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The Oxidation of Pyrite and its Environmental Consequences

by

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Summary

This thesis concentrates on pyrite in colliery spoil - its oxidation and the effect of the oxidation products on the environment of the spoil tip - in particular the problems caused due to the production of acid. Chemical studies were used to determine the important steps of the oxidation pathway so that suitable treatments could be developed which would inhibit or reduce the rate of the oxidation. The oxidation was studied in laboratory experiments so that, hopefully, practical treatments based on chemical principles, could be developed which would reduce the rate of acid production in the field.

In Chapter 1 the literature on pyrite is reviewed - not only that concerning pyrite in colliery spoil but also pyrite in other situations such as acid sulphate soils. Pyrite formation and morphology in sedimentary environments are discussed. The oxidation of pyrite, the problems arising from the oxidation and the possible treatments of these problems are all considered.

The oxidation of pyrite was studied in incubation studies and the central role of ferric iron in the oxidation pathway established - these experiments are reported in Chapter 2. Ferric iron is produced when <u>Thiobacillus Ferrooxidans</u> oxidises the ferrous iron which is initially released from the pyrite. The ferric iron can then oxidise pyrite which will thus release more ferrous iron, the ferric iron also being reduced back to ferrous iron. The ferrous iron is again oxidised to ferric iron by bacteria thus establishing a cyclic process. This pathway is much faster than the oxidation of pyrite by oxygen. Once the solubility limit of ferric iron is reached, some of it will be precipitated, which ultimately releases four moles of acid per mole of pyrite oxidised. Pyrite oxidation can be inhibited by interfering with

the role of ferric iron. This was done successfully in the laboratory experiments - by using a bactericide (panacide) to stop the bacterial oxidation of ferrous iron to ferric iron; by the use of specific chemicals (o-phenanthroline, EDPHA and citrate) to complex ferrous iron or ferric iron; by the use of specific chemicals to precipitate ferric iron (phosphates and silicates) and by the use of waste materials (chicken manure, woodwaste and P.F.A.) to complex either ferrous iron or ferric iron.

The inhibition of pyrite oxidation in the pot experiments was not so successful. Some of the amendments used in the inhibition of pyrite oxidation in the incubation studies were used in conjunction with lime to treat pyritic spoil in pots (reported in Chapter 3). Although it could not be proved that the amendments were directly inhibiting pyrite oxidation, the grass grown in the amended and limed pots showed much better growth than did the limed only pots, showing that the amendments were having a beneficial effect. However the addition of phosphate actually enhanced acid production and the growth of grass in the phosphate plus lime pots was very poor.

The application of lime to pyritic colliery spoils, which is the usual way of controlling the acidity in the spoil, was examined in Chapter 4. The uneven distribution of pyrite in the spoil causes problems in adequate sampling of the spoil in order to calculate the lime requirement and in the spreading of the lime at the time of reclamation. Experiments were performed which involved using lime applied in solution as limewater and these indicated that this controlled the spoil pH more effectively than the addition of solid liming material. The important factor was the saturation of the exchange sites with calcium, which was easier to achieve when the calcium was added in solution. The cation exchange capacity of the spoil was highly pH dependent - the value at pH 5 was about half of that at pH 7.

Different samples of pyrite oxidise at different rates and this is thought to be related to its morphology. In Chapter 5 highly reactive pyrite samples from colliery spoil from the Scottish and Durham coalfields were compared with unreactive pyrite from slate waste from Ballachulish. The visible appearance, the infra-red spectra and the electron micrographs of the samples are compared. The difference in the reactivity of the samples may be due to structural, but not chemical, differences. The method used to determine pyrite is also critically examined in this chapter.

In Chapter 6 the practical applications of the study are considered and suggestions made as to ways of extending the study.

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CHAPTER 1

Pyrite in Sedimentary Environments

1.1 Occurrences of Pyrite

Pyrite (FeS_2) is the most abundant of the sulphide minerals, occurring throughout the world in different environments. Its origin is varied - it occurs as large masses and veins of hydrothermal origin, in igneous rocks as primary or secondary minerals and in contact metamorphic rocks (Deer et al. 1966). It is also found extensively in sedimentary rocks (mainly carbonaceous and argillaceous rocks) as well as unconsolidated sediments.

In some countries pyrite is mined mainly for the manufacture of sulphuric acid, for example, in Spain, Cyprus and Japan; and in other places it is obtained as a by product of mining for non-ferrous base-metal deposits, for example, in Canada and U.S.A.. In Huelva in Southern Spain there is a pyritic zone about 160 kilometres long and up to 29 kilometres wide which extends into Portugal (Lamey 1966). In Japan there are two main mines for pyrite - one is the Matsuo deposit (an area of diameter 1000 metres and depth 152 metres) and the other is the Yanahara mine in Okayama district- both are on the main island (Deer et al. 1962). The pyrite in the latter occurrence and in the Spanish deposit is thought to be of hydrothermal origin.

In the Samreid Lake, Ontario, pyrite is found which is thought to be of volcanic origin, as is the case for the pyritic ores of the Urals (Deer et al 1962). Pyrite can be of magmatic origin, crystallising from a sulphide-rich liquid, as is the case for the Skaergaard intrusion in East Greenland (Deer et al. 1966).

Pyrite is often found associated with valuable ore deposits, for example, in Spain gold and silver are found in the pyritic zone (Lamey 1966), in the Witwatersrand in South Africa pyrite occurs in the conglomerate gold-uranium bearing mines (Deer et al. 1962), in Australia it is found in uranium bearing rocks as well as in a variety of lead, zinc, copper and silver ores (Baker 1960), in Canada in gold-copper areas of Quebec and in Tennessee, U.S.A. in copper deposits (Lamey 1966).

Pyrite is also found in oil shale, for example, as one percent of the weight of the oil shale in an area covering 43000 square kilometres of Colorado, Utah and Wyoming in the U.S.A. (U.S. Bureau of Mines 1960).

Pyrite is also found in coal deposits, the best known example is that of the Appalachian coalfields in the U.S.A., but it also occurs in many other coalfields including many in Britain. It can occur either as a primary or secondary mineral i.e. formed at the same time as the coal or deposited within the solid coal seam (Williams and Keith 1963, Caruccio et al. 1977). Acid sulphate soils contain varying quantities of pyrite and occur throughout the world, especially in tropical areas.

The last two occurences of pyrite will be concentrated on in this chapter as the presence of pyrite causes widespread problems in these cases, although other sources of pyrite and associated problems will be mentioned. Both acid sulphate soils and coal are formed in sedimentary environments, which also often favour the formation of primary pyrite (although pyrite is also found as a secondary mineral in coal). Acid sulphate soils are unconsolidated sediments whereas coal is a sediment which has been consolidated over thousands of years.

1.1.1 Sedimentary Pyrite

Pyrite is a stable mineral under low Eh and low pS^{2-} conditions, (i.e. high dissolved sulphide conditions as $pS^{2-} = -\log a_{S^{2-}}(aq)$), as shown in Fig 1.1.

