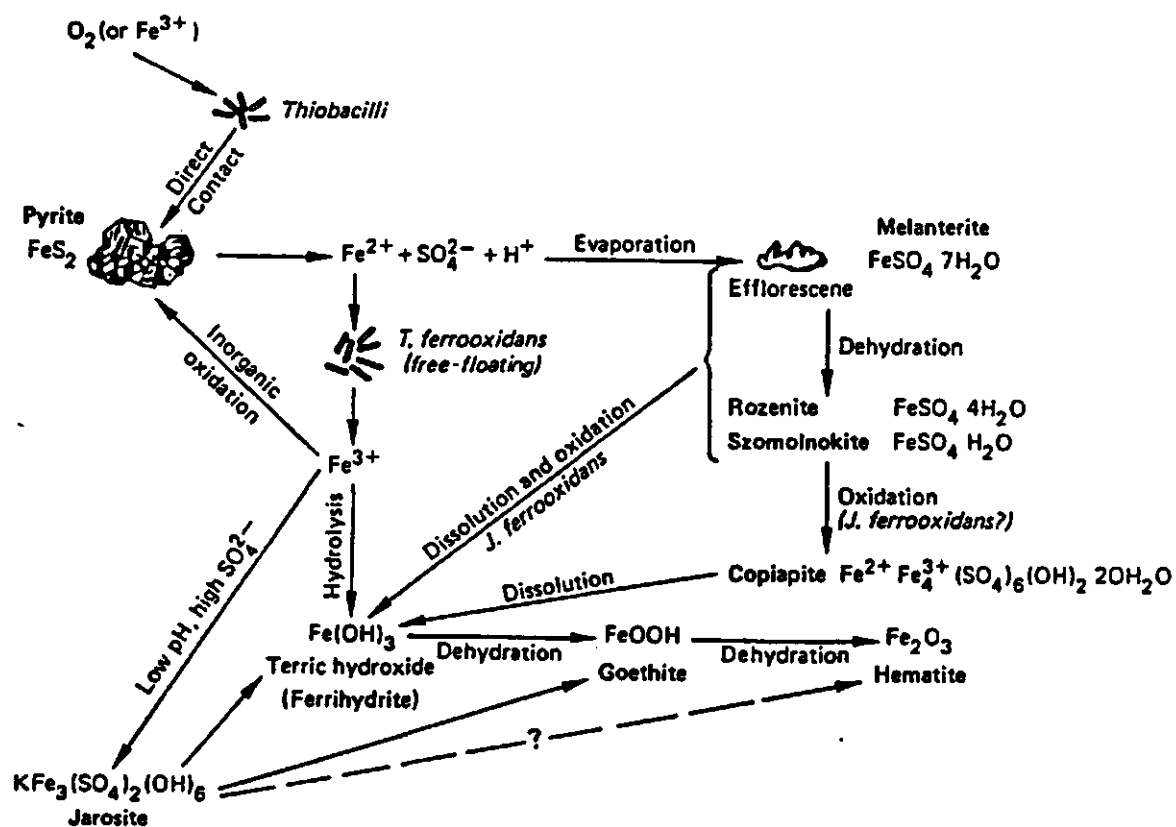


Fig. 3. The overall sequence of mineral reactions for pyrite oxidation showing the relationships between oxidizing agents, catalysts, and mineral products (after NORDSTROM, 1982).

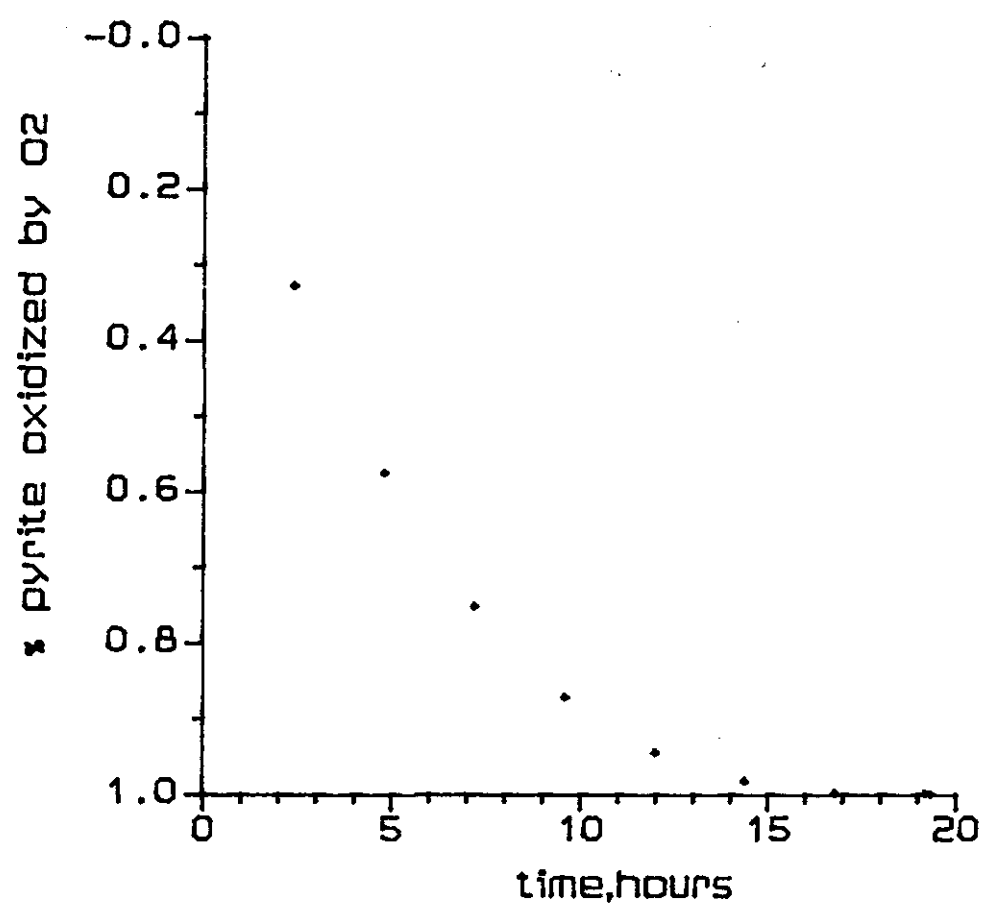


Fig. 4a. Fractional mass losses of pyrite due to oxidation by O₂ versus time
particle size (d_0) = 2 μm

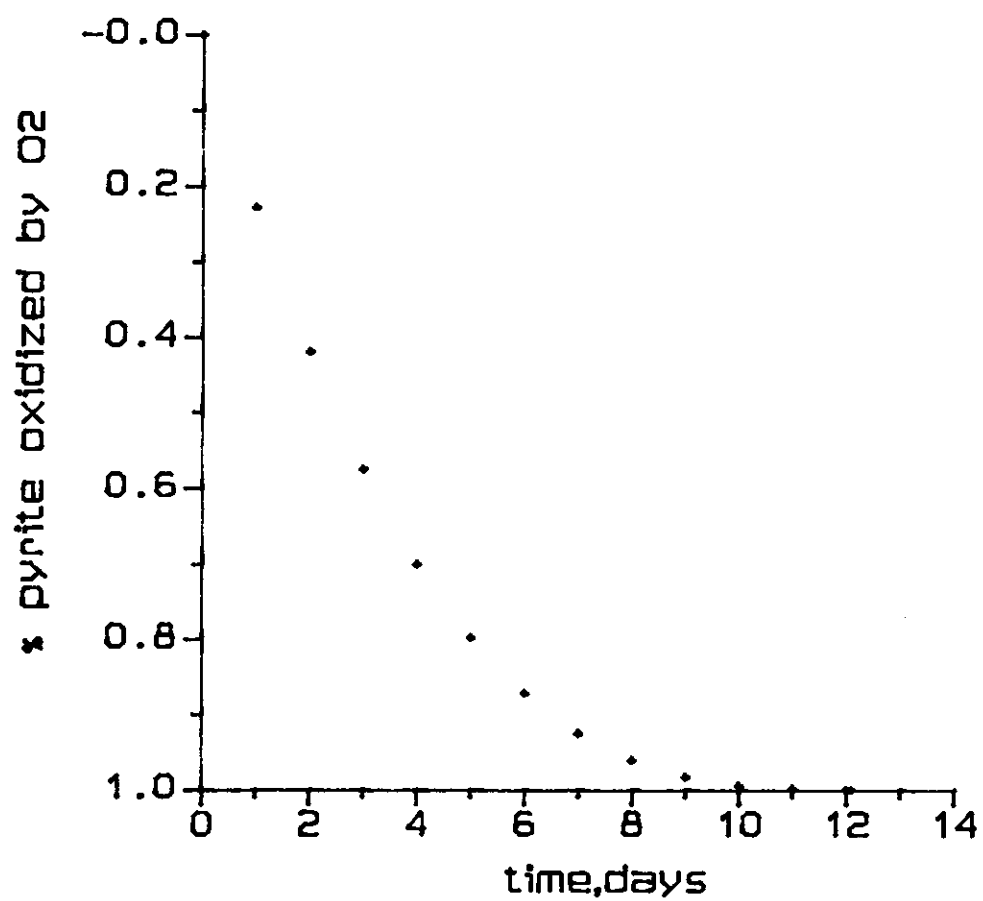


Fig. 4b. Fractional mass losses of pyrite due to oxidation by O₂ versus time
particle size (d_0) = 30 μ m

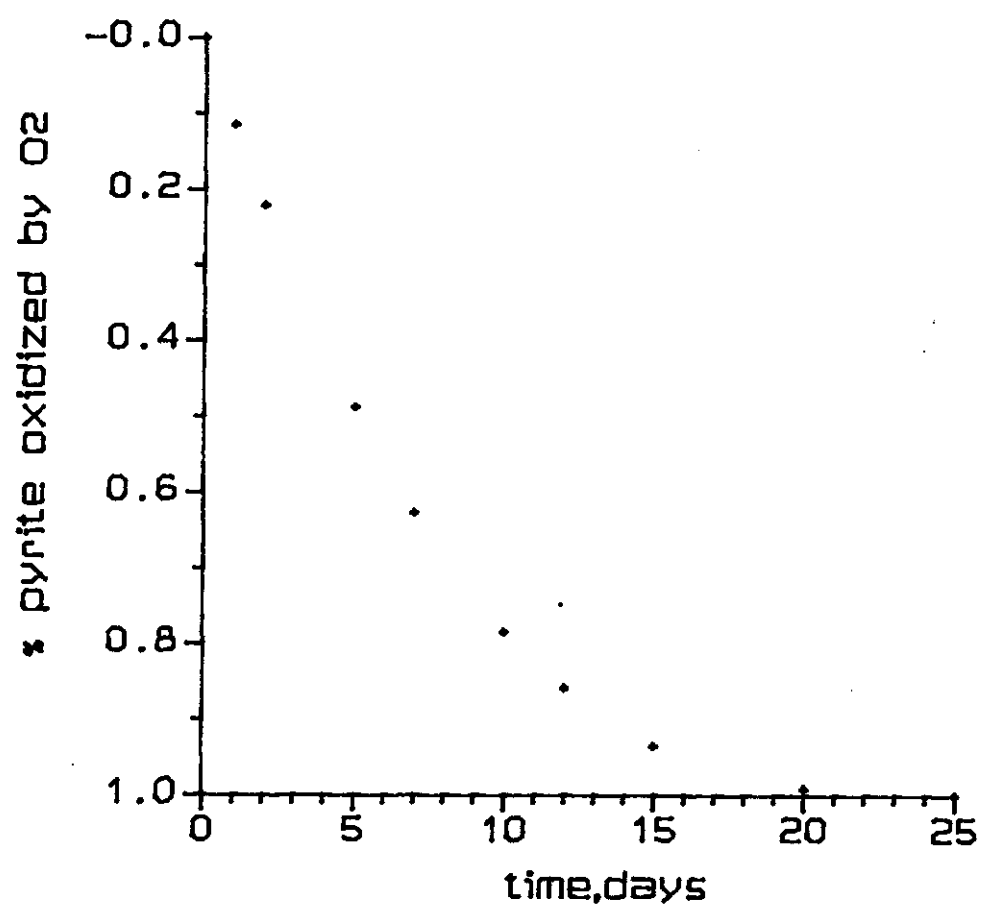


Fig. 4c. Fractional mass losses of pyrite due to oxidation by O₂ versus time
particle size (d_0) = 62 μm

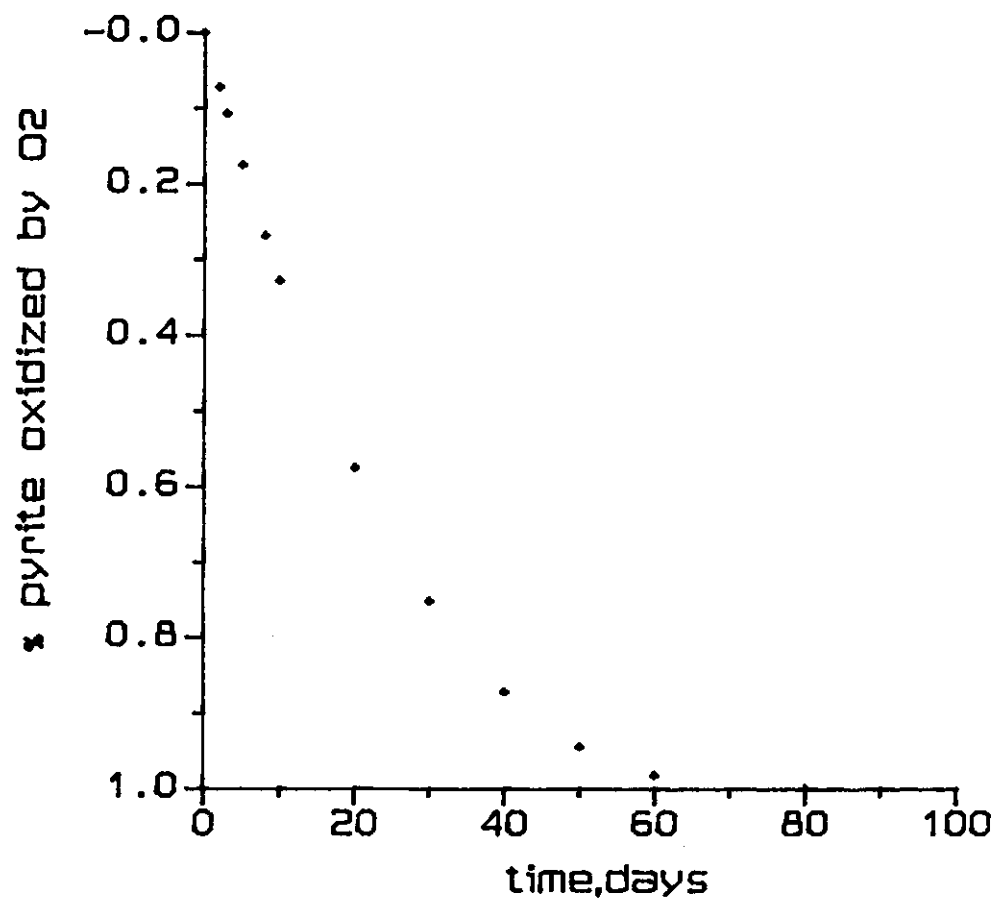


Fig. 4d. Fractional mass losses of pyrite due to oxidation by O₂ versus time

particle size (d_0) = 200 μm

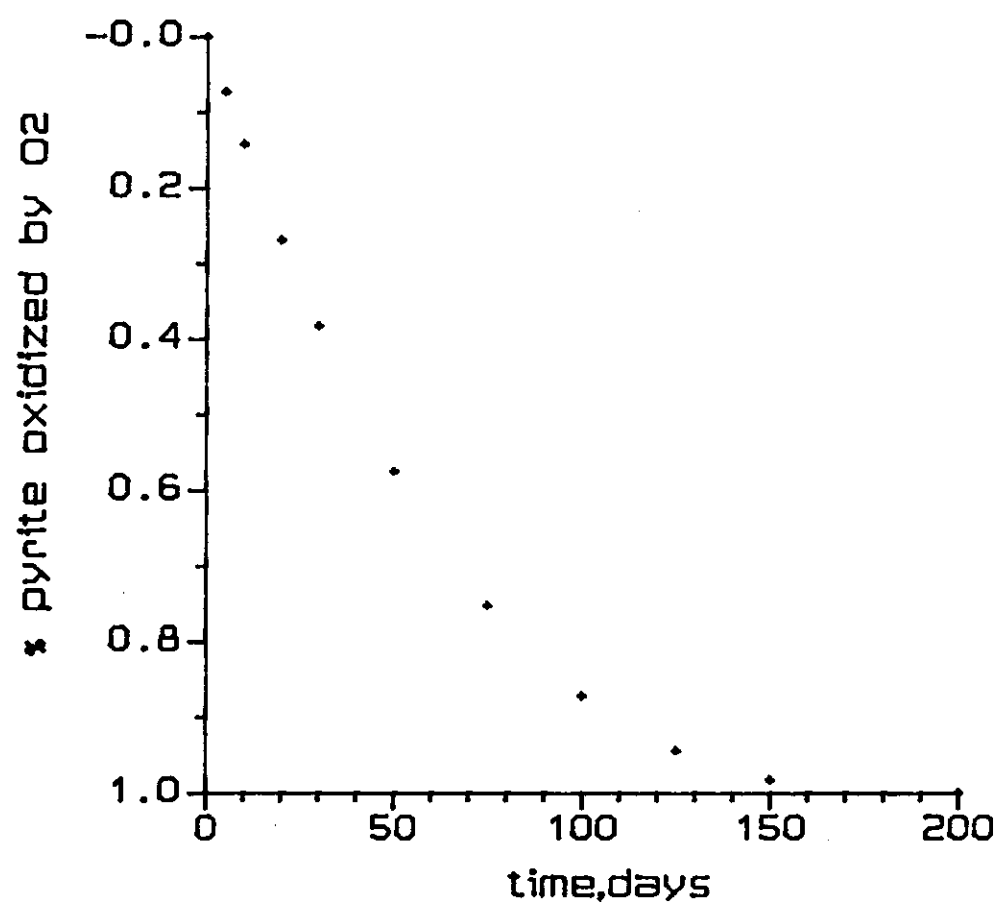


Fig. 4e. Fractional mass losses of pyrite due to oxidation by O₂ versus time
particle size (d_0) = 500 μm

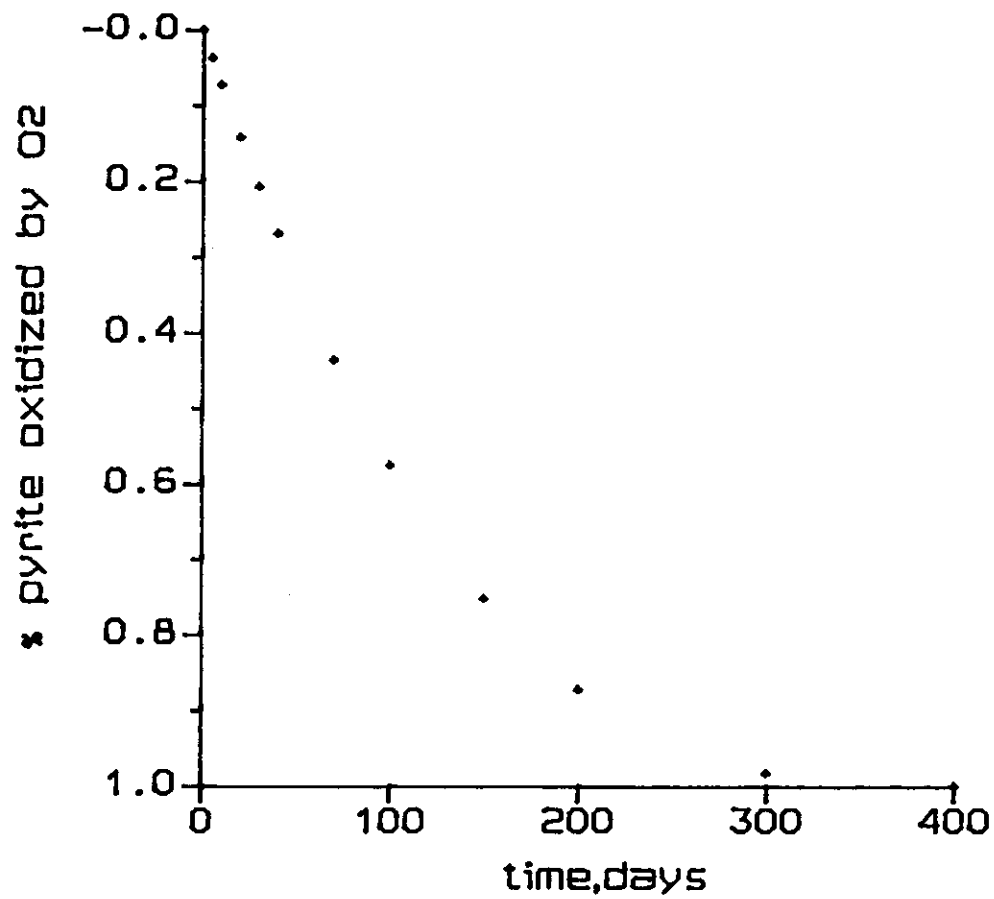


Fig. 4f. Fractional mass losses of pyrite due to oxidation by O₂ versus time

particle size (d_0) = 1000 μm

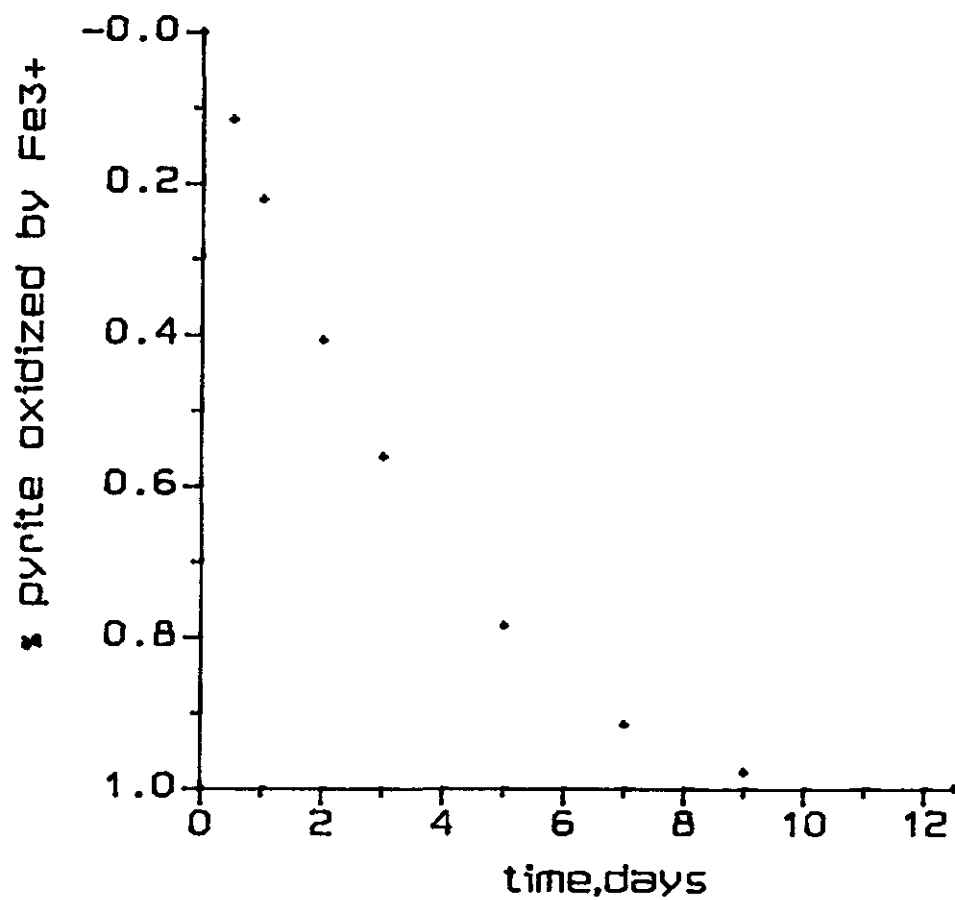


Fig. 5a. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 4$

$\text{Fe}^{2+} = 1.8 \times 10^{-5} \text{ mol.l}^{-1} (= 10^0 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \times 10^{-4} \text{ mol.l}^{-1}$

$K = 4.0 \times 10^{-5} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

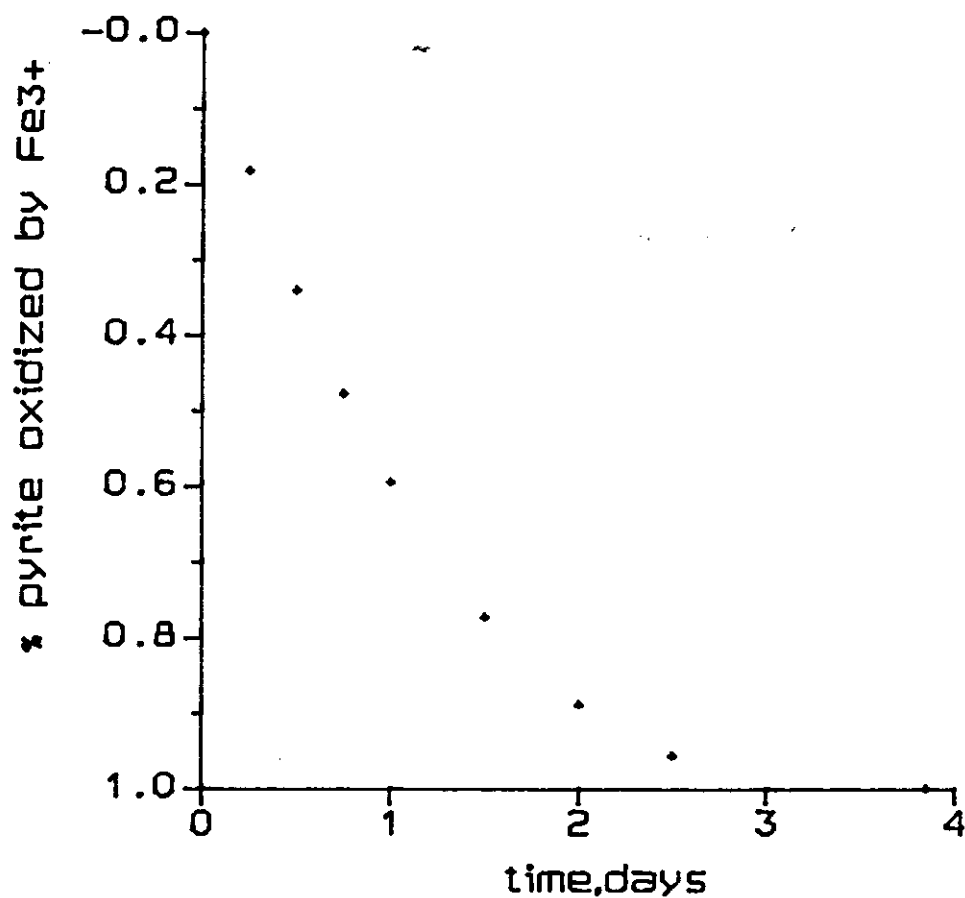


Fig. 5b. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 4$

$\text{Fe}^{2+} = 1.8 \times 10^{-4} \text{ mol.l}^{-1} (= 10^1 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \times 10^{-3} \text{ mol.l}^{-1}$

$K = 1.3 \times 10^{-4} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

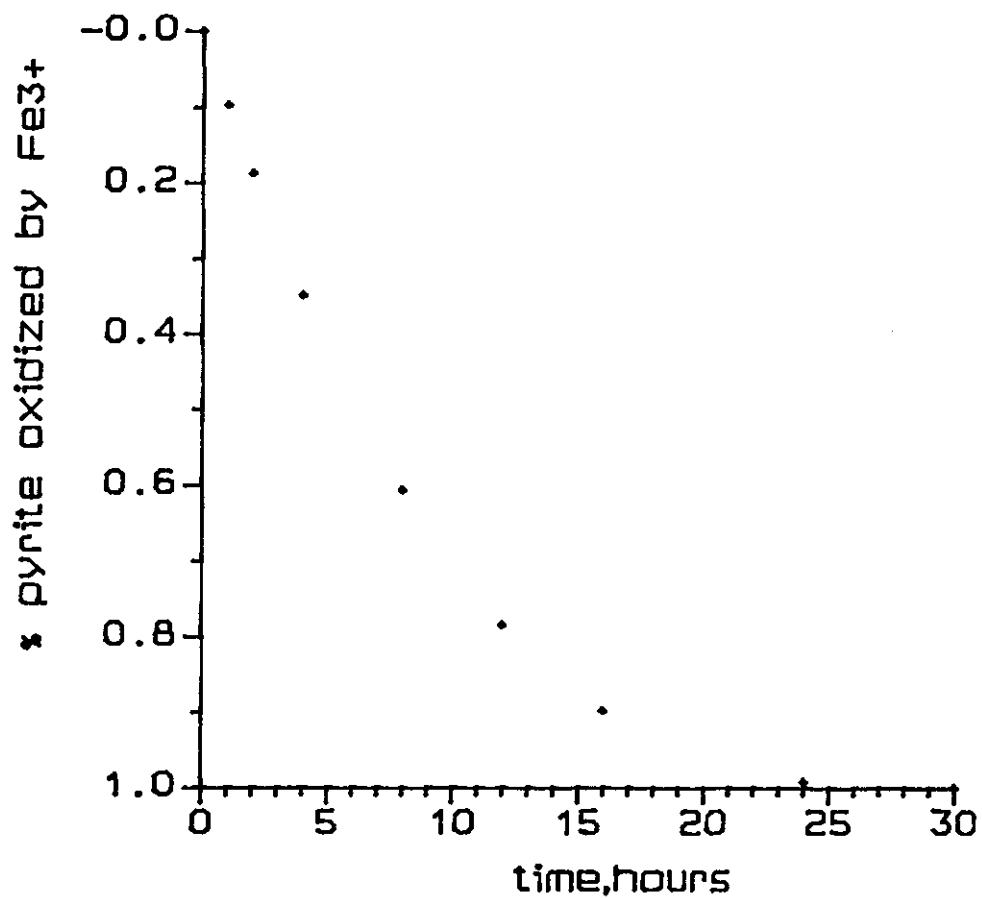


Fig. 5c. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$p_e = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 4$

$\text{Fe}^{2+} = 1.8 \times 10^{-3} \text{ mol.l}^{-1} (= 10^2 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \times 10^{-2} \text{ mol.l}^{-1}$

$K = 4.0 \times 10^{-4} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

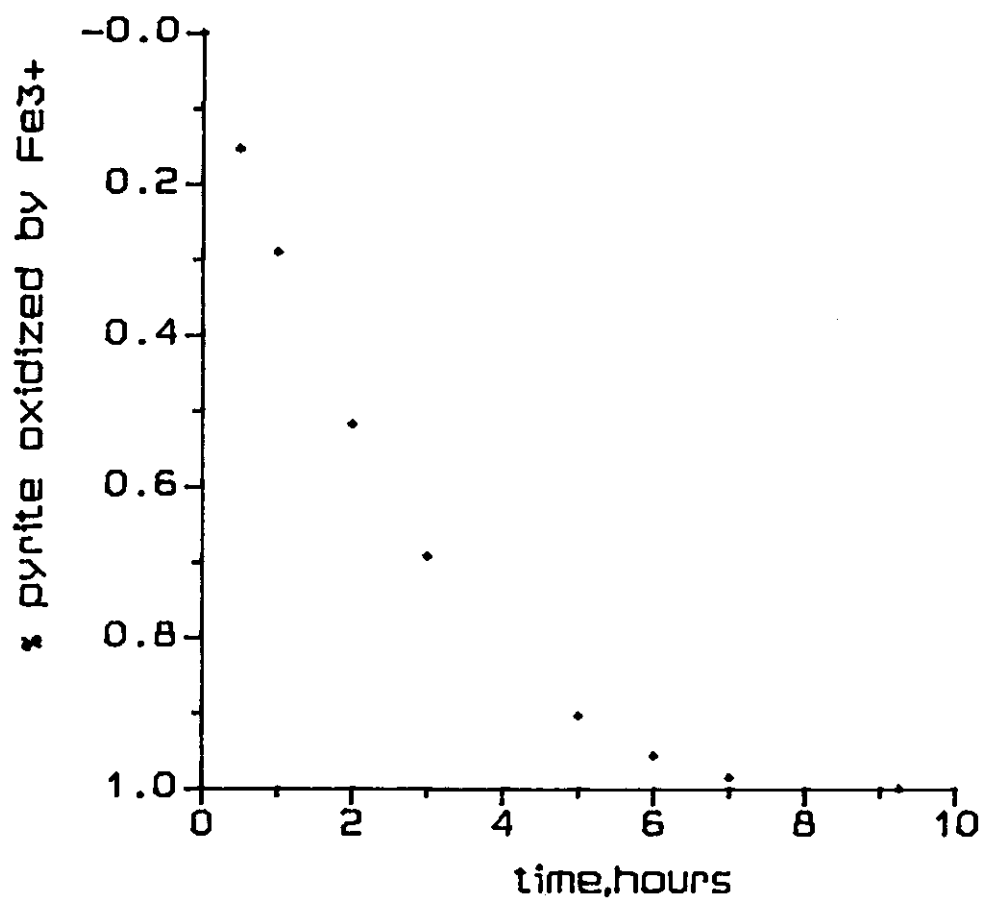


Fig. 5d. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 4$

$\text{Fe}^{2+} = 1.8 \times 10^{-2} \text{ mol.l}^{-1} (= 10^3 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \times 10^{-1} \text{ mol.l}^{-1}$

$K = 1.3 \times 10^{-3} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

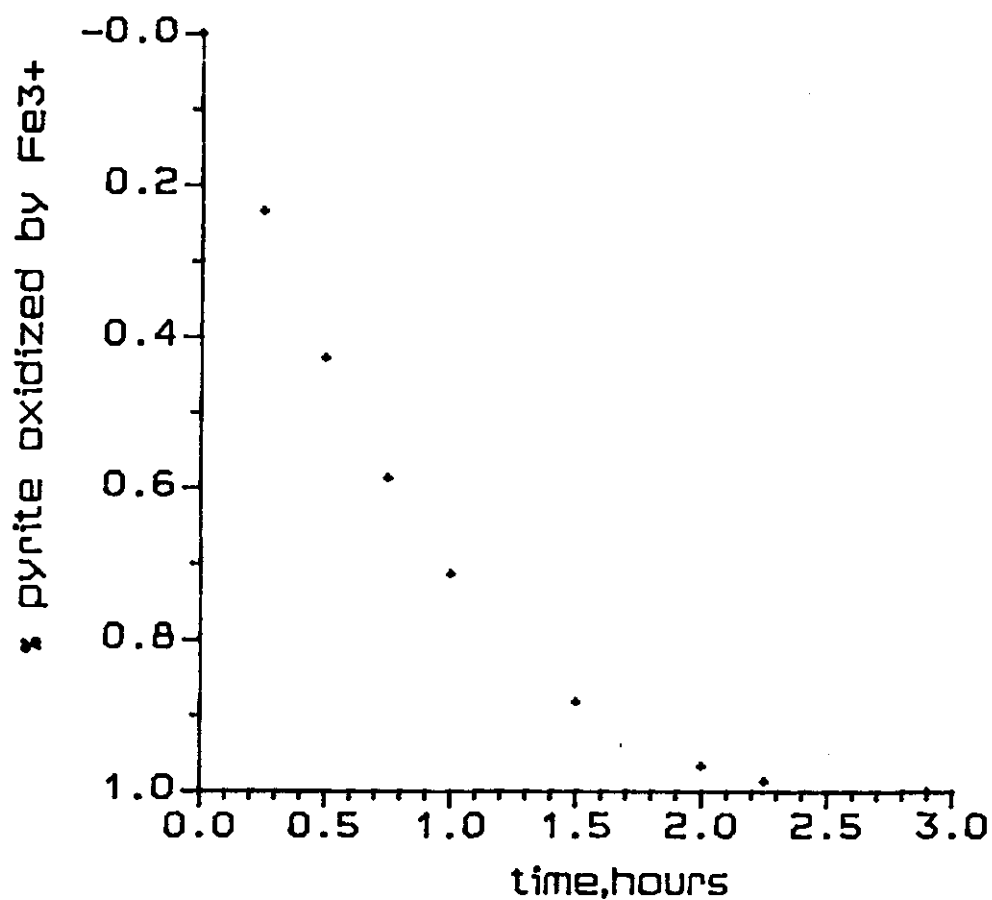


Fig. 5e. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 4$

$\text{Fe}^{2+} = 1.8 \times 10^{-1} \text{ mol.l}^{-1} (= 10^4 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \text{ mol.l}^{-1}$