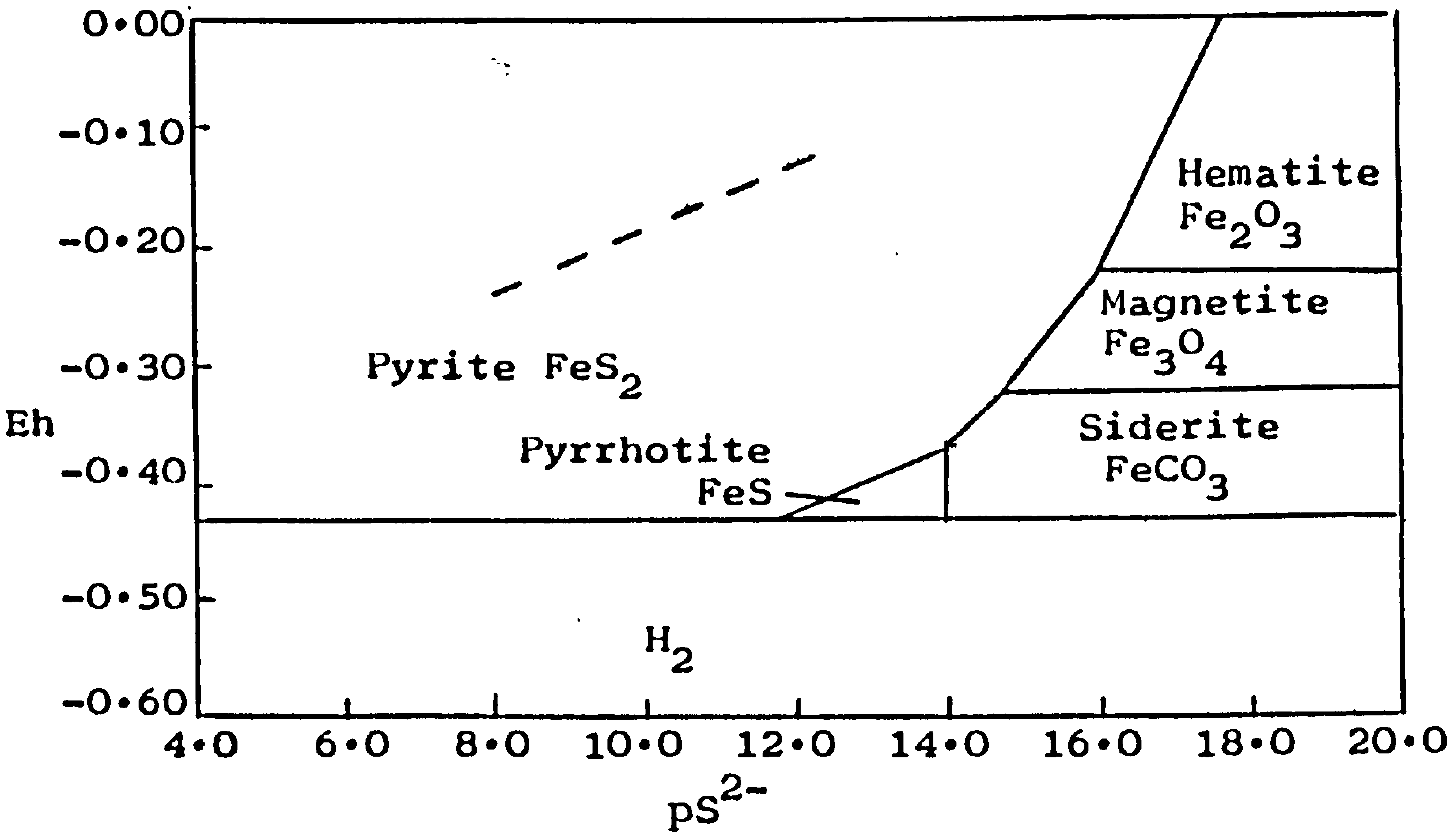


Fig 1.1 Eh - pS^{2-} diagram for pyrite, pyrrhotite, hematite, magnetite and siderite. pH = 7.37, log P_{CO_2} = -2.40, T = 25 °C, P_{total} = 1 atm. Field marked H_2 corresponds to area where water is unstable relative to H_2 gas. Meaurements of natural sulphidic measurements fall closely along the dotted line (Berner 1964, 1971).

These conditions are characteristic of fine grained marine sediments which have a high content of organic matter and where bacterial sulphate reduction is occurring (Berner 1971). Shelf, deltaic, estuarine and hemipelagic muds (muds further out into the open ocean which contain land derived material as well as marine material) are typical anoxic terrigenous sediments where pyrite is formed. Sediments in the open ocean tend not to have enough reactive organic matter or they are aerobic. Sands also tend not to have enough reactive organic matter (Berner 1982).

Postma (1982) found pyrite being formed in brackish water sediments and siderite ($FeCO_3$) in fresh water sediments in a swamp area of Denmark. Siderite is only stable with respect to pyrite at low dissolved sulphide concentrations which will obviously occur in fresh water environments as opposed to marine environments. However pyrite is found in fresh water sediments, but in much lower concentrations than in marine sediments due to the lower concentrations of sulphate available for conversion into pyrite (Williams and Keith 1963, Curtis 1967). Cassagrande et al.(1977) found much lower pyrite concentrations in freshwater peats than marine peats:- 0.90 - 1.94% of total sulphur was present as pyrite in freshwater peat compared to 14.34% of total sulphur as pyrite in marine peat. These are the modern equivalents of coal forming environments under either freshwater or marine conditions.

Marcasite has also been reported as being formed under sedimentary conditions (marcasite and pyrite are polymorphic forms of iron disulphide). Marcasite is only formed at low pH, whereas pyrite is formed also at more neutral to basic conditions. Marcasite is not found in recent sediments, only in ancient ones (Goldhaber and Kaplan 1974). Pyrite is the most important of the two minerals as its occurrence is far more widespread.

1.1.2 Formation of Pyrite in a Sedimentary Environment

The factors affecting pyrite formation and possible mechanisms of formation will be briefly discussed.

Pyrite and other iron sulphides are formed due to the reaction between dissolved hydrogen sulphide and iron minerals. The hydrogen sulphide is formed from the bacterial reduction of dissolved sulphates or from the decomposition of organic sulphur compounds. The first source is thought to be the dominant one (Berner 1971), and in areas of high pyrite content there must have been a continuous diffusion of sulphates into the sediments from the overlying waters (Berner 1970).

Bacterial sulphate reduction will only occur under anaerobic conditions - due to aerobic respiration rapidly consuming oxygen, anoxic conditions are often formed just below the surface of marine sediments (Goldhaber and Kaplan 1975). The water must have a low oxygen content if the organic matter is to be deposited without being completely destroyed. Restricted circulation of water will favour stagnation and oxygen depletion, eg., in the Black Sea (Berner 1972). If the water is fully oxygenated but there is a high rate of deposition bacterial sulphate reduction can also occur. These conditions tend to prevail in near-shore subtidal and intertidal sediments (Berner 1972). The rate of oxygen uptake is temperature dependent and reducing conditions are often found in sediments containing fine-grained organic matter in warm waters. The rate of bacterial sulphate reduction will depend on temperature and pressure, and is independent of sulphate concentration at concentrations above 10 millimolar. The total amount of organic carbon preserved in the sediment and its suitability and availability for bacterial degradation will also affect the rate of reduction.
It has been suggested that these factors are in turn controlled by the environment of deposition and the rate of sediment accumulation (Goldhaber and Kaplan 1975).

The pyritic sulphur content of modern fine grained sediments has been estimated to be 0.22%S compared to a previously estimated amount for ancient shales of 0.27 - 0.40%S (Berner 1982). He estimated a burial rate for sulphur of 39 megatons (megaton = 10^{12}g) per year. This is less than other estimated rates but is explained by different burial rates in different geological periods. Most of the hydrogen sulphide produced by sulphate reduction is reoxidised by oxygen in the overlying water as the rate of pyritic sulphur burial is much less than the rate of reduction of sulphate (Berner 1982).

The chief source of iron for iron sulphide formation is detrital minerals. Adsorbed coatings of colloidal ferric oxides, (for example, hematite and goethite) on detrital clays and silt grains are the most reactive forms of iron. Iron-containing chlorites can also be reactive if they are finely crystallised, whereas silt and sand sized grains of hematite, goethite and magnetite and ferruginous silicates tend to be unreactive (Berner 1971, 1972). Other sources of iron can also be the adsorbed surface oxide coatings on carbonate shell material, and iron that is present in organic matter (Goldhaber and Kaplan 1974). The various ferric oxide coatings on detrital grains have to be solubilized - the ferric iron is reduced to ferrous iron by hydrogen sulphide, humic acids, amino acids, other organic reducing agents present in the sediment or by bacteria (Berner 1971, Goldhaber and Kaplan 1974).

Other metal sulphides could be formed (for example, zinc, lead and copper could be incorporated into sphalerite, galena and chalcopyrite respectively) but iron tends to be the only metal present in any great amount, other metals tending to be present only in trace amounts (Goldhaber and Kaplan 1974).

Iron sulphide formation is limited and controlled by the concentration and reactivity of iron compounds, the availability of dissolved sulphates and the concentration and nature of the organic matter. The last is thought to be the most important as the majority of sedimentary environments would contain some reactive iron compounds and dissolved sulphates, but may contain no organic matter that can be used by sulphate reducing bacteria. If the overlying water contains dissolved hydrogen sulphide then the amount of pyrite formed will be controlled by the availability of iron, as is the case in the Black Sea (Berner 1971).

The overall reaction describing pyrite formation, assuming that the iron source is adsorbed ferric oxide coatings, is:

$$FeO.OH + 6[CH_2O] + 3SO_4^{2-} \longrightarrow 6HCO_3^- + FeS + FeS_2 + 4H_2O$$

where $[CH_2O]$ represents organic matter (Goldhaber and Kaplan 1974).

Thus this reaction causes an overall increase in alkalinity. The bacterial reduction of sulphate to sulphide causes an increase in alkalinity. When the sulphide ion is precipitated there is a decrease in the alkalinity, but the reduction of the ferric ion to ferrous ion causes an increase in alkalinity due to the production of hydroxide ion. The consequent overall increase in alkalinity is equivalent to that occurring from the bacterial sulphate reduction alone. Berner et al. (1970) found that sulphate reduction (or pyrite formation) together with the bacterial production of ammonium ion could cause an increase in alkalinity of the pore waters of anoxic marine sediments to 30 times that of the overlying sea water.