$K = 4.0 \times 10^{-3} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

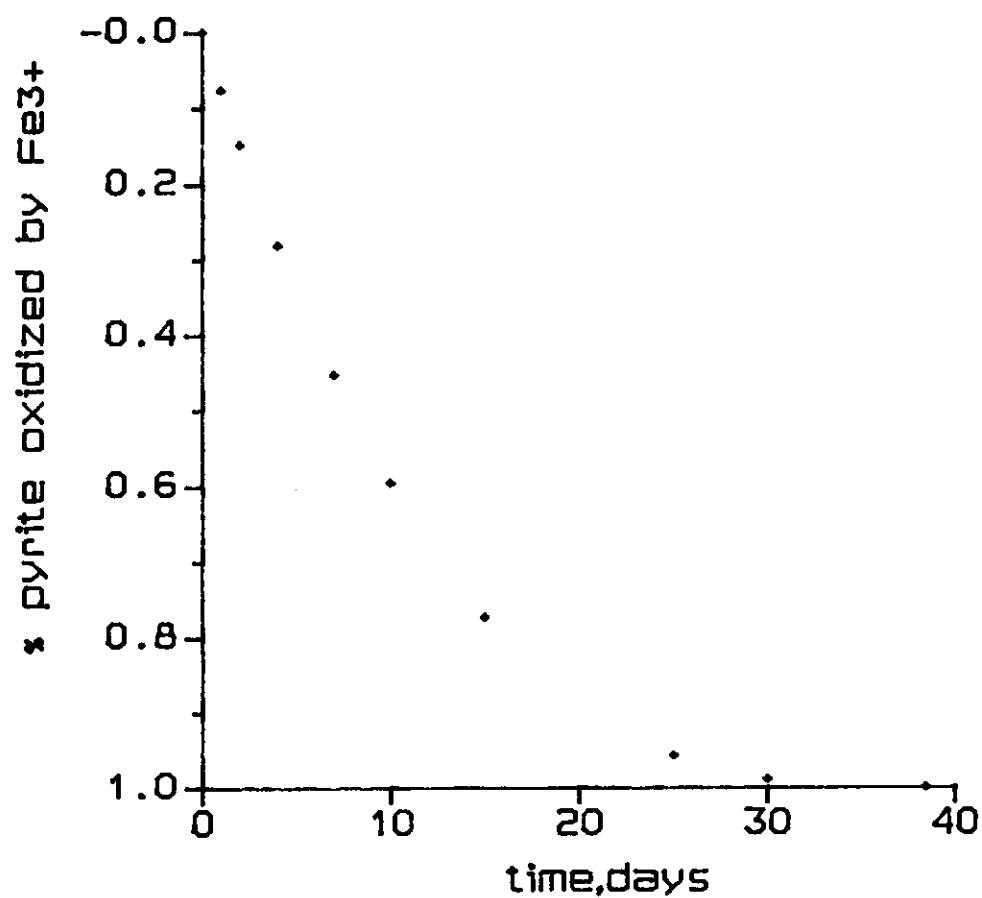


Fig. 5f. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$p_e = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 3$

$\text{Fe}^{2+} = 1.8 \times 10^{-5} \text{ mol.l}^{-1} (= 10^0 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \times 10^{-4} \text{ mol.l}^{-1}$

$K = 1.3 \times 10^{-5} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

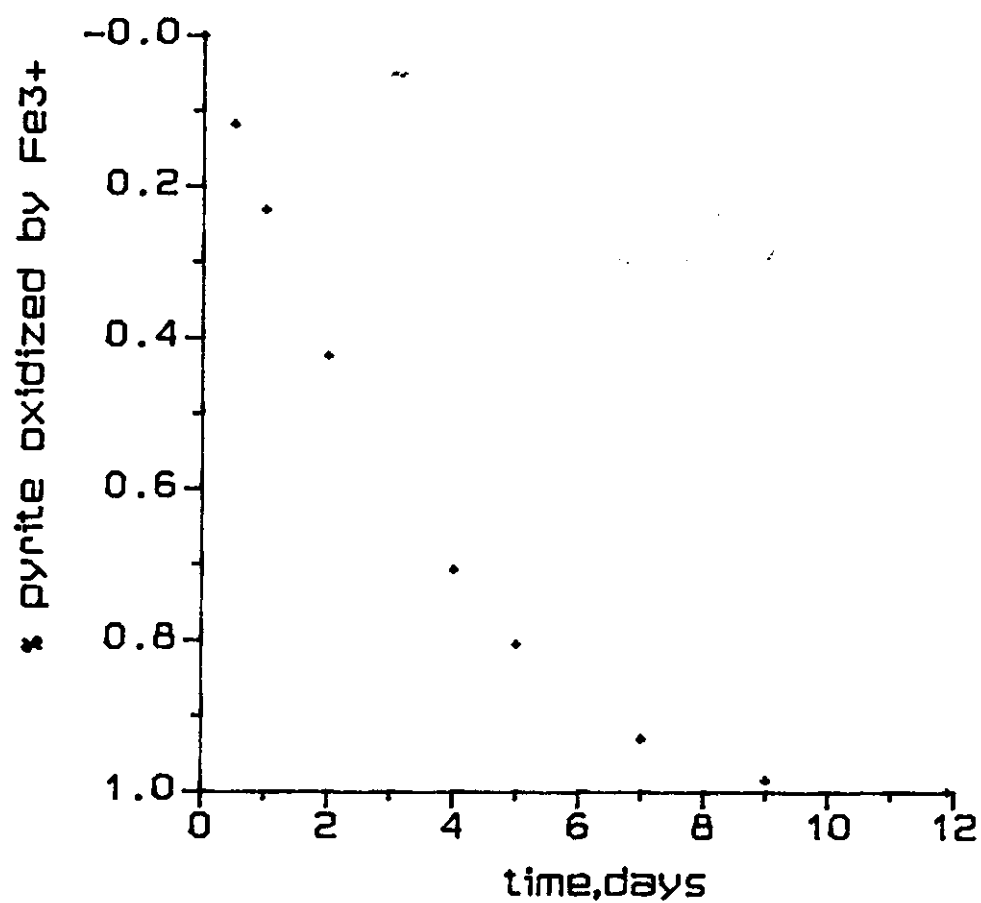


Fig. 5g. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 3$

$\text{Fe}^{2+} = 1.8 \times 10^{-4} \text{ mol.l}^{-1} (= 10^1 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \times 10^{-3} \text{ mol.l}^{-1}$

$K = 4.2 \times 10^{-5} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

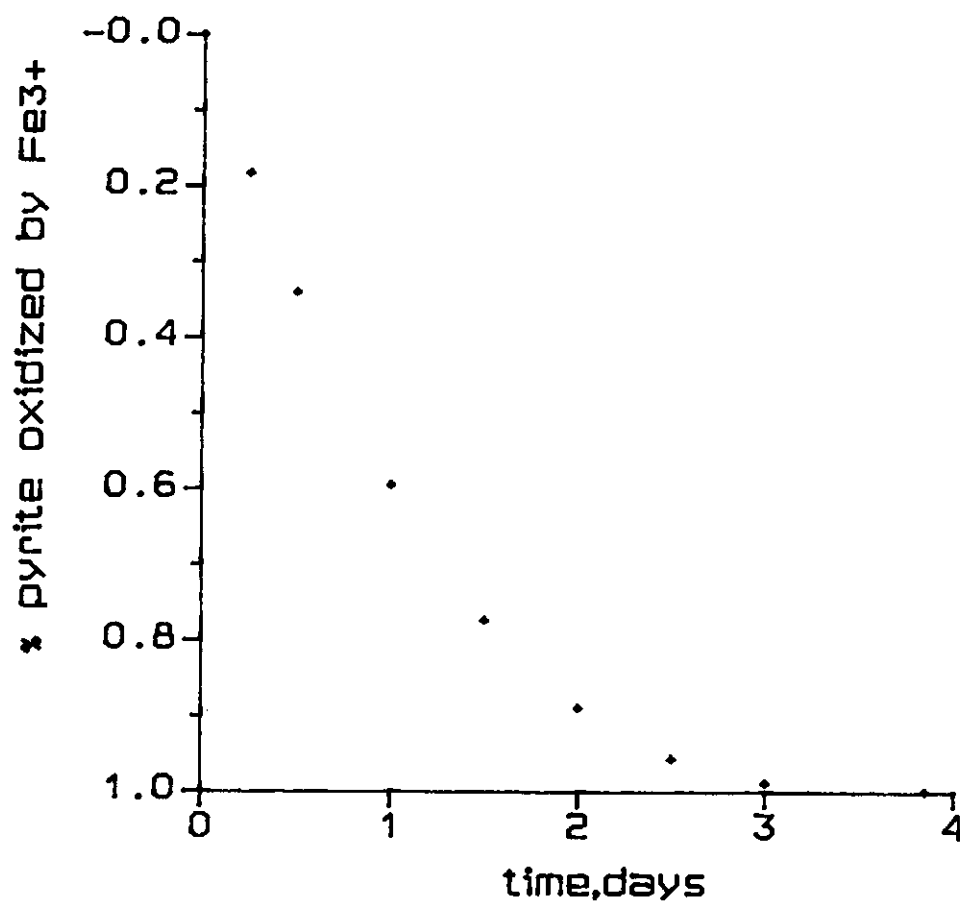


Fig. 5h. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 3$

$\text{Fe}^{2+} = 1.8 \times 10^{-3} \text{ mol.l}^{-1} (= 10^2 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \times 10^{-2} \text{ mol.l}^{-1}$

$K = 1.3 \times 10^{-4} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

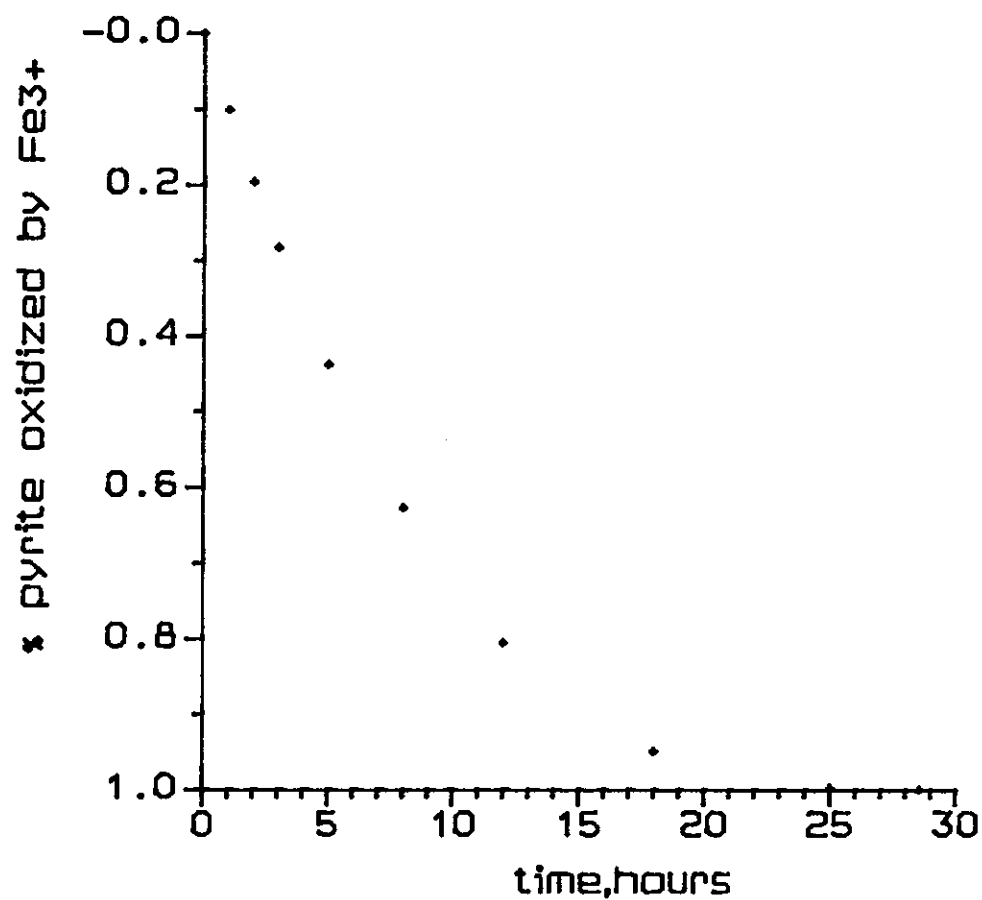


Fig. 5i. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 3$

$\text{Fe}^{2+} = 1.8 \times 10^{-2} \text{ mol.l}^{-1} (= 10^3 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \times 10^{-1} \text{ mol.l}^{-1}$

$K = 4.2 \times 10^{-4} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

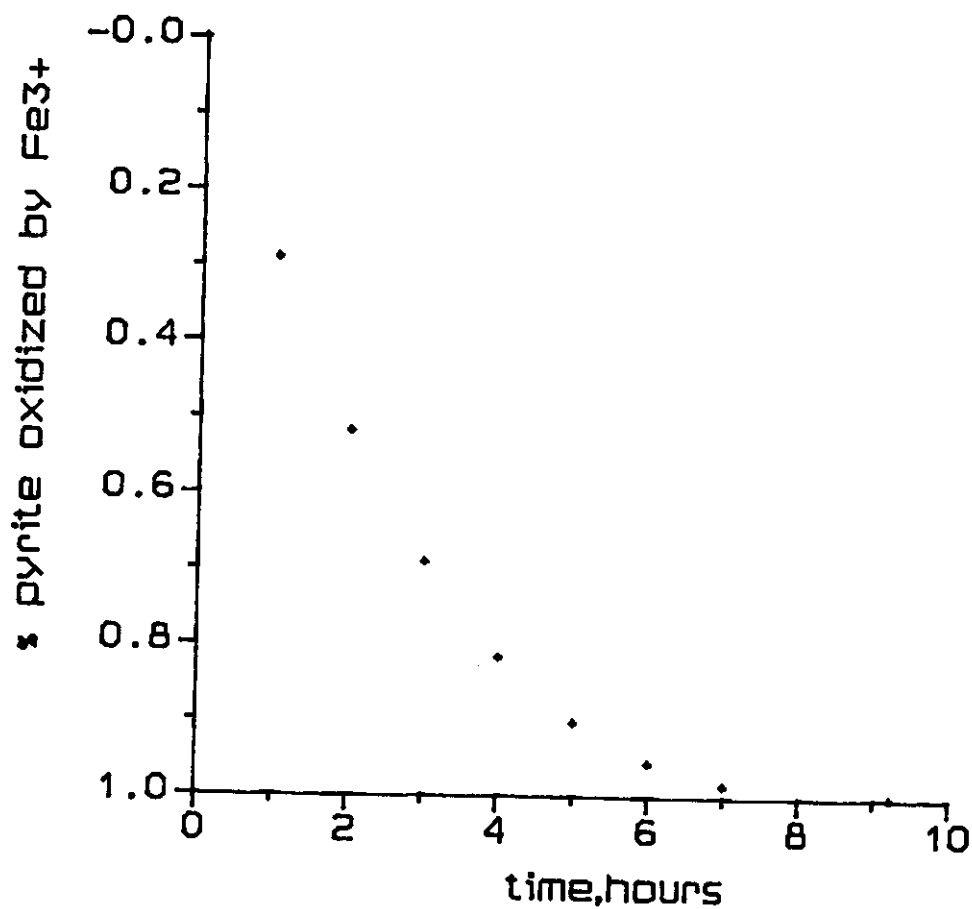


Fig. 5j. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$p_e = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 3$

$\text{Fe}^{2+} = 1.8 \times 10^{-1} \text{ mol.l}^{-1} (= 10^4 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \text{ mol.l}^{-1}$

$K = 1.3 \times 10^{-3} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

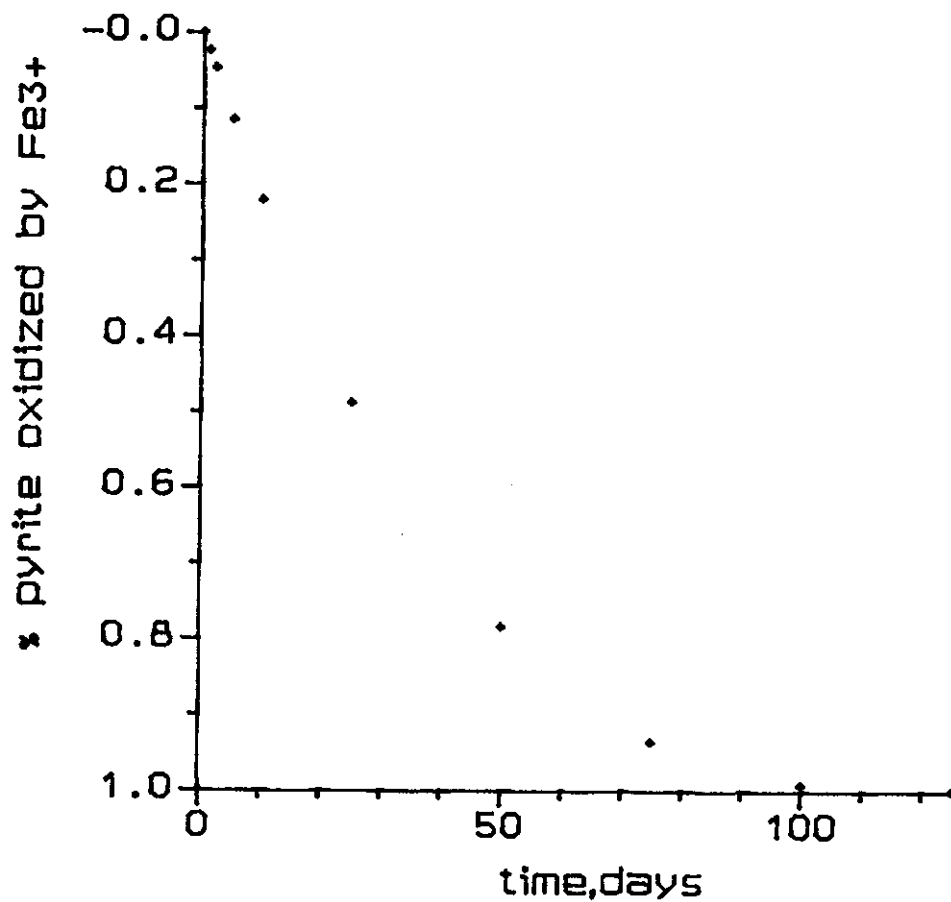


Fig. 5k. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 2$

$\text{Fe}^{2+} = 1.8 \times 10^{-5} \text{ mol.l}^{-1} (= 10^0 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \times 10^{-4} \text{ mol.l}^{-1}$