The increase in the bicarbonate ion concentration tends to lead to a supersaturation of $CaCO_3$ in the pore waters. Although some calcium carbonate does precipitate, it is often inhibited from precipitating, probably by dissolved organic compounds (Berner et al. 1970). The alkalinity can be removed by leaching or diffusion into the overlying waters, resulting in a separation of the potentially acid material (pyrite) from actual alkalinity (van Breemen 1973). Hardan (1973) found that calcium carbonate formed due to sulphate reduction had been redistributed throughout the soils of the reduction area and associated areas, due to centuries of irregular agricultural practices and flooding.

The actual mechanism leading to the formation of sedimentary pyrite has not been completely solved, it being quite possible that there is more than one pathway depending on the conditions of the sediment and the nature of the pyrite formed i.e. framboidal versus non-framboidal.

1.1.3 Possible Pyrite Forming Mechanisms

There have been various laboratory experiments to try and deduce the pathway of pyrite formation. Most of the experiments have tried to reproduce the probable sedimentary environments prevailing during pyrite formation and various different pathways have been suggested.

It is generally thought that metastable iron sulphides other than pyrite are formed initially. Mackinawite (tetragonal FeS) and greigite (cubic Fe_3S_4) are the dominant sulphides formed at low temperature and neutral pH, from the reaction of either H_2S or HS^- and fine grained iron oxides or ferrous iron (Berner 1971, Sweeney and Kaplan 1973, Rickard 1975). Both of these are unstable with respect to pyrite and stoichiometric pyrrhotite (FeS) and are not found in most recent marine sediments as they are transformed to pyrite (Berner 1967). At neutral pH and 65 °C Berner (1970) reported the formation of black non-crystalline FeS from the reaction of H_2S and reactive iron. In the absence of additional elemental sulphur this will crystallise to greigite, mackinawite and pyrrhotite. If continued sulphate reduction takes place, some of the H_2S or FeS can be oxidised. Oxygen can be mixed into the sediment by burrowing mechanisms of benthenic organisms, by current and wave stirring or by diffusion. The oxidation can be chemical but will often be mediated by bacteria, for example, Thiobacilli, which oxidise the sulphide to elementary sulphur and also to sulphate - this explains the fact that there is never a very high concentration of elementary sulphur found in sediments (Berner 1970). Elemental sulphur will slowly react with the iron monosulphides to give pyrite, which will crystallise as minute framboidal spheres (Berner 1970). The complete conversion of iron monosulphide to pyrite takes several years and needs an abundant supply of elemental sulphur and H_2S.

Sweeney and Kaplan (1973) found that framboidal pyrite was not formed in the absence of air. On reacting ferrous chloride and hydrogen sulphide they found that pyrite was formed at 85 °C and greigite was formed at 60 °C. Pyrite spheres and framboids were formed as well as greigite spheres when oxygen was present in the reaction vessel. In anhydrous conditions at 150 °C only euhedral pyrite was formed. They suggested that iron monosulphide, which is probably mackinawite, is converted to pyrrhotite (FeS) which is in the form of hexagonal platelets which can be transformed to pyrite framboidal aggregates by sulphurisation. Alternatively mackinawite could be transformed to greigite by the addition of sulphur. The spherical shape of greigite could be retained to give pyrite spheres or it could be changed by internal nucleation of pyrite crystals to give pyrite framboids upon addition of more sulphur.

Rickard (1975) performed experiments at low temperature and neutral pH, observing the reaction of aqueous sulphide, elementary sulphur and ferrous sulphide. The conditions were similar to that of pyrite forming environments. In the absence of oxygen non-framboidal pyrite was formed, as previously observed by Sweeney and Kaplan (1973). From the kinetics of the reaction Rickard suggested that the pyrite was formed by a direct solution reaction between ferrous ions and polysulphide ions:

$$Fe^{2+} + S_xS^{2-} + HS^- \longrightarrow FeS_2 + S_{x-1}S^{2-} + H^+$$

The polysulphide ions and ferrous ions come from the dissolution of elementary sulphur and iron monosulphide, so this reaction scheme also involves the initial formation of iron monosulphide.

In salt marsh peat, Howarth (1979) found pyrite forming rapidly (one day or less). High sulphate reduction rates were occurring due to the high availability of organic substrates, and due to the rapid replacement of sulphates into the peat by tidal waters. Sulphate reduction was actually the major form of respiration in the marsh. This rapid formation of pyrite was explained by Howarth in terms of the saturation of pyrite and iron monosulphides. The solubility product for mackinawite has been shown to be:

$$[Fe^{2+}][S^{2-}] = Ksp_{mack} = 2.8 \text{ X } 10^{-18}$$

The solubility product of pyrite may be written (Goldhaber and Kaplan 1976):

$$FeS_2 \longrightarrow S^{2-} + S^{o} + Fe^{2+}$$

$$[Fe^{2+}][S^{2-}] = K_{sp\ pyrite} = 2.4 \text{ X } 10^{-28}$$

This assumes saturation with solid orthorhombic sulphur whose activity is unity. The activity of the sulphide ion depends on the total concentration of the sulphide ion and pH. Goldhaber and Kaplan (1974) suggested that at high pH (above 6.5), the solution is supersaturated with respect to mackinawite and pyrite, but mackinawite will precipitate preferentially for kinetic reasons and only slowly convert to pyrite. However at low pH, mackinawite maybe undersaturated, but pyrite could still be supersaturated due to its smaller solubility product and would be able to precipitate without interference from mackinawite. Raiswell (1982) suggested that the direct precipitation of pyrite gave euhedral (well crystallised) pyrite, whereas the intermediate formation of mackinawite gave framboidal pyrite.

The exact pathway of pyrite formation will obviously depend on the environmental conditions, which may well dictate the final structure of the pyrite. However three possible pathways for the formation of pyrite from iron oxide can be identified. Framboidal pyrite is probably formed by the reaction of iron monosulphide and elementary sulphur in the presence of air (Berner 1970), probably with greigite as an intermediate (Sweeney and Kaplan 1973). The other two possible pathways concern the formation of euhedral pyrite. Direct precipitation of euhedral pyrite can occur when the pore water chemistry is such that mackinawite is undersaturated. Euhedral pyrite can also be formed from the reaction of mackinawite and elementary sulphur, shown in anhydrous conditions at 150 °C by Sweeney and Kaplan (1973). In aqueous conditions at low temperatures the kinetics of the reaction were shown to support the mechanism whereby pyrite precipitated from polysulphide ions and ferrous ions, formed by the dissolution of elementary sulphur and iron monosulphide (Rickard 1975).

1.1.4 Types of Pyrite

Pyrite is one of the two forms of iron disulphide, the other is marcasite. They have different physical properties and different crystal structures - pyrite is isometric and marcasite is orthorhombic. Pyrite is mainly found as cubes, pyritohedrons and octahedrons (Deer 1966) and is the more important of the two forms, because of its more widespread occurrence.

There have been various studies of the different morphologies of pyrite, especially of those found in coal. Table 1.1 is a summary of some of the studies. However it can be difficult to condense

MORPHOLOGY	LOCATION	REFERENCE
Primary - 'sulphur ball' - framboidal and polyframboidal	Not specified	Lowson 1982*
Primary - disseminated pyrite - framboidal and polyframboidal	Pennsylvanian age coal - Eastern Kentucky	Caruccio et al. 1977
	Lignite coal - East Texas	Arora et al. 1978
	Bituminous coal - Illinois Basin	Price and Shieh 1979
	Not specified	Lowson 1982
	Pennsylvanian age shale - Missouri	Ainsworth et al. 1982
Primary - replacement pyrite - individual grains	Pennsylvanian age coal - Indiana	Boctor et al. 1976
	Pennsylvanian age coal - Eastern Kentucky	Caruccio et al. 1977
	Not specified	Lowson 1982
Primary - massive pyrite	Pennsylvanian age coal - Eastern Kentucky	Caruccio et al. 1977
	Bituminous coal - Illinois Basin	Price and Shieh 1979
Primary - euhedral pyrite - disseminated as individual crystals, as layers or in spherical agglomerations	Pennsylvanian age coal - Eastern Kentucky	Caruccio et al. 1977
	Bituminous coal - Illinois Basin	Price and Shieh 1979
	Pennsylvanian age shale - Missouri	Ainsworth et al. 1982

* Lowson (1982) - this classification is that of the Ohio State University Research Foundation for pyritic material in coal.