$K = 4.0 \times 10^{-6} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

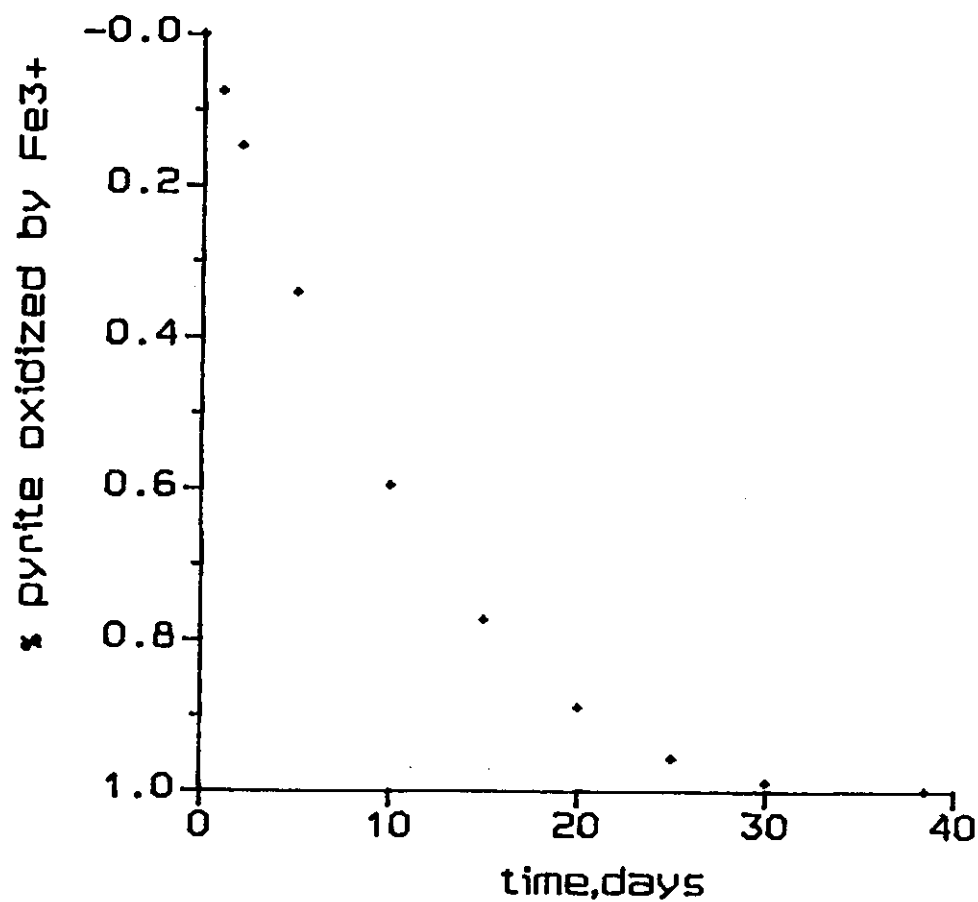


Fig. 51. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 2$

$\text{Fe}^{2+} = 1.8 \times 10^{-4} \text{ mol.l}^{-1} (= 10^1 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \times 10^{-3} \text{ mol.l}^{-1}$

$K = 1.3 \times 10^{-5} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

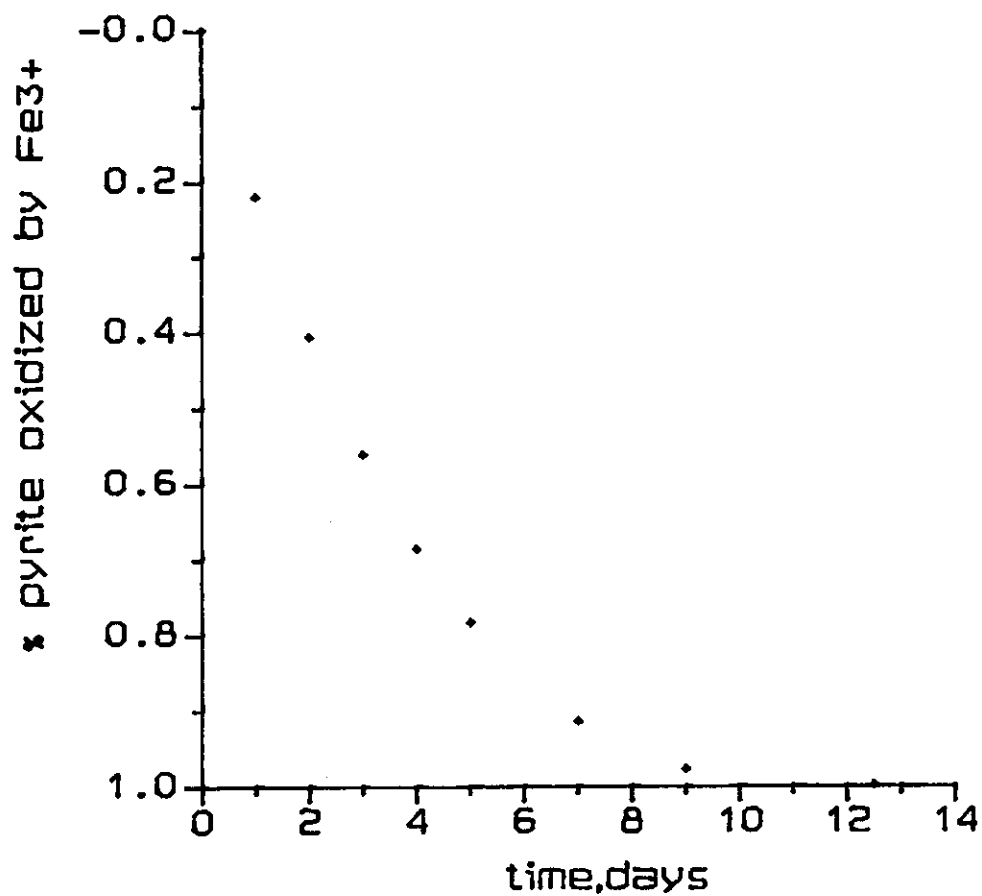


Fig. 5m. Fractional mass losses of pyrite due to oxidation by Fe^{3+}

versus time

$\text{pe} = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 2$

$\text{Fe}^{2+} = 1.8 \cdot 10^{-3} \text{ mol.l}^{-1} (= 10^2 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \cdot 10^{-2} \text{ mol.l}^{-1}$

$K = 4.0 \cdot 10^{-4} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

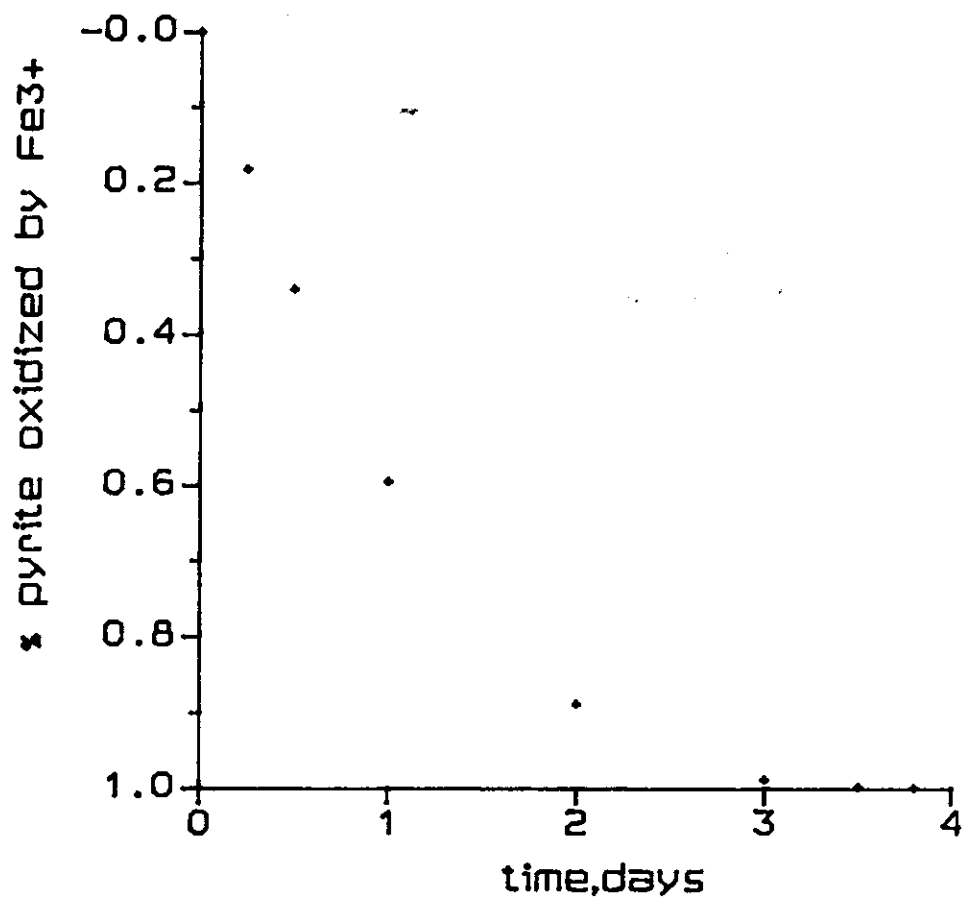


Fig. 5n. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$p_e = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 2$

$\text{Fe}^{2+} = 1.8 \times 10^{-2} \text{ mol.l}^{-1} (= 10^3 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \times 10^{-1} \text{ mol.l}^{-1}$

$K = 1.3 \times 10^{-4} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

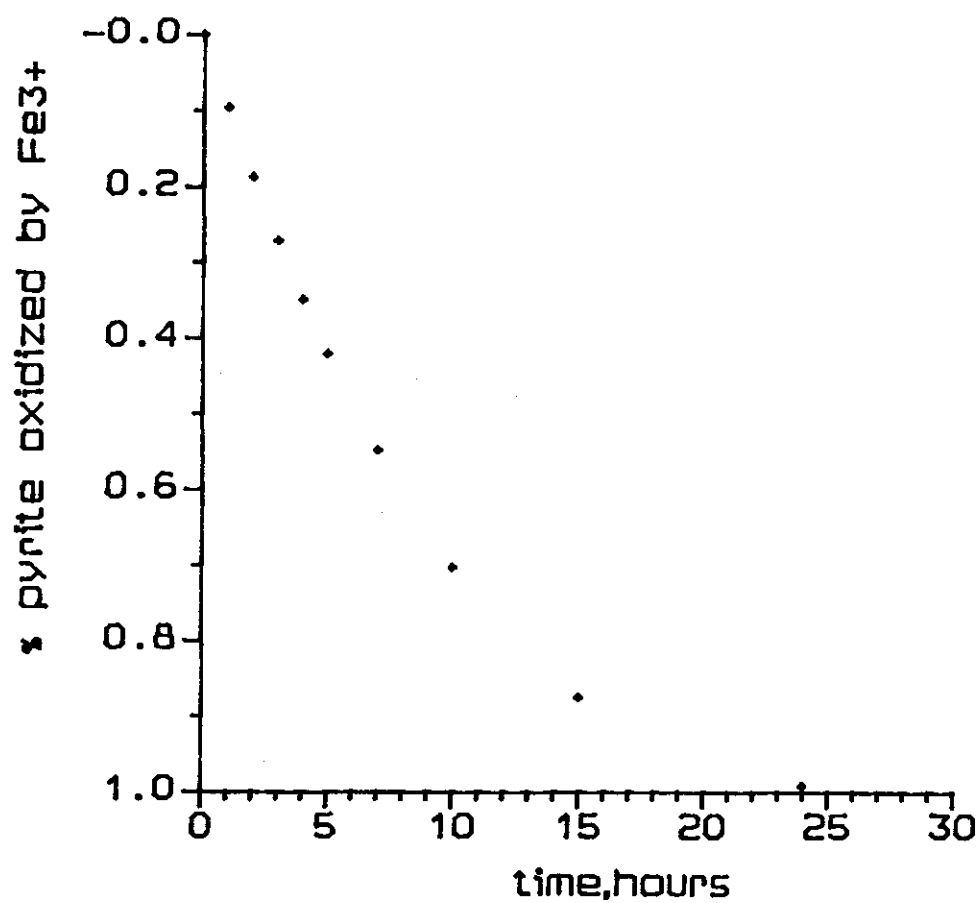


Fig. 5a. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 14$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 2$

$\text{Fe}^{2+} = 1.8 \times 10^{-1} \text{ mol.l}^{-1} (= 10^4 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.64 \text{ mol.l}^{-1}$

$K = 4.0 \times 10^{-4} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

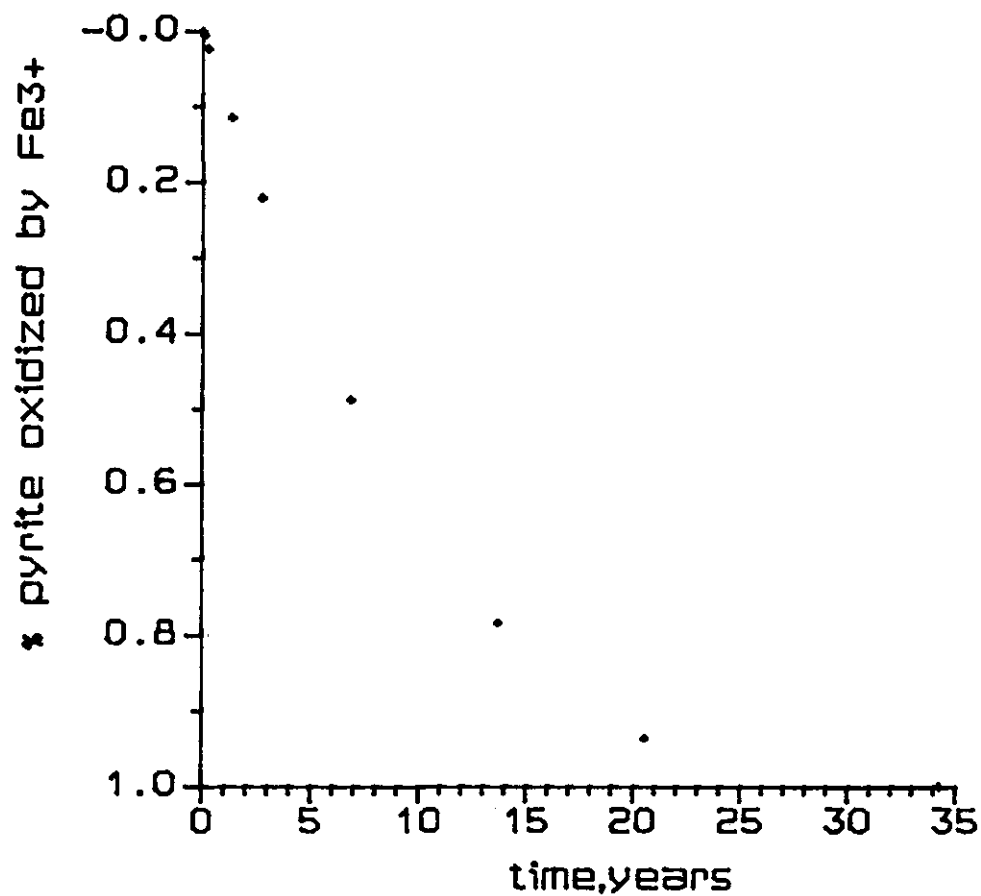


Fig. 6a. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 8$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 4$

$\text{Fe}^{2+} = 1.8 \times 10^{-5} \text{ mol.l}^{-1} (= 10^0 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.6 \times 10^{-10} \text{ mol.l}^{-1}$

$K = 4.0 \times 10^{-8} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

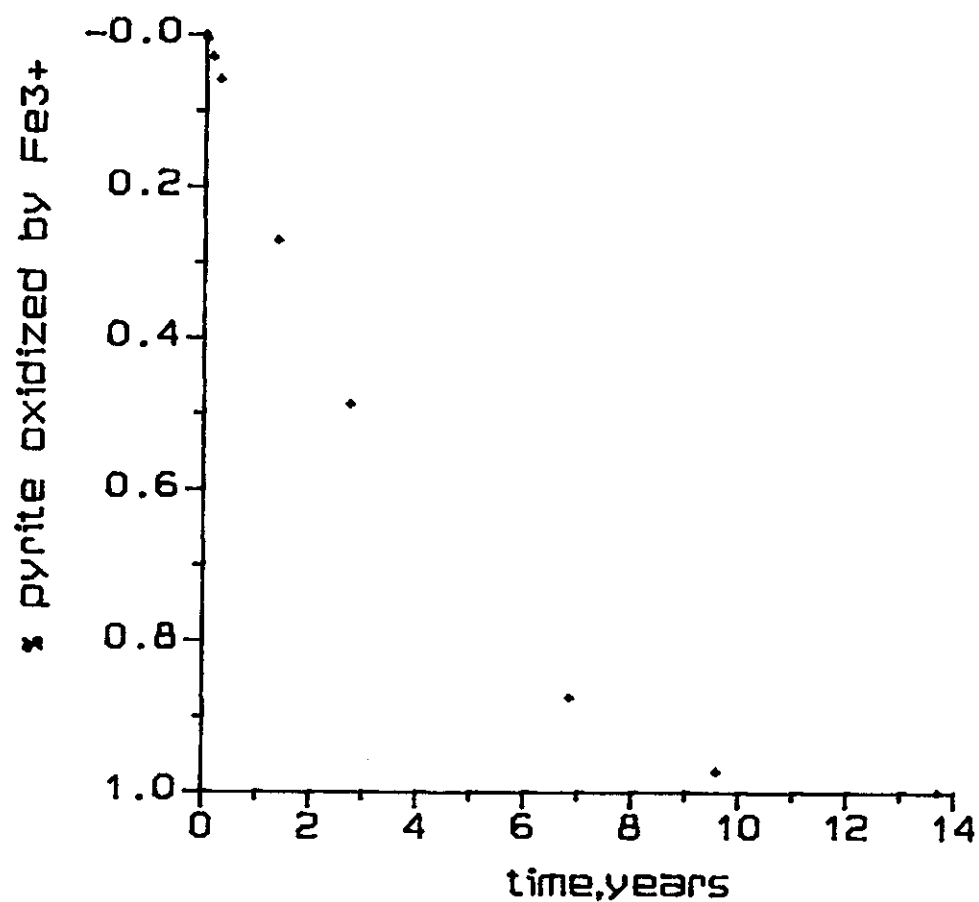


Fig. 6b. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 8$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 4$

$\text{Fe}^{2+} = 1.8 \times 10^{-4} \text{ mol.l}^{-1} (= 10^1 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.6 \times 10^{-9} \text{ mol.l}^{-1}$