Table 1.1 Common Morphologies of Pyrite in Coal and Associated Strata

MORPHOLOGY	LOCATION	REFERENCE
Secondary - replacement pyrite - well-developed crystal faces	Not specified	Lowson 1982
Secondary - fracture or cleat (macro and micro) filling	Pennsylvanian age coal - Indiana	Boctor et al.1976
	Pennsylvanian age coal - Eastern Kentucky	Caruccio et al.1977
	Bituminous coal - Illinois Basin	Price and Shieh 1979
	Not specified	Lowson 1982
Porous masses	Lignite coal - East Texas	Arora et al.1978
	Pennsylvanian age shale - Missouri	Ainsworth et al.1982
Solid non-porous grains	Lignite coal - East Texas	Arora et al.1978
	Pennsylvanian age shale - Missouri	Ainsworth et al.1982
Cell filling	Bituminous coal - Illinois Basin	Price and Shieh 1979
Lenses and layers of fibrous pyrite	Pennsylvanian age coal - Indiana	Boctor et al.1976
	Bituminous coal - Illinois coal	Price and Shieh 1979

Table 1.1 (contd.) Common Morphologies of Pyrite in Coal and Associated Strata

different classification systems, due to the numerous possible ways of describing an occurrence of pyrite, for example, it is uncertain whether either of the porous masses and non-porous grains of Arora et al. (1978) and Ainsworth et al. (1982) could be classified as the same type of pyrite as the massive pyrite described by Caruccio et al. (1977).

Most of the morphologies can clearly be described as primary or secondary, for example, cleat filling pyrite can only occur once the coal has solidified enough to undergo fracturing. Some reports state size ranges of the various forms of pyrite, for example, Caruccio et al. (1977) found massive pyrite and plant replacement pyrite to be 150 to 600 µm and euhedral crystals to be 0.5 to 2 µm in size; Arora et al. (1978) found solid non porous grains to be less than 2 mm in size.

Different proportions of the various types of pyrite occur in different environments. Arora et al. (1978) and Ainsworth et al. (1982) found that the conglomerate masses of pyrite, both porous and non-porous, were the predominant morphology of pyrite in their studies. Boctor et al. (1976) found more disseminated pyrite than lenticular pyrite, and more pyrite in the form of lenses or layers and framboids than as cleat and cell cavity fillings. Ainsworth et al. (1982) found framboidal pyrite to account for less than one percent of the total volume of pyrite.

Van Dam and Pons (1973) reported on different types of pyrite found in acid sulphate soils. Primary pyrite occurred scattered throughout the soil, associated with organic matter, in soil pores and filling the diatoms and foraminifers. That associated with organic matter could also be of secondary origin. Framboidal pyrite was often found in the first two distributions. The size of the framboids and crystals were different depending on the type of sediment - those occurring in sediments rich in clay were smaller than those occurring in sediments rich in silt. They suggested that this showed the pyrite was formed during sedimentation.

1.1.5 Framboidal Pyrite

Framboidal pyrite tends to be considered the most reactive form of pyrite, so consequently there is a great deal of attention given to this particular morphology in the literature.

Caruccio (1970) found that the fine grained framboidal pyrite oxidised much quicker than coarse grained pyrite. Williams and Keith (1963) showed that there was a greater proportion of sulphur in coal overlain by marine rocks than in coal overlain by non-marine rocks and Caruccio et al.(1977) found that framboidal pyrite showed the same kind of distribution, although it is found in both environments.

There is some confusion amongst various reports as to what actually constitutes framboidal pyrite. Framboidal pyrite consists of minute grains of pyrite but some authors reported that these grains can include microcrystals (Boctor et al. 1976, Caruccio et al. 1977, Arora et al. 1978, Ainsworth et al. 1982) whereas others reported that framboidal pyrite only contains crystallites or microcrysts - microscopic embryonic crystals (Rickard 1970, Lowson 1982). Lowson (1982) suggested the broad classification of pyrite into euhedral pyrite and framboidal pyrite, where euhedral pyrite consists of well crystallised pyrite and framboidal pyrite of grains of pyrite with few or no crystal faces grouped together into aggregates.

Rickard (1970) defined the essential features of framboids as being spheriod, or a modification of spheriod, in shape and consisting of discrete equant microcrysts, either randomly or non randomly distributed within the framboid. Arora et al.(1978) found framboids from 20 to 50 µm in size, with a microcrystal size of 0.25 to 1.5 µm.

They estimated that a typical framboid of their study would contain about 47, 400 microcrystals and Rickard (1970) estimated that a framboid of 40 µm diameter and centre-to-centre diameter of 0.1 µm would contain one thousand times this number of microcrysts (this would be an extreme case). This kind of structure would obviously lead to an increased surface area over other kinds of pyrite structure - Pugh et al. (1981) found that framboidal pyrite of mean diameters of 35 and 12.5 µm had four to five times the surface area of massive pyrite of equivalent sizes. Polyframboids are also found (Hossain 1975, Arora et al. 1978) and have been described by Love (1971) as an agglomeration of framboids, increasing the size and complexity of the body, but retaining its spheriod shape. He identified framboids as 5 to 50 µm in size, with up to 150 framboids in a polyframboid. The increased surface area of framboidal and polyframboidal pyrite is normally used to explain the greater reactivity of these forms of pyrite compared to other forms of pyrite (Pugh et al. 1981). However Caruccio (1970) found that finely ground pyrite (non-framboidal) did not oxidise even after two months exposure to conditions which caused other pyrite to decompose. Lowson (1982) suggested that the increased reactivity of framboidal pyrite was due to it being composed of essentially non-crystalline material, whereas euhedral pyrite was crystalline and therefore much less reactive.

The origin of the shape of framboids is not clear. Love (1971) suggested that the spherical shape of the polyframboids was inherited from the earlier monosulphides which were converted to pyrite framboids retaining their globular shape but undergoing internal crystallisation. This is similar to the argument of Sweeney and Kaplan (1973) concerning the formation of framboids. However, Rickard (1970) argued that the shape is caused by pyrite infilling globular organic compounds in sediments or spherical vacuoles in sediments, lavas and veins which were formed by entrapped gases.

Raiswell (1982) found that framboids had euhedral overgrowths but that there was no euhedral pyrite within the framboids. He suggested that framboidal pyrite was formed initially while there was an abundant supply of iron and sulphate ions which led to the intermediate formation of monosulphides, but that euhedral pyrite was formed once the supply of iron and sulphate had been depleted allowing the pyrite to crystallise without the formation of the monosulphide, (the iron being transported from adjacent horizons) - this is similar to the arguments used by Howarth (1979) and Goldhaber and Kaplan (1974) on the preferential formation of pyrite or iron monosulphides depending on the state of saturation of both species.

1.1.6 Trace Elements Associated with Pyrite

Various trace elements are found associated with pyrite either as other sulphides or actually incorporated into the pyrite structure. Fleisher (1955) summarized the occurrence of minor elements in pyrite- arsenic, copper, lead and zinc may all occur as other sulphides or may actually be present in the pyrite structure, whilst cobalt and nickel are also found in the actual pyrite structure. Different elements have been used to distinguish between different pyrite forming environments - Keith and Degens (1959) found higher concentrations of arsenic, silver and copper in fresh water pyrite compared to sea water pyrite. Other elements present in trace amounts have also been used to distinguish between pyrite formed in different environments, but levels of different elements can vary greatly in pyrite from the same environment (Raiswell and Plant 1980). Element ratios have also been used, for example, Co/Ni for the same purpose, but these also are not that reliable. Raiswell and Plant (1980) found copper, nickel, zinc, arsenic and molybdenum to be the only elements to occur in the sulphide phase at an appreciable concentration. Molybdenum, arsenic and copper were the only elements to occur at greater concentrations in the pyrite compared to the host sediment. They also found different elements present in different amounts in euhedral compared to framboidal pyrite, and related this to different sources of iron for the two forms of pyrite in the original sedimentary conditions, i.e. an immediate source or from adjacent horizons.

1.2 Oxidation of Pyrite

There have been many investigations to try to elucidate the mechanism and products of pyrite oxidation. This has been done mainly by studying acid mine drainage and acid sulphate soils.

The overall reaction which is generally used to describe the oxidation is:

$$FeS_2(s) + 15/4\ O_2(aq) + 7/2\ H_2O(l) \longrightarrow Fe(OH)_3(s) + 2H_2SO_4(aq) \qquad (1)$$

Thus ferric hydroxide and sulphuric acid are the ultimate products of the oxidation. However this simple equation hides many steps - the sulphur changes its oxidation state by seven and iron is hydrolysed and precipitated, which obviously must involve more than one step. Also other ferric compounds and sulphate compounds can be formed depending on the immediate environment.

1.2.1 Oxidation Pathway

Pyrite has been shown to be inert over a wide Eh range (Garrels and Thompson 1960, van Breemen 1973). Fig 1.2 shows the stability relationships between the most important iron and sulphur compounds. However van Breemen (1973) showed that pyrite would only

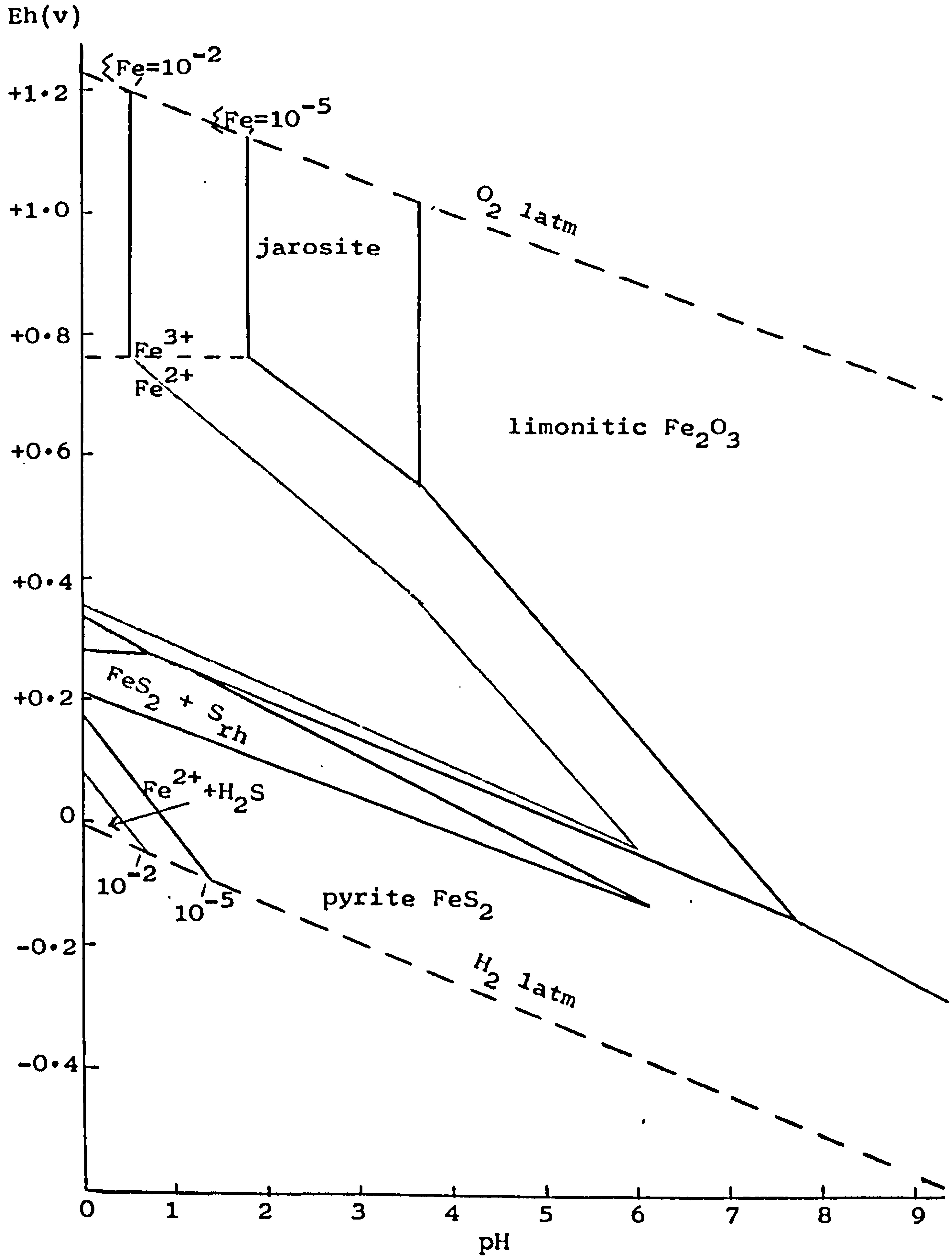


Fig 1.2 Stability relationships among most important iron and sulphur compounds - using dissolved sulphur compounds (H_2S, HS^-, HSO_4^- or SO_4^{2-}), activities of 5 x 10^{-3} and K^+, activity of 5 x 10^{-4}. Solid-solution contours show activities of uncomplexed Fe^{2+} or Fe^{3+} equal to 10^{-5} and 10^{-2} (van Breemen 1973).

oxidise at higher values of Eh than those shown by the upper limit for pyrite in the diagram. Consequently pyrite will only oxidise in relatively good oxidising conditions. Water has been suggested as an oxidant for pyrite (Barnes and Clark 1964), but this is not feasible as the reaction would have to take place just above the stability field of pyrite (Clark 1966, van Breemen 1973).

The two main oxidising agents for pyrite under natural conditions are oxygen and ferric ion. The following reactions have been suggested to describe the oxidation (Temple and Delchamps 1953, Le Roux et al. 1973, van Breemen 1973, Stumm and Morgan 1981):

$$FeS_2 + 1/2\ O_2 + 2H^+ \longrightarrow Fe^{2+} + 2S^o + H_2O \qquad (2)$$

$$Fe^{2+} + 1/4\ O_2 + H^+ \longrightarrow Fe^{3+} + 1/2\ H_2O \qquad (3)$$

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ \qquad (4)$$

$$FeS_2 + 2Fe^{3+} \longrightarrow 3Fe^{2+} + 2S^o \qquad (5)$$

$$2S^o + 12Fe^{3+} + 8H_2O \longrightarrow 12Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (6)$$

$$2S^o + 3O_2 + 2H_2O \longrightarrow 2SO_4^{2-} + 4H^+ \qquad (7)$$

Le Roux et al. (1973) did not include the formation of ferric hydroxide as they maintained the pH at too low a value for its formation. Reaction 2, the oxidation of pyrite by oxygen is very slow, shown by the rather inert behaviour of pyrite electrodes and from the very slow oxidation of pyrite in solutions where ferric ion is absent (Temple and Delchamps 1953, Singer and Stumm 1970).

The second reaction is obviously necessary if ferric ion is going to be generated from the oxidation of pyrite and then itself act as an oxidant of pyrite. At pH less than 3.5 this has been shown to be a very slow reaction (Singer and Stumm 1970) and the rate is independent of pH. In a solution containing 9×10^{-4} moles ferrous iron per litre only five percent of it would be oxidised in 150 days, but certain bacteria can accelerate the reaction by a factor of over 10 (Singer and Stumm 1970). These bacteria are commonly found in acid mine drainage and acid sulphate soils, and have been shown to actively promote pyrite oxidation (Temple and Delchamps 1953, Bloomfield 1972, Noike et al. 1983). The type and involvement of bacteria will be discussed later.

Ferric ion will only stay in solution at pH of less than 3.5, above this it will precipitate rapidly. It has been shown ferric ion oxidises pyrite rapidly at room temperature according to:

$$FeS_2 + 14Fe^{3+} + 8H_2O \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (8)$$

(Garrels and Thompson 1960). This is a combination of reactions 5 and 6. Between pH 0 and 2 the rate has been shown to be independent of pH, although it may vary considerably for pyrite from different places (Garrels and Thompson 1960). They suggested that the rate of pyrite oxidation was proportional to the fraction of pyrite surface covered by ferric ions, which in turn could be controlled by the fraction of ferric ions in solution compared to ferrous ions. This explained their observation that the rate of pyrite oxidation increased dramatically as the ferric ion fraction in solution became close to unity (i.e. the majority of iron was present as ferric ions), as the fraction of occupied surface would increase disproportionally as ferrous ion concentration became very low.

Reaction 7 is also catalysed by bacteria (Temple and Delchamps 1953), the air oxidation of it being very slow (Bloomfield 1972, van Breemen 1973). The oxidation can therefore be described as cyclic, assuming the ferric ion stays in solution - ferric ion oxidises pyrite, itself being reduced, it is then oxidised back to ferric ion by bacteria and can oxidise further pyrite. Obviously the oxidation of pyrite releases more ferrous ion into solution which joins in the cyclic process.