$K = 10^{-7} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

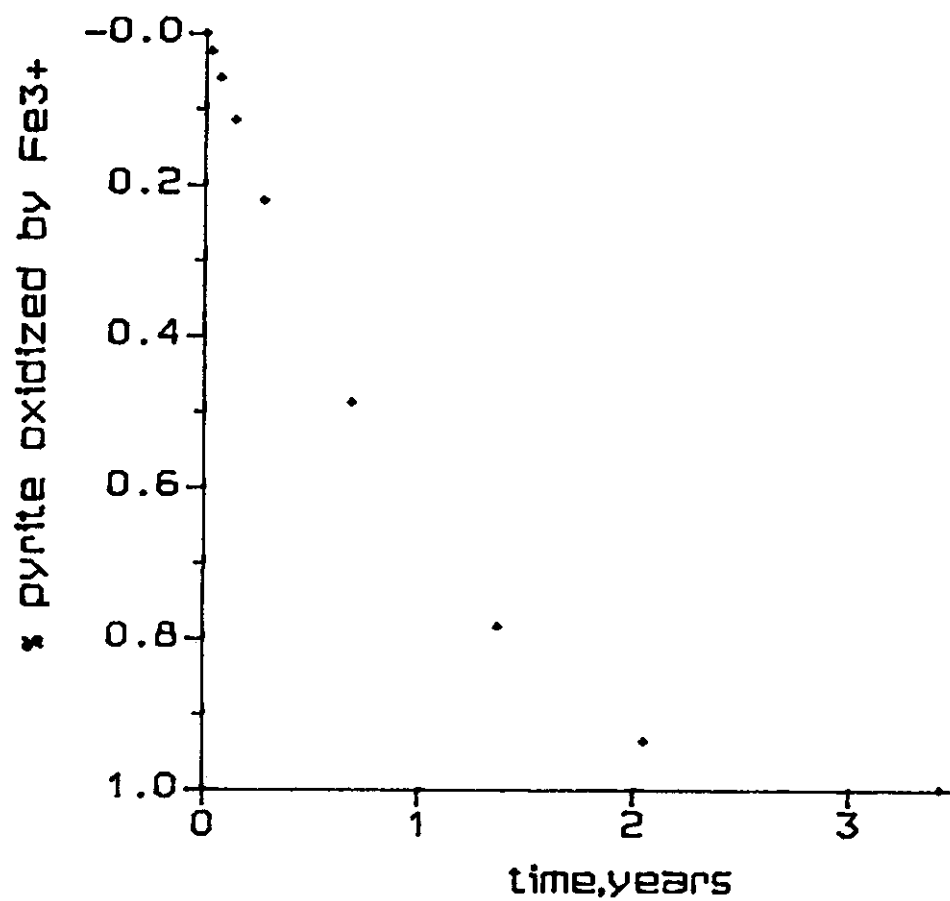


Fig. 6c. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 8$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 4$

$\text{Fe}^{2+} = 1.8 \times 10^{-3} \text{ mol.l}^{-1} (= 10^2 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.6 \times 10^{-8} \text{ mol.l}^{-1}$

$K = 4.0 \times 10^{-7} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

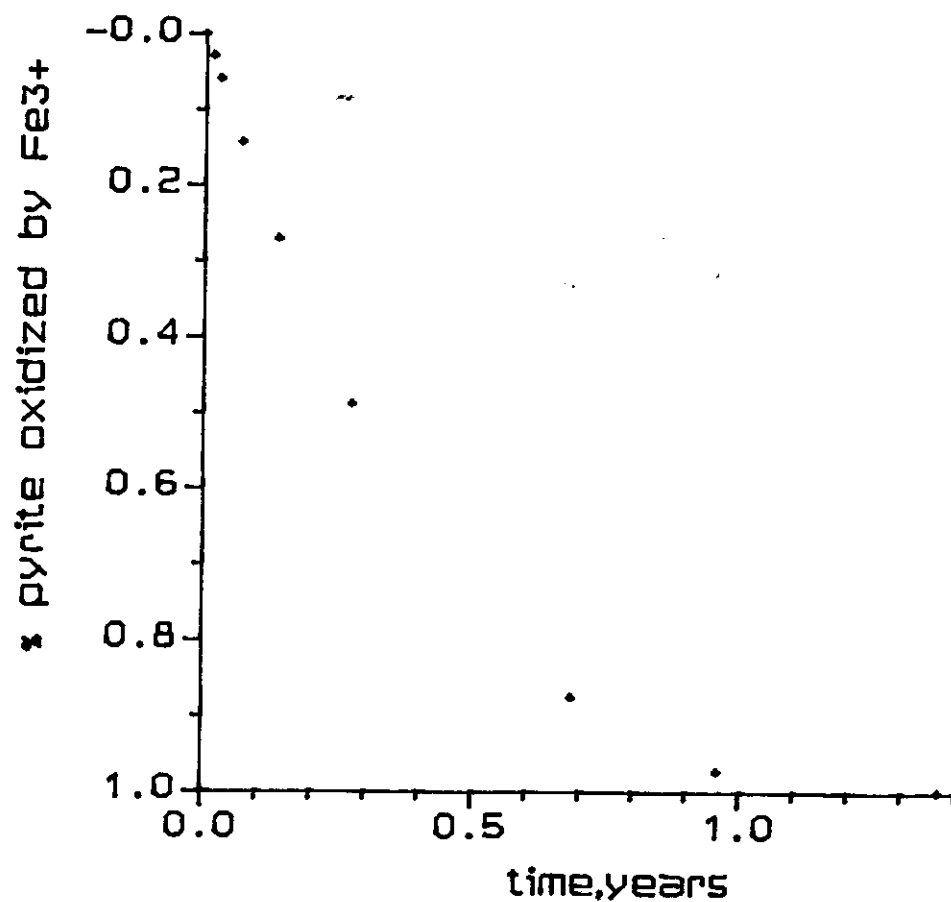


Fig. 6d. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 8$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 4$

$\text{Fe}^{2+} = 1.8 \times 10^{-2} \text{ mol.l}^{-1} (= 10^3 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.6 \times 10^{-7} \text{ mol.l}^{-1}$

$K = 10^{-6} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

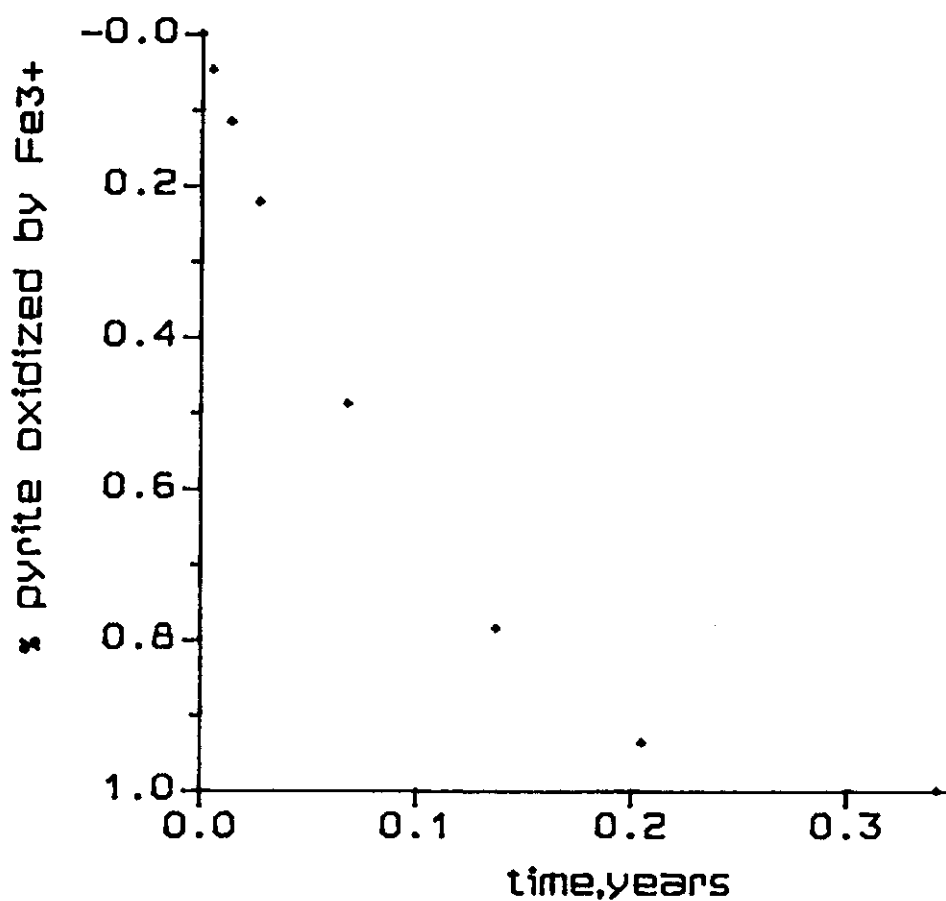


Fig. 6e. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 8$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 4$

$\text{Fe}^{2+} = 1.8 \times 10^{-1} \text{ mol.l}^{-1} (= 10^4 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.6 \times 10^{-6} \text{ mol.l}^{-1}$

$K = 4.0 \times 10^{-6} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

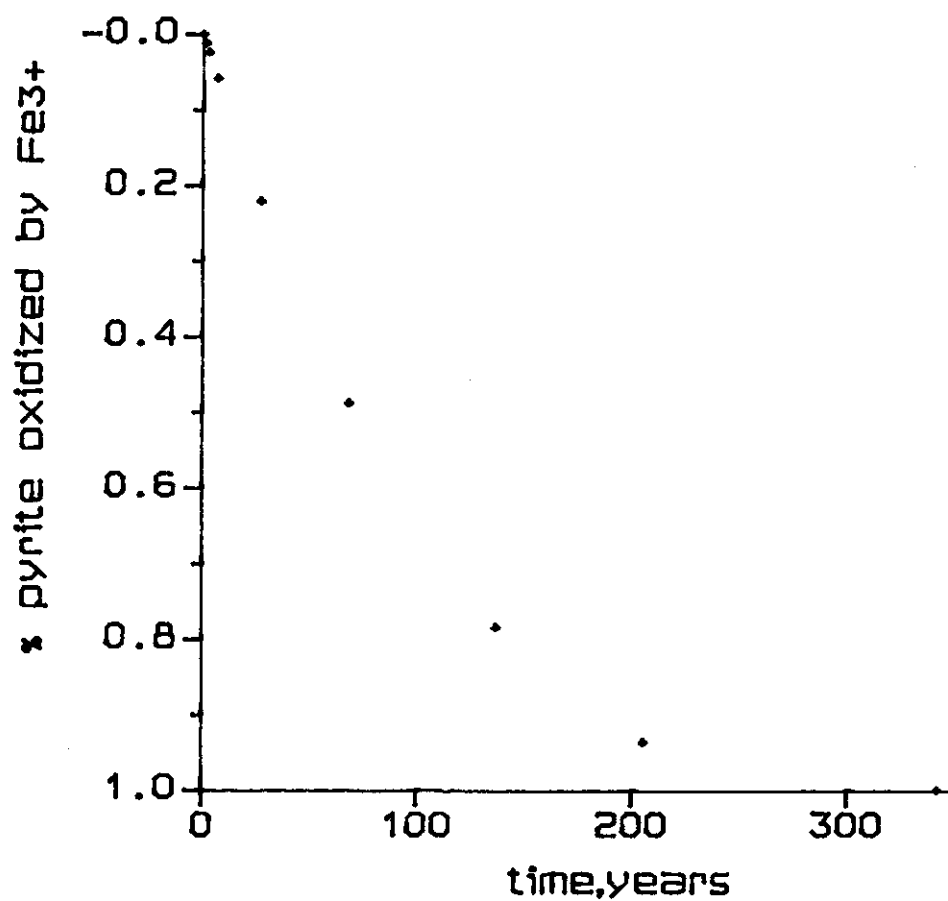


Fig. 6f. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$p_e = 8$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 2$

$\text{Fe}^{2+} = 1.8 \times 10^{-5} \text{ mol.l}^{-1} (= 10^0 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.6 \times 10^{-10} \text{ mol.l}^{-1}$

$K = 4.0 \times 10^{-9} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

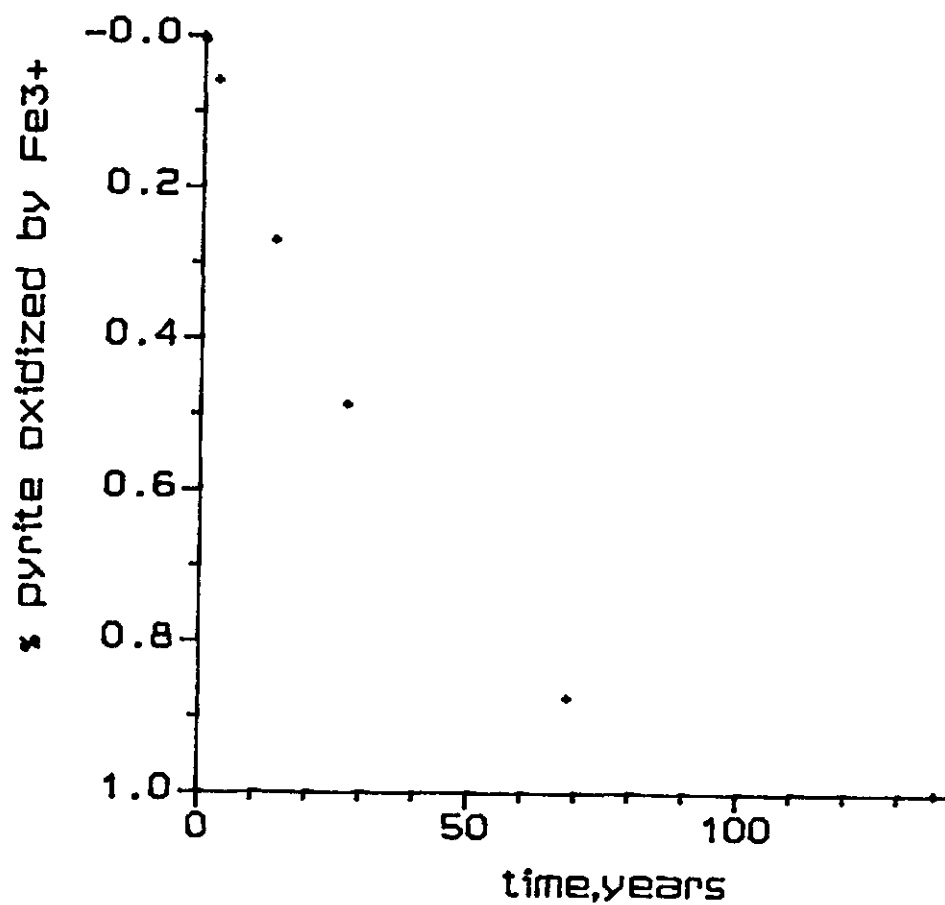


Fig. 6g. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$p_e = 8$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 2$

$\text{Fe}^{2+} = 1.8 \times 10^{-4} \text{ mol.l}^{-1} (= 10^1 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.6 \times 10^{-9} \text{ mol.l}^{-1}$

$K = 10^{-8} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

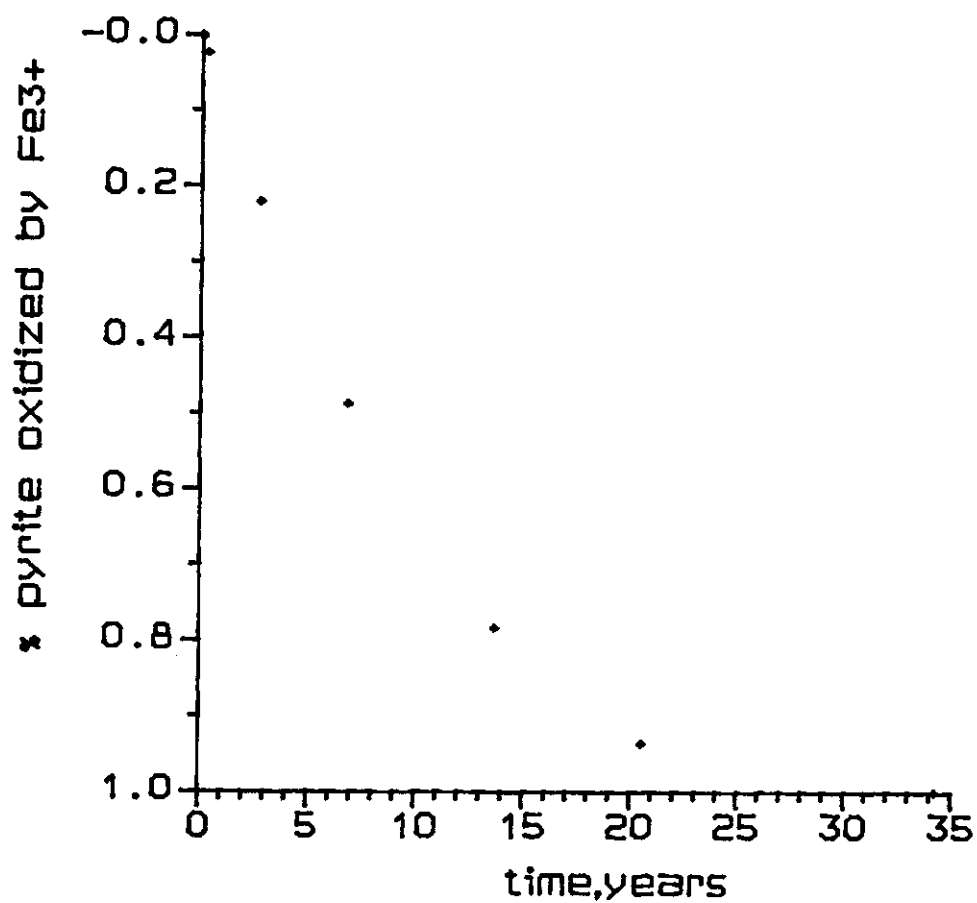


Fig. 6h. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 8$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 2$

$\text{Fe}^{2+} = 1.8 \times 10^{-3} \text{ mol.l}^{-1} (= 10^2 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.6 \times 10^{-8} \text{ mol.l}^{-1}$

$K = 4.0 \times 10^{-8} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

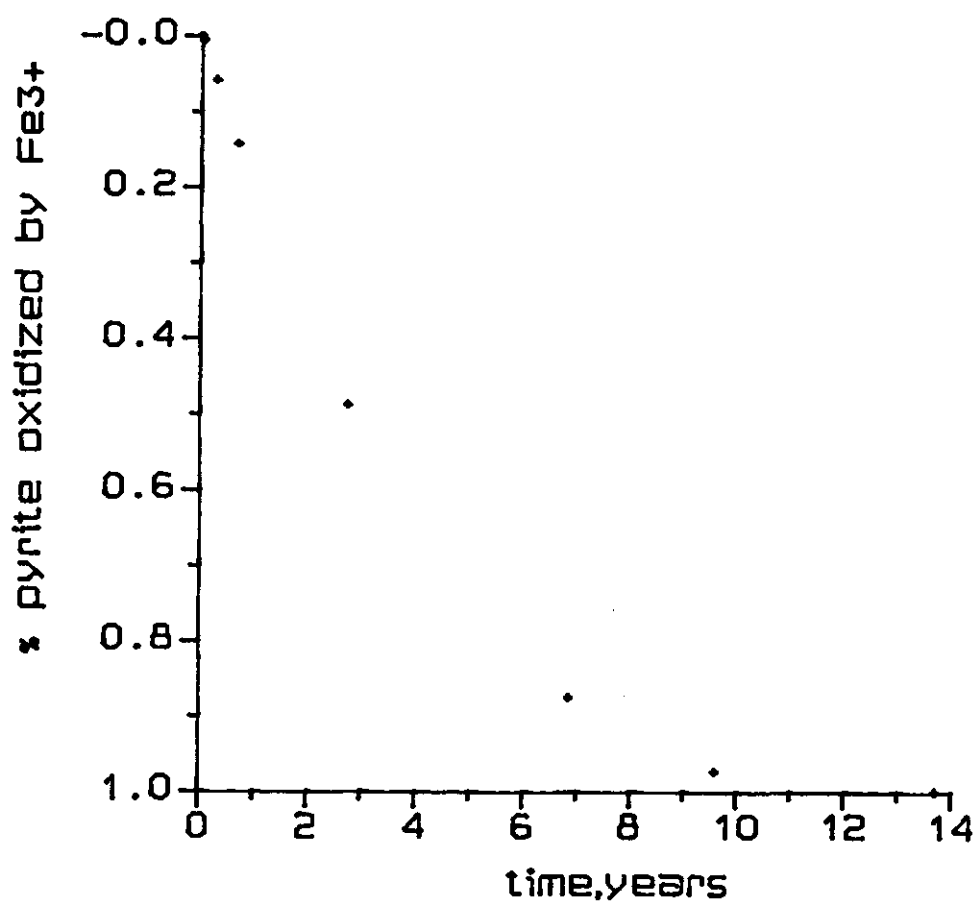


Fig. 61. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 8$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 2$