However this will not occur in more basic environments, as the ferric ion will precipitate. Initially when mine waste is dumped, or before acid sulphate soils are drained, the environment is neutral, so something must cause the initial pH drop. This is an important aspect as it is only at low pH that relatively rapid pyrite oxidation takes place, the oxidation by oxygen alone being very slow. Various reasons have been suggested for the initial pH fall. Nordstrom (1982) suggested it was due to the oxidation of the elemental sulphur (reaction 7) produced by reaction 2, but Arkesteyn (1980) showed that microorganisms were not responsible for the initial pH drop (the oxidation of elemental sulphur is mediated by microorganisms). Hart (1959) suggested that it was the oxidation of iron monosulphide which caused the drop in pH, but Bloomfield (1973) pointed out that there would not be enough of this present to produce such a decrease in pH. It has been postulated that it is the presence of a small, probably poorly crystallised fraction of pyrite present that is oxidised non-biologically releasing enough acid to cause the pH to drop (van Breemen 1973). It has been estimated that the pH of a pyritic soil would drop from 7 to 4 due to the non-biological oxidation of about 0.9% pyrite within one month if the pyritic soil was exposed to air, although it would take longer than this in the field where the diffusion of oxygen into the soil is restricted (van Breemen 1982). However there is no concensus amongst different workers on the reason for the initial pH drop.

There has been some discussion as to whether elemental sulphur is found at least as an initial oxidation product. Various authors report that they found elemental sulphur, although in small amounts (Bloomfield 1972, Silverman 1967) but it would seem that it is usually oxidised essentially instantaneously to sulphate (Garrels and Thompson 1960). Steger and Desjardins (1978) reported that there is some evidence that thiosulphate is an intermediate oxidation product of sulphur to sulphate. However it does not persist, and sulphate is the only major sulphur species found as a result of pyrite oxidation.

1.2.2 Bacterial Involvement in Pyrite Oxidation

Bacteria have been invoked to play three different roles in the oxidation pathway of pyrite - oxidation of sulphur, oxidation of ferrous ion and oxidation of pyrite itself.

As early as 1922 Waksman and Joffe isolated *Thiobacillus thiooxidans* from composts of soil, sulphur and rock phosphate, and reported that it would oxidise elemental sulphur to sulphuric acid, obtaining its carbon requirement from the carbon dioxide of the atmosphere and nitrogen from inorganic nitrogen salts. They also demonstrated that it lived in a very acid medium. In 1947, Colmer and Hinkle isolated two organisms from acid mine drainage, one of which was similar to if not identical to *T. thiooxidans* oxidising elemental sulphur to sulphate. The other organism oxidised ferrous ion to ferric ion, but they did not characterize it. It has since been confirmed by many authors that *T. thiooxidans* is indeed capable of oxidising sulphur to sulphate and is consistently found in acid mine drainage (Leathen et al. 1953, Parker and Prisk 1953, Temple and Delchamps 1953, Belly and Brock 1974) and also in acid sulphate soils (Hart 1959, Bloomfield 1972). The relative importance of *T. thiooxidans* in pyrite oxidation is debateable as both these bacteria and ferric ion can oxidise the elemental sulphur - two studies have found that it is the ferric ion which is the major oxidiser of the sulphur (Silverman et al. 1961, Arkesteyn 1980).

The bacteria responsible for oxidising ferrous ion to ferric ion was isolated by various workers (Leathen et al.1953, Colmer et al. 1950, Temple and Colmer 1951, Temple and Delchamps 1953) and identified as belonging to the genus Thiobacilli and named Thiobacillus ferrooxidans. There have been various different iron oxidising bacteria mentioned in the literature but they have all been identified as belonging to the same species, T. ferrooxidans (Silverman and Ehrlich 1964, Hutchinson et al. 1966). It has been suggested that not only does this bacterium assist the oxidation of pyrite by oxidising ferrous to ferric ion, but that it can also oxidise the pyrite itself - termed direct contact mechanism (Silverman 1967). To substantiate this there is evidence that T. ferrooxidans can leach metals from sulphides where iron is not present (Zajic 1969, Silver and Torma 1974, Nielsen and Beck 1972). Some authors consider the direct contact mechanism more important than the oxidation of ferrous to ferric ion (Duncan et al.1967, Beck and Brown 1968) but others consider the oxidation of ferrous to ferric ion to be the only role of T. ferrooxidans in pyrite oxidation (Leathen et al.1953, Silverman et al.1963, Le Roux et al.1973, Stumm and Morgan 1981). It has also been suggested that this bacterium will oxidise sulphur, (for example, Le Roux et al.1973, Beck and Brown 1968, Hutchinson et al.1966) but T. thiooxidans or ferric ion can do this as well.

The important fact is that T. ferrooxidans has been shown conclusively to increase the rate of pyrite oxidation (for example, Temple and Delchamps 1953, Bloomfield 1972, Noike et al.1983).

Various other iron oxidising bacteria have been implicated in the oxidation of pyrite (Walsh and Mitchell 1972). It has been suggested that they may be responsible for the initial attack on pyrite causing the pH to fall, and Beck (1960) found other bacteria that could oxidise both ferrous ion and sulphur at low pH. It has also been reported that cultures containing other bacteria in addition to *Thiobacilli* can be more effective in oxidising pyrite than pure cultures of *T. ferrooxidans* or mixtures of *T. ferrooxidans* and *T. thiooxidans* (Norris and Kelly 1978, Norris et al. 1980), invoking yet other organisms to play a part. However Arkesteyn (1980) failed to isolate any of the bacteria in question in acid sulphate soils and reported that only *T. ferrooxidans* were important in the oxidation of pyrite and that the initial pH drop was non-biological. In spoil from a coal mine Dacey et al. (1980) found bacteria which were capable of causing a pH drop from 8 to 1.3. They tentatively suggested at least four types of bacteria to be present including a mixotrophic *Thiobacillus* and a *Norcardia*, as well as a fungal species. However the culture was not capable of oxidising all kinds of pyrite at high pH, depending on the chemical and mineralogical characteristics of the pyrite. Thus the role of other microorganisms in pyrite oxidation is not clear cut, but the role of *T. ferrooxidans* is definitely of great importance. Therefore it is obviously useful to consider the environments it can survive in, and the optimum conditions for its growth and oxidation of iron.

Thiobacillus ferrooxidans obtains the carbon necessary for its growth by fixing atmospheric carbon dioxide. By studying the $^{14}CO_2$ uptake on a coal waste tip, Belly and Brock (1974) reported that there was little bacterial activity below 8 - 10 cm depth in the tip probably due to a lack of oxygen below that depth. Periodic rainfall would provide the oxygen and carbon dioxide requirement into the top of the tip, and would also remove oxidation products, exposing fresh surfaces for oxidation. They also found very little activity in freshly dumped coal waste, the maximum activity was in 3 to 5 year old dumps - this length of time was needed for a significant number of bacteria (approx. 10^5 bacteria per gram) to develop to show $^{14}CO_2$ uptake. They also found a decrease in bacterial activity in 40 year old tips - either the bacteria had exhausted the readily available energy sources or toxic products had built up. They concluded that most of the acid found in older tips was due to earlier activity. At neutral or only slightly acid conditions the bacteria were not active (Belly and Brock 1974, Arkestyn 1980). T. ferrooxidans has been found in sediments and mine waters that are not acidic (Olson et al.1979). The number of bacteria in the neutral to alkaline waters of a mine sedimentation pond's influent waters was very high. It was suggested that T. ferrooxidans was active in the coal bearing strata in small areas or microzones but the bicarbonate in the ground water was so high that any acid produced was neutralised. The bacteria were not active at neutral pH and no evidence of acid was found in the water. The optimum conditions for growth of T. ferrooxidans have been found to be a temperature of 20 - 30 °C and a moisture content of 23 - 35% (Belly and Brock 1974). Although the bacteria are tolerant to many metal ions, for example, iron, zinc, nickel, cobalt, they are susceptible to others, for example, silver at concentrations as low as 0.1 mgl^{-1}, or uranium at 250 mgl^{-1}, can inhibit oxidation of pyrite by T. ferrooxidans (Roy and Mishra 1981). The growth is more sensitive to these metals than the oxidation so at levels below these inhibitory levels (for oxidation) the oxidation is not coupled to the growth, i.e. bacterial oxidation can occur even in periods of non-growth of the bacteria.

Sulphate ions must be present in the media for oxidation to occur (Lazaroff 1963). Chloride ions can inhibit the oxidation but this is probably a reflection of the sulphate requirement, as a high relative proportion of sulphate ions to chloride ions or other anions is required for the oxidation to take place. Adaption of the bacteria can occur so that they are able to oxidise iron in a high chloride/ low sulphate environment. However, sulphate will obviously be present when pyrite is oxidising. Nutrient requirements are not limiting to growth as such small concentrations are needed. It has been reported that high phosphate concentrations can limit the bacterial activity, but it may depend on which particular strain of the bacteria is present (Le Roux et al. 1973). It has also been shown that T. ferrooxidans can fix atmospheric nitrogen (Mackintosh 1978) and thus can exist in the absence of nitrogen compounds.