$\text{Fe}^{2+} = 1.8 \times 10^{-2} \text{ mol.l}^{-1} (= 10^3 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.6 \times 10^{-7} \text{ mol.l}^{-1}$

$K = 10^{-7} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

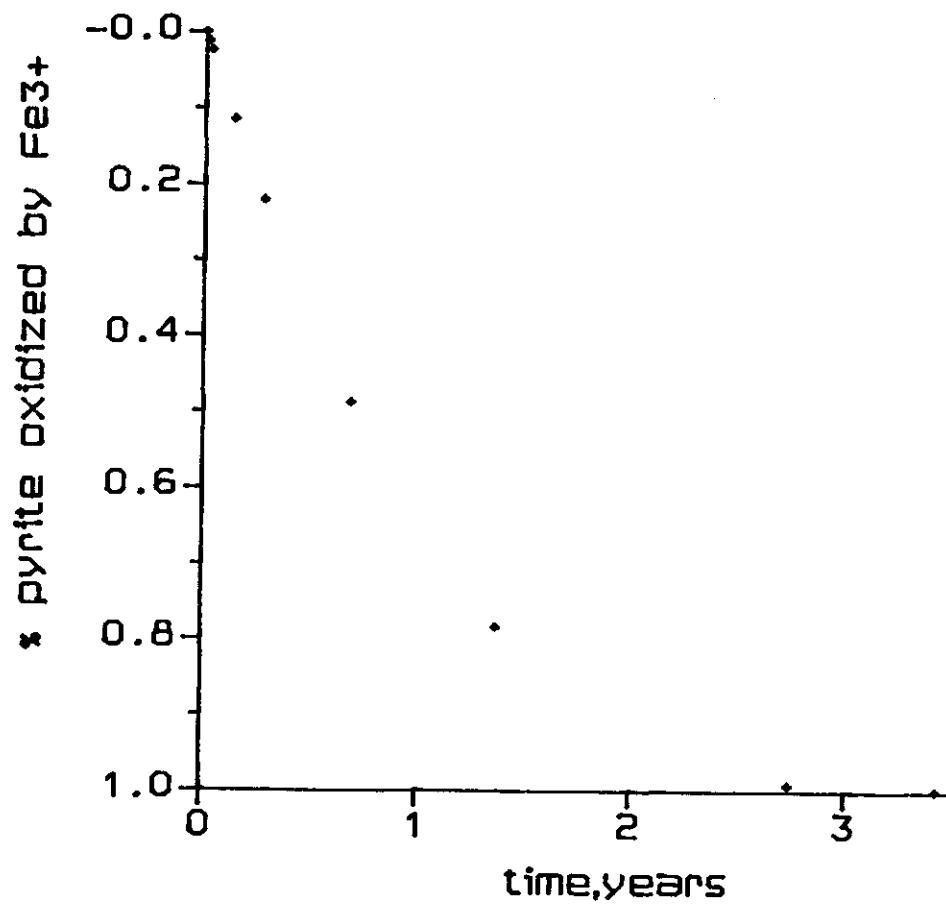


Fig. 6j. Fractional mass losses of pyrite due to oxidation by Fe^{3+} versus time

$\text{pe} = 8$

$d_0 = 2 \mu\text{m}$

$\text{pH} = 2$

$\text{Fe}^{2+} = 1.8 \times 10^{-1} \text{ mol.l}^{-1} (= 10^4 \text{ mg.l}^{-1})$

$\text{Fe}^{3+} = 1.6 \times 10^{-6} \text{ mol.l}^{-1}$

$K = 4.0 \times 10^{-7} \text{ g pyrite.cm}^{-2}.\text{day}^{-1}$

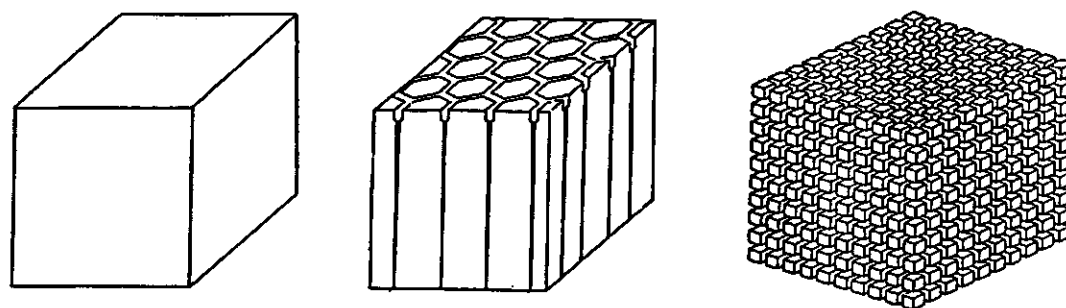


Fig. 7. Development of soil structure in potential acid sulphate soil

- a) Unripe, no macroporosity**
- b) Somewhat ripened, cracked**
- c) Completely ripe, well structured**

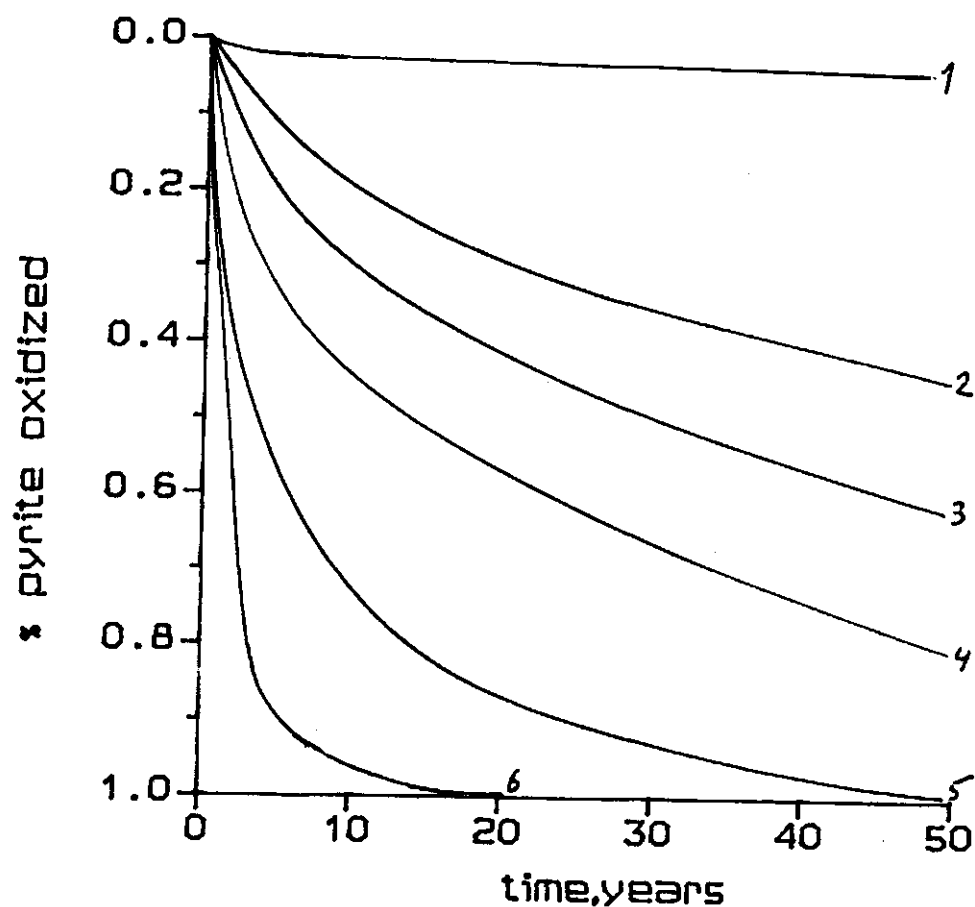


Fig. 8. Effect of soil structure on oxygen diffusion and pyrite oxidation

- 1 : Fully unripe, no structure, $S = 0.01 \text{ cm}^2/\text{cm}^3$
- 2 : Cracked, crack distance 30 cm, $S = 0.13 \text{ cm}^2/\text{cm}^3$
- 3 : Cracked, crack distance 20 cm, $S = 0.2 \text{ cm}^2/\text{cm}^3$
- 4 : Well structured, clod diameter 20 cm, $S = 0.3 \text{ cm}^2/\text{cm}^3$
- 5 : Well structured, clod diameter 10 cm, $S = 0.6 \text{ cm}^2/\text{cm}^3$
- 6 : Well structured, clod diameter 5 cm, $S = 1.2 \text{ cm}^2/\text{cm}^3$

S: Specific surface area of peds. (cm^2/cm^3 soil matrix)

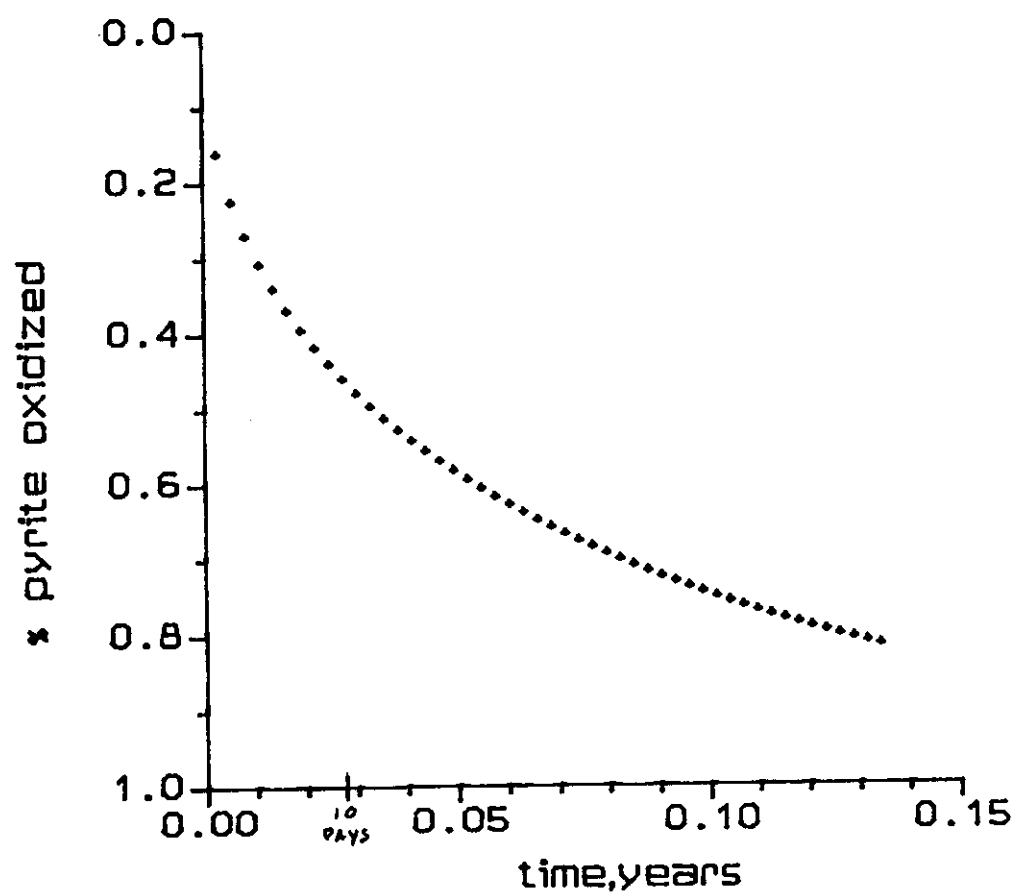


Fig. 9. Oxygen diffusion and pyrite oxidation in a situation with large surface area of aggregates through which oxygen diffusion takes place.
Calculation for aggregates with diameter of 1 cm and specific surface area of $6 \text{ cm}^2/\text{cm}^3$

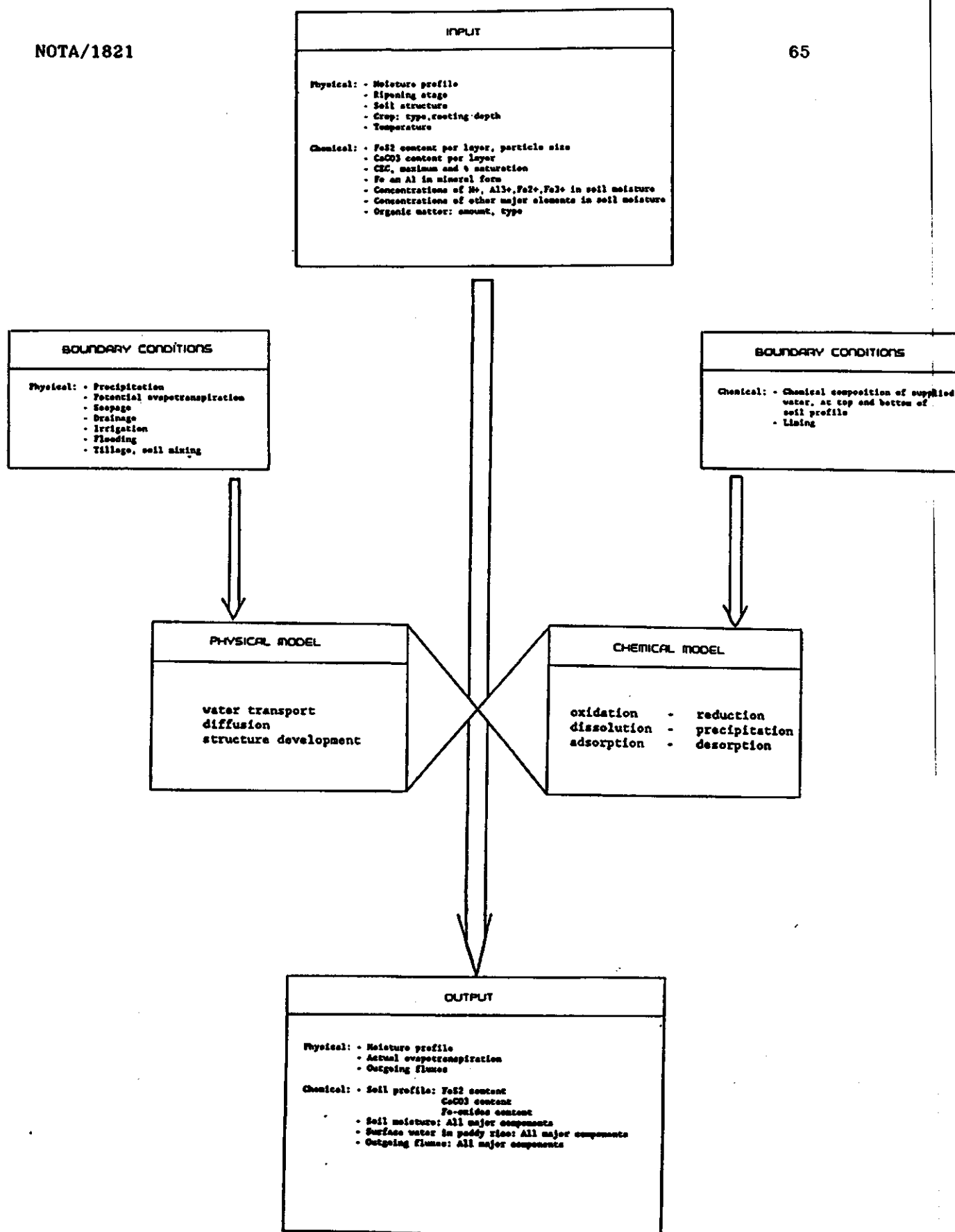


Fig. 10. Model for simulation of physical and chemical processes in acid sulfate soils

**Table 3. Diffusion of oxygen and corresponding pyrite oxidation in
acid sulfate soils with different structure**

OXYGEN DIFFUSION AND PYRITE OXIDATION IN SOILS WITH DIFFERENT STRUCTURE

Volume of soil matrix: 1 m3
 Volume of solids: 0.23 m3 Mass of solids: 624 Kg
 Volume of water: 0.77 m3

Initial amount of pyrite in soil system (mol): 344.0
 (Kg): 41.3
 (% by weight): 6.6

Oxygen concentration in water (moles/l): 0.000458
 Diffusion coefficient (+ reaction) oxygen in water (cm2.s-1): 0.0000000072

Diffusion of oxygen into soil block with area (cm2): 10000.0
 Specific area in contact with oxygen (cm2/cm3 soil matrix): 0.010

Time (years)	Pyrite oxidized (m3/m3) (moles)		Acidity produced (moles)	
			Jarosite	Goethite

1.0	0.007	2.46	7.39	9.85
2.0	0.010	3.48	10.45	13.93
3.0	0.012	4.27	12.80	17.06
4.0	0.014	4.93	14.78	19.70
5.0	0.016	5.51	16.52	22.03
6.0	0.018	6.03	18.10	24.13
7.0	0.019	6.52	19.55	26.06
8.0	0.020	6.97	20.90	27.86
9.0	0.021	7.39	22.16	29.55
10.0	0.023	7.79	23.36	31.15
11.0	0.024	8.17	24.50	32.67
12.0	0.025	8.53	25.59	34.12
13.0	0.026	8.88	26.64	35.52
14.0	0.027	9.21	27.64	36.86
15.0	0.028	9.54	28.61	38.15
16.0	0.029	9.85	29.55	39.40
17.0	0.030	10.15	30.46	40.61
18.0	0.030	10.45	31.34	41.79
19.0	0.031	10.73	32.20	42.94
20.0	0.032	11.01	33.04	44.05
21.0	0.033	11.28	33.85	45.14
22.0	0.034	11.55	34.65	46.20
23.0	0.034	11.81	35.43	47.24
24.0	0.035	12.06	36.19	48.26
25.0	0.036	12.31	36.94	49.25
26.0	0.037	12.56	37.67	50.23
27.0	0.037	12.80	38.39	51.18
28.0	0.038	13.03	39.09	52.12
29.0	0.039	13.26	39.78	53.05
30.0	0.039	13.49	40.46	53.95
31.0	0.040	13.71	41.13	54.84
32.0	0.040	13.93	41.79	55.72
33.0	0.041	14.15	42.44	56.59
34.0	0.042	14.36	43.08	57.44
35.0	0.042	14.57	43.71	58.28
36.0	0.043	14.78	44.33	59.10
37.0	0.044	14.98	44.94	59.92
38.0	0.044	15.18	45.54	60.72
39.0	0.045	15.38	46.14	61.52
40.0	0.045	15.57	46.72	62.30
41.0	0.046	15.77	47.30	63.07