1.2.3 Oxidation Products

The immediate environment of the pyrite will dictate the amount of acid produced and whether or not it is neutralised. The iron liberated from the pyrite will stay in solution as ferrous or ferric ion or will be precipitated as ferric compounds. Le Roux et al. (1973) found that the iron stayed in solution as ferric iron (this needs very acidic conditions to stop the iron precipitating):

$$FeS_2 + 15/4\ O_2 + 1/2\ H_2O \longrightarrow Fe^{3+} + 2SO_4^{2-} + H^+ \qquad (9)$$

This produces only one mole of acid per mole of pyrite oxidised. If the iron stays in solution as ferrous ion then two moles of acid per mole of pyrite oxidised are produced (van Breemen 1973):

$$FeS_2 + 7/2\ O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (10)$$

The maximum amount of acid is produced when the iron is precipitated as ferric hydroxide, four moles of acid being produced per mole of pyrite oxidised (van Breemen 1973):

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \longrightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \qquad (11)$$

The stoichometric hydroxide $Fe(OH)_3$ does not actually exist, although it is used here to describe the end product of the oxidation as opposed to intermediate ferric oxides. The red-brown compound generally called $Fe(OH)_3$ is actually a hydrated ferric oxide, $Fe_2O_3nH_2O$ or FeO.OH.

Jarosite is often found as yellow mottles in acid sulphates soils (Ivarson 1973, Calvert and Ford 1973, Ross and Ivarson 1981 Postma 1983) and represent an incomplete hydrolysis of ferric ion:

$$\begin{aligned} &FeS_2 + 15/4\ O_2 + 5/2\ H_2O + 1/3\ K^+ \longrightarrow \\ &1/3\ KFe_3(SO_4)_2(OH)_6 + 4/3\ SO_4^{2-} + 3H^+ \qquad (12) \end{aligned}$$

In this reaction slighly less acid is produced than in reaction 11. The formation of jarosite and its analogues (the substitution of NH_4^+, Na^+, H_3O^+ for K^+) and the controls upon which form dominates has been investigated by many authors (van Breemen 1973, Ivarson 1973, Ivarson et al. 1979, Ivarson et al. 1980). Jarosite is more stable than ferric hydroxide at low pH, but over a number of years it will hydrolise to ferric hydroxide, causing the release of a small amount of acid.

Other iron compounds can be formed, ranging from insoluble iron oxides to soluble iron sulphate hydrates (Caruccio 1978, Nordstom 1982), various transformations between the different species being possible but eventually iron hydroxide or jarosite will precipitate. Jarosite and ferric hydroxide appear as yellow and reddish-brown coatings on spoils and acid sulphate muds (Bloomfield 1972, van Breemen 1973, Infanger and Hood 1980, Caruccio et al. 1981, Nordstrom 1982). Acidic mine drainage is often of a yellow to red colour due to dissolved ferric ion (Caruccio et al. 1981). The solid iron compounds can dissolve if the pH is lowered (Portma 1983), or when natural waters flow over the iron salts (Caruccio et al. 1981). Ferric iron will also dissolve if the bacterial oxidation of ferrous ion ceases (Stumm and Morgan 1981). Any ferric ion which is released back into solution will obviously be able to oxidise more pyrite.

The acid produced by the oxidation of pyrite can be buffered by various constituents of the soil or water. Van Breemen (1973) identified the substances capable of this as (carbonate) alkalinity in solution, exchangeable bases and weatherable minerals. He reported that the alkalinity of the waters of acid sulphate soils tends to be rather low and therefore are not particularly effective buffering agents. The exchangeable bases on clays will be removed and replaced by hydrogen ions, but often these clays undergo spontaneous decomposition to become clays saturated with aluminium (Bloomfield and Coulter 1973, van Breemen 1973). Clays with exchangeable hydrogen ions tend to exist only at very low pH. Carbonate minerals in the soil including calcium carbonate and ankerite (a mineral consisting of carbonates of calcium, magnesium, iron and manganese) will be attacked by acid. Gypsum is often found (van Dam and Pons 1973) as a result of acid attack on calcium carbonate:

$$CaCO_3 + 2H^+ \longrightarrow Ca^{2+} + CO_2(\text{gas}) + H_2O$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O \longrightarrow CaSO_4.2H_2O(\text{gypsum})$$

Silicate minerals will hydrolyse at low pH to form H_4SiO_4 and this will precipitate as cryptocrystalline or amorphous silica (van Breemen 1973, van Dam and Pons 1973):

$$\text{M-Al-Silicate} + a\text{H}^+ + b\text{H}_2\text{O} \longrightarrow \text{M}^{a+} + c\text{H}_4\text{SiO}_4 + \text{Al(silicate)residue}$$

(M = Metal)

Kaolinite is often found as the aluminium-silicate product of this reaction and is widespread in acid sulphate soils, but it can also be attacked by acid. Other reactions will also be important in buffering the acid, including the weathering of feldspars and micas. Depending on which reactions predominate, the system will be buffered at different pH's - typical acid sulphate soils have a pH in the range 3 to 4, - the jarosite-goethite system and kaolinite-AlOHSO_4 + amorphous silica system both buffer the pH at about 3.7 (van Breemen 1973).

Caruccio and co-workers (Caruccio and Pelletier 1980, Caruccio et al. 1981), discussed the neutralising capacity of strata associated with coal. The presence of calcareous material in the strata can result in alkaline drainage as opposed to acidic drainage. The alkalinity content of the water will depend to a large extent on the solubility of the particular carbonate mineral in question, which tends to be low (except siderite which in any case oxidises to lower the pH, Postma 1983). If the water is kept alkaline it will not only neutralise any acid produced but the pH will be maintained in a range unfavourable for pyrite oxidation. Clays, micas and feldspars will also be important in buffering the acid produced, depending on the particular constituents of the associated strata.

Obviously the capacity of various constituents of the soil or rock strata to neutralise any acid will depend on the amount of acid produced and the actual amount of neutralising material present. Thus soils of different pH, waste tips of different pH and mine drainage of different pH will result upon the oxidation of pyrite.

1.2.4 Factors Affecting the Rate of Pyrite Oxidation

Environmental factors affecting microbial growth, partial pressure of oxygen, temperature and type of pyrite will all affect the rate of pyrite oxidation in the field.

Clark (1966) found the rate of sulphate production was related to the dissolved oxygen content. By doing experiments at a fixed partial pressure of oxygen, in closed containers, he found the rate of sulphate production could be expressed:

$$\frac{d[SO_4^{2-}]}{dt} = a \times [O_2]^b$$

where $[O_2]$ = dissolved oxygen in mgl^{-1} and the rate is expressed in $mgl^{-1}h^{-1}(g\ pyrite)^{-1}$

At pH 1 and in sterile conditions he found a = 0.23 and b = 2/3. Oxygen consumption figures for pyrite oxidation under favourable conditions i.e. low pH, microbial activity and available oxygen, have been found (Silverman 1967) but they cannot be compared to the real situation. Van Breemen (1973) calculated that at the most one-tenth of the necessary oxygen for optimum pyrite oxidation to occur would be available in a 2 mm layer of soil. Therefore, oxygen diffusion is probably a rate limiting factor for pyrite oxidation under field conditions. An increase in temperature of 10 °C will double the rate of oxidation by oxygen (Clark 1966, Nordstrom 1982).

Framboidal pyrite is frequently reported as the most reactive type of pyrite (Caruccio 1970). This type of pyrite has the largest surface area for a specific diameter. Museum grade pyrite which has a much smaller surface area than framboidal pyrite for the equivalent diameter (Pugh et al. 1981) is normally reported to be inactive (for example, Leathen et al. 1953), although others report it will react if it is very finely ground (for example, Temple and Delchamps 1953).

Most authors agree that the occurrence of trace metals has no effect on the oxidation rate of pyrite, although Caruccio (1972) found that titanium tended to be associated with stable pyrite whilst silver was associated with reactive pyrite. Other sulphides such as chalcopyrite and sphalerite which can occur with the pyrite can decrease the rate of oxidation of pyrite (Nordstrom 1982). Mixtures of sulphides will release more metals into solution than just one sulphide and cause a greater decrease in pH. Pyrite will increase the rate of metal release from other sulphides whilst its own oxidation rate is decreased (Nordstrom 1982).

The presence of calcite does inhibit pyrite oxidation, because it maintains the pH at too high a value for bacterial activity and ferric hydroxide will precipitate out (Clark 1966). Acid washing of inactive pyrite samples has been found to activate them (Temple and Delchamps 1953).