42.0	0.046	15.96	47.88	63.84
43.0	0.047	16.15	48.44	64.59
44.0	0.047	16.33	49.00	65.34
45.0	0.048	16.52	49.56	66.08
46.0	0.049	16.70	50.11	66.81
47.0	0.049	16.88	50.65	67.53
48.0	0.050	17.06	51.18	68.25
49.0	0.050	17.24	51.71	68.95
50.0	0.051	17.41	52.24	69.65

OXYGEN DIFFUSION AND PYRITE OXIDATION IN SOILS WITH DIFFERENT STRUCTURE

Volume of soil matrix: 1 m3
 Volume of solids: 0.23 m3 Mass of solids: 624 Kg
 Volume of water: 0.77 m3

Initial amount of pyrite in soil system (mol): 344.0
 (Kg): 41.3
 (% by weight): 6.6

Oxygen concentration in water (moles/l): 0.000458
 Diffusion coefficient (+ reaction) oxygen in water (cm².s⁻¹): 0.0000000072

Diffusion of oxygen into cylinders with radius (cm): 50.0
 Specific area in contact with oxygen (cm²/cm³ soil matrix): 0.040

Time (years)	Pyrite oxidized (m3/m3) (moles)		Acidity produced (moles)	
			Jarosite	Goethite
1.0	0.037	12.82	38.47	51.29
2.0	0.041	14.23	42.68	56.91
3.0	0.045	15.57	46.71	62.28
4.0	0.049	16.86	50.58	67.44
5.0	0.053	18.10	54.30	72.40
6.0	0.056	19.29	57.88	77.18
7.0	0.059	20.44	61.33	81.78
8.0	0.063	21.55	64.66	86.22
9.0	0.066	22.63	67.88	90.50
10.0	0.069	23.66	70.99	94.65
11.0	0.072	24.67	74.00	98.67
12.0	0.075	25.64	76.93	102.57
13.0	0.077	26.59	79.76	106.35
14.0	0.080	27.51	82.52	110.02
15.0	0.083	28.40	85.20	113.60
16.0	0.085	29.27	87.81	117.08
17.0	0.088	30.12	90.35	120.47
18.0	0.090	30.94	92.83	123.77
19.0	0.092	31.75	95.25	127.00
20.0	0.095	32.54	97.61	130.15
21.0	0.097	33.31	99.92	133.23
22.0	0.099	34.06	102.18	136.24
23.0	0.101	34.80	104.39	139.19
24.0	0.103	35.52	106.56	142.08
25.0	0.105	36.23	108.69	144.92
26.0	0.107	36.92	110.77	147.69
27.0	0.109	37.61	112.82	150.42
28.0	0.111	38.27	114.82	153.10
29.0	0.113	38.93	116.80	155.73
30.0	0.115	39.58	118.73	158.31
31.0	0.117	40.21	120.64	160.85
32.0	0.119	40.84	122.52	163.35
33.0	0.121	41.45	124.36	165.81
34.0	0.122	42.06	126.18	168.24
35.0	0.124	42.66	127.97	170.62
36.0	0.126	43.24	129.73	172.98
37.0	0.127	43.82	131.47	175.29
38.0	0.129	44.39	133.18	177.58
39.0	0.131	44.96	134.88	179.83
40.0	0.132	45.51	136.54	182.06
41.0	0.134	46.06	138.19	184.26
42.0	0.135	46.61	139.82	186.42

43.0	0.137	47.14	141.42	188.56
44.0	0.139	47.67	143.01	190.68
45.0	0.140	48.19	144.58	192.77
46.0	0.142	48.71	146.13	194.83
47.0	0.143	49.22	147.66	196.88
48.0	0.145	49.72	149.17	198.90
49.0	0.146	50.22	150.67	200.89
50.0	0.147	50.72	152.15	202.87

OXYGEN DIFFUSION AND PYRITE OXIDATION IN SOILS WITH DIFFERENT STRUCTURE

Volume of soil matrix: 1 m3
 Volume of solids: 0.23 m3 Mass of solids: 624 Kg
 Volume of water: 0.77 m3

Initial amount of pyrite in soil system (mol): 344.0
 (Kg): 41.3
 (% by weight): 6.6

Oxygen concentration in water (moles/l): 0.000458
 Diffusion coefficient (+ reaction) oxygen in water (cm2.s-1): 0.0000000072

Diffusion of oxygen into cylinders with radius (cm): 25.0
 Specific area in contact with oxygen (cm2/cm3 soil matrix): 0.080

Time (years)	Pyrite oxidized (m3/m3) (moles)		Acidity produced (moles)	
			Jarosite	Goethite
1.0	0.049	16.86	50.58	67.44
2.0	0.063	21.55	64.66	86.22
3.0	0.075	25.64	76.93	102.57
4.0	0.085	29.27	87.81	117.08
5.0	0.095	32.54	97.61	130.15
6.0	0.103	35.52	106.56	142.08
7.0	0.111	38.27	114.82	153.10
8.0	0.119	40.84	122.52	163.35
9.0	0.126	43.24	129.73	172.98
10.0	0.132	45.51	136.54	182.06
11.0	0.139	47.67	143.01	190.68
12.0	0.145	49.72	149.17	198.90
13.0	0.150	51.69	155.07	206.76
14.0	0.156	53.58	160.73	214.30
15.0	0.161	55.39	166.17	221.56
16.0	0.166	57.14	171.43	228.57
17.0	0.171	58.84	176.51	235.34
18.0	0.176	60.48	181.43	241.91
19.0	0.180	62.07	186.21	248.28
20.0	0.185	63.62	190.85	254.47
21.0	0.189	65.12	195.37	260.49
22.0	0.194	66.59	199.77	266.36
23.0	0.198	68.02	204.06	272.09
24.0	0.202	69.42	208.26	277.68
25.0	0.206	70.79	212.36	283.14
26.0	0.210	72.12	216.37	288.49
27.0	0.213	73.43	220.29	293.72
28.0	0.217	74.71	224.14	298.85
29.0	0.221	75.97	227.91	303.88
30.0	0.224	77.20	231.61	308.81
31.0	0.228	78.41	235.24	313.66
32.0	0.231	79.60	238.81	318.41
33.0	0.235	80.77	242.32	323.09
34.0	0.238	81.92	245.76	327.68
35.0	0.241	83.05	249.15	332.21
36.0	0.245	84.16	252.49	336.66
37.0	0.248	85.26	255.78	341.04
38.0	0.251	86.34	259.01	345.35
39.0	0.254	87.40	262.20	349.60
40.0	0.257	88.45	265.34	353.79
41.0	0.260	89.48	268.44	357.92
42.0	0.263	90.50	271.50	362.00

43.0	0.266	91.50	274.51	366.02
44.0	0.269	92.50	277.49	369.99
45.0	0.272	93.48	280.43	373.90
46.0	0.275	94.44	283.33	377.77
47.0	0.277	95.40	286.19	381.59
48.0	0.280	96.34	289.02	385.36
49.0	0.283	97.27	291.82	389.09
50.0	0.285	98.19	294.58	392.78

OXYGEN DIFFUSION AND PYRITE OXIDATION IN SOILS WITH DIFFERENT STRUCTURE

Volume of soil matrix: 1 m3
 Volume of solids: 0.23 m3 Mass of solids: 624 Kg
 Volume of water: 0.77 m3

Initial amount of pyrite in soil system (mol): 344.0
 (Kg): 41.3
 (% by weight): 6.6

Oxygen concentration in water (moles/l): 0.000458
 Diffusion coefficient (+ reaction) oxygen in water (cm2.s-1): 0.0000000072

Diffusion of oxygen into cylinders with radius (cm): 15.0
 Specific area in contact with oxygen (cm2/cm3 soil matrix): 0.133

Time (years)	Pyrite oxidized (m3/m3) (moles)		Acidity produced (moles)	
			Jarosite	Goethite
1.0	0.072	24.78	74.33	99.11
2.0	0.099	34.23	102.68	136.90
3.0	0.121	41.66	124.97	166.63
4.0	0.139	47.90	143.71	191.61
5.0	0.155	53.37	160.11	213.48
6.0	0.169	58.28	174.83	233.11
7.0	0.182	62.76	188.29	251.05
8.0	0.195	66.91	200.73	267.64
9.0	0.206	70.79	212.36	283.14
10.0	0.216	74.43	223.29	297.72
11.0	0.226	77.88	233.64	311.51
12.0	0.236	81.16	243.47	324.63
13.0	0.245	84.29	252.86	337.15
14.0	0.254	87.28	261.85	349.13
15.0	0.262	90.16	270.49	360.65
16.0	0.270	92.93	278.80	371.73
17.0	0.278	95.61	286.82	382.43
18.0	0.285	98.19	294.58	392.78
19.0	0.293	100.70	302.10	402.80
20.0	0.300	103.13	309.39	412.52
21.0	0.307	105.49	316.47	421.96
22.0	0.313	107.79	323.36	431.14
23.0	0.320	110.02	330.06	440.08
24.0	0.326	112.20	336.60	448.80
25.0	0.332	114.33	342.98	457.31
26.0	0.338	116.40	349.21	465.61
27.0	0.344	118.43	355.30	473.73
28.0	0.350	120.42	361.25	481.67
29.0	0.356	122.36	367.08	489.44
30.0	0.361	124.26	372.79	497.06
31.0	0.367	126.13	378.39	504.52
32.0	0.372	127.96	383.87	511.83
33.0	0.377	129.75	389.26	519.01
34.0	0.382	131.51	394.54	526.06
35.0	0.387	133.24	399.73	532.98
36.0	0.392	134.94	404.83	539.78
37.0	0.397	136.62	409.85	546.46
38.0	0.402	138.26	414.78	553.04
39.0	0.407	139.88	419.63	559.50
40.0	0.411	141.47	424.40	565.86
41.0	0.416	143.03	429.10	572.13
42.0	0.420	144.57	433.72	578.30

43.0	0.425	146.09	438.28	584.37
44.0	0.429	147.59	442.77	590.36
45.0	0.433	149.07	447.20	596.26
46.0	0.438	150.52	451.56	602.08
47.0	0.442	151.95	455.86	607.82
48.0	0.446	153.37	460.11	613.48
49.0	0.450	154.77	464.30	619.06
50.0	0.454	156.14	468.43	624.57

OXYGEN DIFFUSION AND PYRITE OXIDATION IN SOILS WITH DIFFERENT STRUCTURE

Volume of soil matrix: 1 m3
 Volume of solids: 0.23 m3 Mass of solids: 624 Kg
 Volume of water: 0.77 m3

Initial amount of pyrite in soil system (mol): 344.0
 (Kg): 41.3
 (% by weight): 6.6

Oxygen concentration in water (moles/l): 0.000458
 Diffusion coefficient (+ reaction) oxygen in water (cm².s-1): 0.0000000072

Diffusion of oxygen into cylinders with radius (cm): 10.0
 Specific area in contact with oxygen (cm²/cm³ soil matrix): 0.200

Time (years)	Pyrite oxidized (m3/m3) (moles)		Acidity produced (moles)	
			Jarosite	Goethite
1.0	0.105	36.23	108.69	144.92
2.0	0.147	50.72	152.15	202.87
3.0	0.179	61.68	185.03	246.70
4.0	0.206	70.79	212.36	283.14
5.0	0.229	78.71	236.14	314.85
6.0	0.249	85.80	257.40	343.20
7.0	0.268	92.25	276.75	369.00
8.0	0.285	98.19	294.58	392.78
9.0	0.302	103.73	311.18	414.90
10.0	0.317	108.91	326.73	435.64
11.0	0.331	113.80	341.40	455.20
12.0	0.344	118.43	355.30	473.73
13.0	0.357	122.84	368.52	491.36
14.0	0.369	127.05	381.14	508.19
15.0	0.381	131.08	393.23	524.31
16.0	0.392	134.94	404.83	539.78
17.0	0.403	138.67	416.00	554.66
18.0	0.414	142.25	426.76	569.01
19.0	0.424	145.72	437.15	582.86
20.0	0.433	149.07	447.20	596.26
21.0	0.443	152.31	456.93	609.24
22.0	0.452	155.46	466.37	621.83
23.0	0.461	158.51	475.53	634.05
24.0	0.469	161.48	484.44	645.92
25.0	0.478	164.37	493.11	657.48
26.0	0.486	167.18	501.55	668.73
27.0	0.494	169.92	509.77	679.69
28.0	0.502	172.60	517.79	690.39
29.0	0.509	175.21	525.62	700.82
30.0	0.517	177.75	533.26	711.01
31.0	0.524	180.24	540.73	720.97
32.0	0.531	182.68	548.03	730.71
33.0	0.538	185.06	555.18	740.24
34.0	0.545	187.39	562.17	749.56
35.0	0.551	189.67	569.02	758.69
36.0	0.558	191.91	575.72	767.63
37.0	0.564	194.10	582.30	776.40
38.0	0.570	196.25	588.74	784.99
39.0	0.577	198.35	595.06	793.42
40.0	0.583	200.42	601.26	801.68
41.0	0.589	202.45	607.35	809.80
42.0	0.594	204.44	613.32	817.76

43.0	0.600	206.40	619.19	825.59
44.0	0.606	208.32	624.95	833.27
45.0	0.611	210.20	630.61	840.82
46.0	0.616	212.06	636.18	848.24
47.0	0.622	213.88	641.65	855.53
48.0	0.627	215.67	647.02	862.70
49.0	0.632	217.44	652.31	869.75
50.0	0.637	219.17	657.51	876.68

OXYGEN DIFFUSION AND PYRITE OXIDATION IN SOILS WITH DIFFERENT STRUCTURE

Volume of soil matrix: 1 m3
 Volume of solids: 0.23 m3 Mass of solids: 624 Kg
 Volume of water: 0.77 m3

Initial amount of pyrite in soil system (mol): 344.0
 (Kg): 41.3
 (% by weight): 6.6

Oxygen concentration in water (moles/l): 0.000458
 Diffusion coefficient (+ reaction) oxygen in water (cm2.s-1): 0.0000000072

Diffusion of oxygen into cylinders with radius (cm): 5.0
 Specific area in contact with oxygen (cm2/cm3 soil matrix): 0.400

Time (years)	Pyrite oxidized		Acidity produced	
	(m3/m3)	(moles)	(moles)	Jarosite Goethite
1.0	0.206	70.79	212.36	283.14
2.0	0.285	98.19	294.58	392.78
3.0	0.344	118.43	355.30	473.73
4.0	0.392	134.94	404.83	539.78
5.0	0.433	149.07	447.20	596.26
6.0	0.469	161.48	484.44	645.92
7.0	0.502	172.60	517.79	690.39
8.0	0.531	182.68	548.03	730.71
9.0	0.558	191.91	575.72	767.63
10.0	0.583	200.42	601.26	801.68
11.0	0.606	208.32	624.95	833.27
12.0	0.627	215.67	647.02	862.70
13.0	0.647	222.55	667.66	890.22
14.0	0.666	229.01	687.02	916.02
15.0	0.683	235.07	705.21	940.27
16.0	0.700	240.78	722.33	963.11
17.0	0.716	246.16	738.49	984.65
18.0	0.730	251.25	753.74	1004.99
19.0	0.744	256.05	768.16	1024.21
20.0	0.758	260.60	781.79	1042.39
21.0	0.770	264.90	794.70	1059.59
22.0	0.782	268.97	806.91	1075.89
23.0	0.793	272.83	818.49	1091.32
24.0	0.804	276.49	829.46	1105.95
25.0	0.814	279.95	839.86	1119.81
26.0	0.823	283.24	849.71	1132.95
27.0	0.832	286.35	859.06	1145.41
28.0	0.841	289.31	867.92	1157.23
29.0	0.849	292.11	876.33	1168.44
30.0	0.857	294.77	884.30	1179.07
31.0	0.864	297.29	891.87	1189.16
32.0	0.871	299.68	899.04	1198.72
33.0	0.878	301.95	905.85	1207.80
34.0	0.884	304.10	912.31	1216.41
35.0	0.890	306.14	918.43	1224.58
36.0	0.896	308.08	924.25	1232.33
37.0	0.901	309.92	929.76	1239.68
38.0	0.906	311.66	934.99	1246.66
39.0	0.911	313.32	939.96	1253.28
40.0	0.915	314.89	944.67	1259.56
41.0	0.920	316.38	949.14	1265.52
42.0	0.924	317.79	953.38	1271.17

43.0	0.928	319.13	957.40	1276.53
44.0	0.931	320.41	961.22	1281.62
45.0	0.935	321.61	964.84	1286.45
46.0	0.938	322.76	968.28	1291.03
47.0	0.941	323.85	971.54	1295.38
48.0	0.944	324.88	974.63	1299.51
49.0	0.947	325.86	977.57	1303.42
50.0	0.950	326.78	980.35	1307.14

OXYGEN DIFFUSION AND PYRITE OXIDATION IN SOILS WITH DIFFERENT STRUCTURE

Volume of soil matrix: 1 m3
 Volume of solids: 0.23 m3 Mass of solids: 624 Kg
 Volume of water: 0.77 m3

Initial amount of pyrite in soil system (mol): 344.0
 (Kg): 41.3
 (% by weight): 6.6

Oxygen concentration in water (moles/l): 0.000458
 Diffusion coefficient (+ reaction) oxygen in water (cm².s⁻¹): 0.0000000072

Diffusion of oxygen into spheres with radius (cm): 20.0
 Specific area in contact with oxygen (cm²/cm³ soil matrix): 0.150

Time (years)	Pyrite oxidized (m3/m3) (moles)	Acidity produced (moles) Jarosite Goethite
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1.0	0.089 30.49	91.48 121.98
2.0	0.114 39.29	117.88 157.18
3.0	0.136 46.81	140.42 187.23
4.0	0.155 53.37	160.11 213.48
5.0	0.172 59.21	177.63 236.84
6.0	0.187 64.49	193.47 257.97
7.0	0.202 69.33	207.98 277.30
8.0	0.215 73.80	221.39 295.19
9.0	0.227 77.97	233.90 311.86
10.0	0.238 81.88	245.64 327.52
11.0	0.249 85.57	256.72 342.30
12.0	0.259 89.08	267.24 356.32
13.0	0.269 92.42	277.25 369.67
14.0	0.278 95.61	286.82 382.43
15.0	0.287 98.67	296.00 394.66
16.0	0.295 101.60	304.81 406.42
17.0	0.304 104.43	313.30 417.73
18.0	0.312 107.16	321.49 428.66
19.0	0.319 109.80	329.41 439.22
20.0	0.327 112.36	337.08 449.44
21.0	0.334 114.84	344.51 459.35
22.0	0.341 117.24	351.73 468.98
23.0	0.348 119.58	358.75 478.33
24.0	0.354 121.86	365.58 487.44
25.0	0.361 124.08	372.23 496.30
26.0	0.367 126.24	378.71 504.95
27.0	0.373 128.35	385.04 513.39
28.0	0.379 130.41	391.22 521.62
29.0	0.385 132.42	397.26 529.68
30.0	0.391 134.39	403.16 537.55
31.0	0.396 136.31	408.94 545.25
32.0	0.402 138.20	414.60 552.80
33.0	0.407 140.05	420.14 560.19
34.0	0.412 141.86	425.57 567.43
35.0	0.418 143.63	430.90 574.54
36.0	0.423 145.38	436.13 581.51
37.0	0.428 147.09	441.26 588.35
38.0	0.432 148.77	446.30 595.07
39.0	0.437 150.42	451.25 601.66
40.0	0.442 152.04	456.11 608.15
41.0	0.447 153.63	460.90 614.53

42.0	0.451	155.20	465.60	620.80
43.0	0.456	156.74	470.22	626.97
44.0	0.460	158.26	474.78	633.04
45.0	0.464	159.75	479.26	639.01
46.0	0.469	161.22	483.67	644.89
47.0	0.473	162.67	488.02	650.69
48.0	0.477	164.10	492.30	656.40
49.0	0.481	165.51	496.52	662.02
50.0	0.485	166.89	500.67	667.56

OXYGEN DIFFUSION AND PYRITE OXIDATION IN SOILS WITH DIFFERENT STRUCTURE

Volume of soil matrix: 1 m3
 Volume of solids: 0.23 m3 Mass of solids: 624 Kg
 Volume of water: 0.77 m3

Initial amount of pyrite in soil system (mol): 344.0
 (Kg): 41.3
 (% by weight): 6.6

Oxygen concentration in water (moles/l): 0.000458
 Diffusion coefficient (+ reaction) oxygen in water (cm².s⁻¹): 0.0000000072

Diffusion of oxygen into spheres with radius (cm): 10.0
 Specific area in contact with oxygen (cm²/cm³ soil matrix): 0.300

Time (years)	Pyrite oxidized (m3/m3) (moles)	Acidity produced (moles) Jarosite Goethite
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1.0	0.155 53.37	160.11 213.48
2.0	0.215 73.80	221.39 295.19
3.0	0.259 89.08	267.24 356.32
4.0	0.295 101.60	304.81 406.42
5.0	0.327 112.36	337.08 449.44
6.0	0.354 121.86	365.58 487.44
7.0	0.379 130.41	391.22 521.62
8.0	0.402 138.20	414.60 552.80
9.0	0.423 145.38	436.13 581.51
10.0	0.442 152.04	456.11 608.15
11.0	0.460 158.26	474.78 633.04
12.0	0.477 164.10	492.30 656.40
13.0	0.493 169.60	508.81 678.42
14.0	0.508 174.81	524.44 699.25
15.0	0.523 179.76	539.27 719.03
16.0	0.536 184.46	553.39 737.85
17.0	0.549 188.95	566.85 755.80
18.0	0.562 193.24	579.72 772.96
19.0	0.574 197.35	592.04 789.39
20.0	0.585 201.29	603.86 805.15
21.0	0.596 205.07	615.22 820.29
22.0	0.607 208.71	626.14 834.85
23.0	0.617 212.22	636.66 848.88
24.0	0.627 215.60	646.80 862.40
25.0	0.636 218.86	656.59 875.45
26.0	0.645 222.01	666.04 888.05
27.0	0.654 225.06	675.18 900.24
28.0	0.663 228.01	684.02 912.03
29.0	0.671 230.86	692.58 923.44
30.0	0.679 233.63	700.88 934.50
31.0	0.687 236.31	708.92 945.23
32.0	0.694 238.91	716.72 955.63
33.0	0.702 241.43	724.29 965.72
34.0	0.709 243.88	731.64 975.52
35.0	0.716 246.26	738.78 985.05
36.0	0.723 248.57	745.72 994.30
37.0	0.729 250.82	752.47 1003.30
38.0	0.735 253.01	759.03 1012.05
39.0	0.742 255.14	765.42 1020.56
40.0	0.748 257.21	771.63 1028.85
41.0	0.754 259.23	777.68 1036.91

42.0	0.759	261.19	783.58	1044.77
43.0	0.765	263.10	789.31	1052.42
44.0	0.770	264.97	794.91	1059.87
45.0	0.776	266.78	800.35	1067.14
46.0	0.781	268.56	805.67	1074.22
47.0	0.786	270.28	810.84	1081.12
48.0	0.791	271.96	815.89	1087.86
49.0	0.795	273.61	820.82	1094.42
50.0	0.800	275.21	825.62	1100.83

OXYGEN DIFFUSION AND PYRITE OXIDATION IN SOILS WITH DIFFERENT STRUCTURE

Volume of soil matrix: 1 m3
 Volume of solids: 0.23 m3 Mass of solids: 624 Kg
 Volume of water: 0.77 m3

Initial amount of pyrite in soil system (mol): 344.0
 (Kg): 41.3
 (% by weight): 6.6

Oxygen concentration in water (moles/l): 0.000458
 Diffusion coefficient (+ reaction) oxygen in water (cm².s⁻¹): 0.0000000072

Diffusion of oxygen into spheres with radius (cm): 5.0
 Specific area in contact with oxygen (cm²/cm³ soil matrix): 0.600

Time (years)	Pyrite oxidized (m3/m3) (moles)		Acidity produced (moles)	
			Jarosite	Goethite
1.0	0.295	101.60	304.81	406.42
2.0	0.402	138.20	414.60	552.80
3.0	0.477	164.10	492.30	656.40
4.0	0.536	184.46	553.39	737.85
5.0	0.585	201.29	603.86	805.15
6.0	0.627	215.60	646.80	862.40
7.0	0.663	228.01	684.02	912.03
8.0	0.694	238.91	716.72	955.63
9.0	0.723	248.57	745.72	994.30
10.0	0.748	257.21	771.63	1028.85
11.0	0.770	264.97	794.91	1059.87
12.0	0.791	271.96	815.89	1087.86
13.0	0.809	278.29	834.88	1113.18
14.0	0.826	284.03	852.10	1136.14
15.0	0.841	289.25	867.75	1157.00
16.0	0.855	294.00	881.99	1175.99
17.0	0.867	298.32	894.96	1193.28
18.0	0.879	302.26	906.79	1209.05
19.0	0.889	305.86	917.58	1223.43
20.0	0.899	309.14	927.42	1236.56
21.0	0.907	312.14	936.42	1248.55
22.0	0.915	314.88	944.63	1259.51
23.0	0.923	317.38	952.13	1269.51
24.0	0.929	319.66	958.99	1278.65
25.0	0.935	321.75	965.26	1287.01
26.0	0.941	323.66	970.98	1294.64
27.0	0.946	325.41	976.22	1301.62
28.0	0.951	327.00	981.00	1308.00
29.0	0.955	328.46	985.38	1313.83
30.0	0.959	329.79	989.37	1319.17
31.0	0.962	331.01	993.03	1324.04
32.0	0.965	332.12	996.37	1328.50
33.0	0.968	333.14	999.43	1332.57
34.0	0.971	334.07	1002.22	1336.29
35.0	0.974	334.92	1004.77	1339.70
36.0	0.976	335.70	1007.11	1342.81
37.0	0.978	336.41	1009.24	1345.66
38.0	0.980	337.06	1011.19	1348.26
39.0	0.982	337.66	1012.98	1350.64
40.0	0.983	338.20	1014.61	1352.81
41.0	0.985	338.70	1016.10	1354.80

42.0	0.986	339.15	1017.46	1356.62
43.0	0.987	339.57	1018.71	1358.28
44.0	0.988	339.95	1019.85	1359.80
45.0	0.989	340.30	1020.89	1361.19
46.0	0.990	340.61	1021.84	1362.46
47.0	0.991	340.90	1022.71	1363.62
48.0	0.992	341.17	1023.51	1364.68
49.0	0.992	341.41	1024.24	1365.65
50.0	0.993	341.63	1024.90	1366.54

OXYGEN DIFFUSION AND PYRITE OXIDATION IN SOILS WITH DIFFERENT STRUCTURE

Volume of soil matrix: 1 m3
 Volume of solids: 0.23 m3 Mass of solids: 624 Kg
 Volume of water: 0.77 m3

Initial amount of pyrite in soil system (mol): 344.0
 (Kg): 41.3
 (% by weight): 6.6

Oxygen concentration in water (moles/l): 0.000458
 Diffusion coefficient (+ reaction) oxygen in water (cm2.s-1): 0.0000000072

Diffusion of oxygen into spheres with radius (cm): 2.5
 Specific area in contact with oxygen (cm2/cm3 soil matrix): 1.200

Time (years)	Pyrite oxidized (m3/m3) (moles)		Acidity produced (moles)	
			Jarosite	Goethite
1.0	0.536	184.46	553.39	737.85
2.0	0.694	238.91	716.72	955.63
3.0	0.791	271.96	815.89	1087.86
4.0	0.855	294.00	881.99	1175.99
5.0	0.899	309.14	927.42	1236.56
6.0	0.929	319.66	958.99	1278.65
7.0	0.951	327.00	981.00	1308.00
8.0	0.965	332.12	996.37	1328.50
9.0	0.976	335.70	1007.11	1342.81
10.0	0.983	338.20	1014.61	1352.81
11.0	0.988	339.95	1019.85	1359.80
12.0	0.992	341.17	1023.51	1364.68
13.0	0.994	342.02	1026.07	1368.09
14.0	0.996	342.62	1027.86	1370.47
15.0	0.997	343.03	1029.10	1372.14
16.0	0.998	343.33	1029.98	1373.30
17.0	0.999	343.53	1030.59	1374.12
18.0	0.999	343.67	1031.01	1374.68
19.0	0.999	343.77	1031.31	1375.08
20.0	1.000	343.84	1031.52	1375.36
21.0	1.000	343.89	1031.66	1375.55
22.0	1.000	343.92	1031.76	1375.69
23.0	1.000	343.95	1031.84	1375.78
24.0	1.000	343.96	1031.89	1375.85
25.0	1.000	343.97	1031.92	1375.89
26.0	1.000	343.98	1031.94	1375.93
27.0	1.000	343.99	1031.96	1375.95
28.0	1.000	343.99	1031.97	1375.96
29.0	1.000	343.99	1031.98	1375.97
30.0	1.000	344.00	1031.99	1375.98
31.0	1.000	344.00	1031.99	1375.99
32.0	1.000	344.00	1031.99	1375.99
33.0	1.000	344.00	1032.00	1375.99
34.0	1.000	344.00	1032.00	1376.00
35.0	1.000	344.00	1032.00	1376.00
36.0	1.000	344.00	1032.00	1376.00
37.0	1.000	344.00	1032.00	1376.00
38.0	1.000	344.00	1032.00	1376.00
39.0	1.000	344.00	1032.00	1376.00
40.0	1.000	344.00	1032.00	1376.00
41.0	1.000	344.00	1032.00	1376.00

42.0	1.000	344.00	1032.00	1376.00
43.0	1.000	344.00	1032.00	1376.00
44.0	1.000	344.00	1032.00	1376.00
45.0	1.000	344.00	1032.00	1376.00
46.0	1.000	344.00	1032.00	1376.00
47.0	1.000	344.00	1032.00	1376.00
48.0	1.000	344.00	1032.00	1376.00
49.0	1.000	344.00	1032.00	1376.00
50.0	1.000	344.00	1032.00	1376.00

OXYGEN DIFFUSION AND PYRITE OXIDATION IN SOILS WITH DIFFERENT STRUCTURE

Volume of soil matrix: 1 m3
 Volume of solids: 0.23 m3 Mass of solids: 624 Kg
 Volume of water: 0.77 m3

Initial amount of pyrite in soil system (mol): 344.0
 (Kg): 41.3
 (% by weight): 6.6

Oxygen concentration in water (moles/l): 0.000458
 Diffusion coefficient (+ reaction) oxygen in water (cm2.s-1): 0.0000000072

Diffusion of oxygen into spheres with radius (cm): 1.0
 Specific area in contact with oxygen (cm2/cm3 soil matrix): 3.000

Time (years)	Pyrite oxidized (m3/m3) (moles)		Acidity produced	
			(moles)	
			Jarosite	Goethite

1.0	0.935	321.75	965.26	1287.01
2.0	0.993	341.63	1024.90	1366.54
3.0	0.999	343.75	1031.25	1374.99
4.0	1.000	343.97	1031.92	1375.89
5.0	1.000	344.00	1031.99	1375.99
6.0	1.000	344.00	1032.00	1376.00
7.0	1.000	344.00	1032.00	1376.00
8.0	1.000	344.00	1032.00	1376.00
9.0	1.000	344.00	1032.00	1376.00
10.0	1.000	344.00	1032.00	1376.00
11.0	1.000	344.00	1032.00	1376.00
12.0	1.000	344.00	1032.00	1376.00
13.0	1.000	344.00	1032.00	1376.00
14.0	1.000	344.00	1032.00	1376.00
15.0	1.000	344.00	1032.00	1376.00
16.0	1.000	344.00	1032.00	1376.00
17.0	1.000	344.00	1032.00	1376.00
18.0	1.000	344.00	1032.00	1376.00
19.0	1.000	344.00	1032.00	1376.00
20.0	1.000	344.00	1032.00	1376.00
21.0	1.000	344.00	1032.00	1376.00
22.0	1.000	344.00	1032.00	1376.00
23.0	1.000	344.00	1032.00	1376.00
24.0	1.000	344.00	1032.00	1376.00
25.0	1.000	344.00	1032.00	1376.00
26.0	1.000	344.00	1032.00	1376.00
27.0	1.000	344.00	1032.00	1376.00
28.0	1.000	344.00	1032.00	1376.00
29.0	1.000	344.00	1032.00	1376.00
30.0	1.000	344.00	1032.00	1376.00
31.0	1.000	344.00	1032.00	1376.00
32.0	1.000	344.00	1032.00	1376.00
33.0	1.000	344.00	1032.00	1376.00
34.0	1.000	344.00	1032.00	1376.00
35.0	1.000	344.00	1032.00	1376.00
36.0	1.000	344.00	1032.00	1376.00
37.0	1.000	344.00	1032.00	1376.00
38.0	1.000	344.00	1032.00	1376.00
39.0	1.000	344.00	1032.00	1376.00
40.0	1.000	344.00	1032.00	1376.00
41.0	1.000	344.00	1032.00	1376.00

42.0	1.000	344.00	1032.00	1376.00
43.0	1.000	344.00	1032.00	1376.00
44.0	1.000	344.00	1032.00	1376.00
45.0	1.000	344.00	1032.00	1376.00
46.0	1.000	344.00	1032.00	1376.00
47.0	1.000	344.00	1032.00	1376.00
48.0	1.000	344.00	1032.00	1376.00
49.0	1.000	344.00	1032.00	1376.00
50.0	1.000	344.00	1032.00	1376.00

OXYGEN DIFFUSION AND PYRITE OXIDATION IN SOILS WITH DIFFERENT STRUCTURE

Volume of soil matrix: 1 m3
 Volume of solids: 0.23 m3 Mass of solids: 624 Kg
 Volume of water: 0.77 m3

Initial amount of pyrite in soil system (mol): 344.0
 (Kg): 41.3
 (% by weight): 6.6

Oxygen concentration in water (moles/l): 0.000458
 Diffusion coefficient (+ reaction) oxygen in water (cm2.s-1): 0.0000000072

Diffusion of oxygen into spheres with radius (cm): 0.5
 Specific area in contact with oxygen (cm2/cm3 soil matrix): 6.000

Time (years)	Pyrite oxidized (m3/m3) (moles)	Acidity produced (moles) Jarosite Goethite
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1.0	1.000 343.97	1031.92 1375.89
2.0	1.000 344.00	1032.00 1376.00
3.0	1.000 344.00	1032.00 1376.00
4.0	1.000 344.00	1032.00 1376.00
5.0	1.000 344.00	1032.00 1376.00
6.0	1.000 344.00	1032.00 1376.00
7.0	1.000 344.00	1032.00 1376.00
8.0	1.000 344.00	1032.00 1376.00
9.0	1.000 344.00	1032.00 1376.00
10.0	1.000 344.00	1032.00 1376.00
11.0	1.000 344.00	1032.00 1376.00
12.0	1.000 344.00	1032.00 1376.00
13.0	1.000 344.00	1032.00 1376.00
14.0	1.000 344.00	1032.00 1376.00
15.0	1.000 344.00	1032.00 1376.00
16.0	1.000 344.00	1032.00 1376.00
17.0	1.000 344.00	1032.00 1376.00
18.0	1.000 344.00	1032.00 1376.00
19.0	1.000 344.00	1032.00 1376.00
20.0	1.000 344.00	1032.00 1376.00
21.0	1.000 344.00	1032.00 1376.00
22.0	1.000 344.00	1032.00 1376.00
23.0	1.000 344.00	1032.00 1376.00
24.0	1.000 344.00	1032.00 1376.00
25.0	1.000 344.00	1032.00 1376.00
26.0	1.000 344.00	1032.00 1376.00
27.0	1.000 344.00	1032.00 1376.00
28.0	1.000 344.00	1032.00 1376.00
29.0	1.000 344.00	1032.00 1376.00
30.0	1.000 344.00	1032.00 1376.00
31.0	1.000 344.00	1032.00 1376.00
32.0	1.000 344.00	1032.00 1376.00
33.0	1.000 344.00	1032.00 1376.00
34.0	1.000 344.00	1032.00 1376.00
35.0	1.000 344.00	1032.00 1376.00
36.0	1.000 344.00	1032.00 1376.00
37.0	1.000 344.00	1032.00 1376.00
38.0	1.000 344.00	1032.00 1376.00
39.0	1.000 344.00	1032.00 1376.00
40.0	1.000 344.00	1032.00 1376.00
41.0	1.000 344.00	1032.00 1376.00

42.0	1.000	344.00	1032.00	1376.00
43.0	1.000	344.00	1032.00	1376.00
44.0	1.000	344.00	1032.00	1376.00
45.0	1.000	344.00	1032.00	1376.00
46.0	1.000	344.00	1032.00	1376.00
47.0	1.000	344.00	1032.00	1376.00
48.0	1.000	344.00	1032.00	1376.00
49.0	1.000	344.00	1032.00	1376.00
50.0	1.000	344.00	1032.00	1376.00