The concentration of ferric ion in solution will obviously affect the oxidation rate. The rate of bacterial oxidation of ferrous ion to ferric ion compared to the rate of oxidation of pyrite by ferric ion will dictate whether ferric ion is found in solution and which of these reactions will have more affect on the rate of oxidation. Van Breemen (1973) reported if the pyrite concentration is high then only ferrous ion is found in solution i.e. the bacterial oxidation of ferrous ion is-slower than the oxidation of pyrite by ferric ion. At lower pyrite concentrations ferric ion is found to predominate over ferrous ion in solution (Bloomfield 1972). No increase in the rate of oxidation was found upon addition of ferric ion over a concentration of 6g l^{-1} (Le Roux et al. 1973). This may well be explained by the theory of Garrels and Thompson (1960) - the rate of pyrite oxidation is proportional to the surface area covered by ferric ions. Van Breemen (1973) also found that above a certain concentration of ferric ions no increase in the oxidation rate was found. If the ferric ion in solution is regulated by jarosite and various ferric sulphate compounds, then the ferric ion concentration in terms of the pH can be calculated (van Breemen 1973). Using rate constants calculated by Hart (1963), he found the dependency of the oxidation rate on pH - the time taken for the complete oxidation of a given quantity of pyrite will increase by a factor of 100 for every unit increase in pH, between pH2 and 4 - 10^3, 10^5 and 10^7 hours for pH 2, 3 and 4 respectively. Although theoretically the rate is independent of the amount of pyrite, the rate involving high concentrations of pyrite will be affected due to the bacterial oxidation of ferrous ion being slower than the oxidation of pyrite by ferric ion. However, these calculations are theoretical and are not substantiated in the field, as shown by the fact that pyrite is still present in aerated soils (for example, Harmsen 1954).

Various experiments have investigated the rate of oxidation. Dent and Raiswell (1982) found the rate of oxidation to be proportional to surface area of the pyrite and the rate of transfer of the oxidants into the system. They found the rate of oxidation at any point was related to the distance of that point from the air-water interface. They also found that a decreased particle size and a decrease in the initial concentration of pyrite increased the rate of oxidation.

It was estimated that it would take 12 to 13 years to remove the pyrite from a soil containing 0.9% pyritic sulphur under the climatic conditions of South-East England (Trafford et al.1973, Bloomfield 1973), but these measurements were done on a soil core which allowed oxygen to diffuse to the bottom of the columns, better leaching occured than would be possible in the field and the temperature was higher than in the field, so this was actually an underestimate of the time required. Harmsen (1954) found 0.4% pyritic sulphur in soils which had been aerated for nine years and also found considerable concentrations of pyrite still present in old soils that had been drained and cultivated. These examples show that pyrite in the field can remain for a considerable number of years and may not be quickly oxidised and leached away. Krothe et al. (1980) found that extensive oxidation and leaching had occurred in the top two metres of coal waste dumps but at greater depths large quantities of pyrite were still present.

1.2.5 Effect of Pyrite Oxidation on Plant Growth

There are four main changes in the soil or spoil status due to pyrite oxidation which can have a detrimental effect on plant growth. These are:

1. increase in hydrogen ion concentration
2. increase in many metal ion concentrations
3. decrease in various nutrient concentrations
4. physical changes in the spoil or soil

As pyrite oxidation releases acid, there is a considerable increase in the hydrogen ion concentration. The hydrogen ion itself can be toxic to some plants if it is present in high concentrations (Berg and Vogel 1973).

As the acidity of the spoil or soil increases, many metal ions can be released into solution. The toxic affects of manganese and aluminium on plant growth were described by Berg and Vogel (1973). The concentration of iron in solution will be increased, due to its release from the pyrite itself, as well as being released from other constituents of the soil or spoil due to these being attacked by the acid. Ferric ion will not exist in solution above a pH of approximately 3.5 and therefore will only be present in toxic concentrations at low pH. However, ferrous ion can stay in solution up to about pH 6 and can be present in toxic concentrations. Potentially toxic concentrations of zinc, copper and nickel as well as iron, manganese and aluminium in acidic coal spoil have been reported (Barnhisel and Massey 1969, Massey and Barnhisel 1972). If other metal sulphides are present as well as pyrite, these other metals can also be leached - Krothe et al. (1980) reported the occurrence of zinc in the leachate from a coal waste dump in Illinois due to the leaching of sphalerite (ZnS). Various factors will affect whether a particular concentration of a metal ion is toxic, for example, for manganese, the presence of certain other metals or calcium can reduce its toxicity to plants (Rorison 1973). Different species of plants will also have different degrees of tolerance to different metal ions.

The two main nutrients found to be deficient in acidic coal waste are nitrogen and phosphorous (Gemmell 1973). The microbiological processes which convert the various forms of nitrogen in the soil to nitrogen in a form available for plants can be impaired at low pH, e.g. Nitrosomonas and Nitrobacter which convert amonium to nitrite and nitrite to nitrate are both affected by low pH and can stop functioning completely (Jackson 1967). Phosphorus can be made unavailable to plants as it can be fixed by either amorphous iron oxides (Pulford and Duncan 1975) or by aluminium (Rorison 1973).

The weathering of pyrite can increase the rate of physical breakdown of other spoil constituents, increasing the proportion of finer particles in the spoil. Another result of pyrite oxidation is an increase in the total salt concentration - carbonates and other minerals will be attacked by the acid (Bloomfield and Coulter 1973, Coulter 1973).

There can be a large increase in soluble salts which will increase the osmatic pressure of the soil solution and decrease the water availability for plant roots (Williamson et al. 1982).

The problems involved in growing plants on colliery spoil have been reviewed by Kent (1982) and the physiological effects on plants due to the effects of pyrite oxidation were discussed by Rorison (1973).

1.3 Pyritic Mine Wastes and Acid Sulphate Soils

Problems arising from pyrite oxidation occur extensively in pyritic mine wastes and acid sulphate soils. Many valuable minerals and coal have pyrite occurring in associated strata and during the course of mining the pyrite is exposed and can thus be oxidised. Acid sulphate soils are widespread, especially in the Tropics and contain pyrite, some or all of which has oxidised, leading to severe problems if the soils is to be used for agriculture. Both these problems and the possible methods of treating them will be discussed briefly.

1.3.1 Pyritic Mine Wastes

In mining operations, pyrite can be uncovered - it can be left in the mine exposed to the air or be dumped with other waste from the mine. Air will then have access to the pyrite which will oxidise, resulting in the production of acid and iron and sulphate salts, as previously described. Acid mine drainage is water that is pumped from mines containing exposed pyrite and its oxidation products, or it is water that has flowed over or through pyritic rocks or pyritic waste heaps. It will dissolve the oxidation products of the pyrite and will become highly acidic. Acidic mine drainages contain varying amounts of its characteristic components - iron, sulphate and acid, depending on the source of the drainage. Caruccio et al.(1981) defined acid mine drainages as having a pH below 2.3, anion concentrations (mainly sulphate) above 10,000 mgl^{-1} and acidities of about 5,000 mgl^{-1} (as $CaCO_3$), whereas Glover (1983) described an average acidic mine drainage of having a pH of about 2.9, iron concentration of 120 mgl^{-1} and a sulphate concentration of 1,250 mgl^{-1} with extremely acidic drainages as having a pH of 2.0 and iron concentrations of 5,000 mgl^{-1}. Kroethe et al.(1980) found acid mine drainages as having acidities ranging from 800 to 82,000 mgl^{-1} (as $CaCO_3$). The drainage can also contain large amounts of dissolved metals, the concentration of the metals depending on the strata that the water is flowing through, for example, the acidic water can attack clays releasing aluminium and manganese (Kroethe et al.1980), or it can attack ankerite and black shales releasing manganese (Pulford et al.1982), or it can solubilize other metal sulphides releasing those metals - copper, nickel, zinc, calcium and lead (Kroethe et al.1980). Acid mine drainage can run into rivers and cause pollution of water and land, even miles from the source of the drainage. Two soils treated with acid mine drainage showed a decrease in pH, calcium content and base saturation whilst the acidity, iron and aluminium increased, iron and aluminium also being released from the soil (Ciolkosz et al.1979). In Southern Australia, acid mine drainage caused the pH of a creek to fall to 2.5 whilst the metal concentration increased dramatically, resulting in the death of fish and vegetation for many miles. In rivers in Ontario, acid mine drainage has caused an increase in the iron content by factors of up to 1,000 (Williamson et al.1982). In the United States the problem of acid mine drainage is vast, but even in Britain where the problem is much smaller there are 10 million litres produced every day (Glover 1983). In South Africa acid mine drainage is a product of both coal and gold mining - in the gold mining area of the Witwatersrand one sand dump can produce over 7,000 tonnes of pure sulphuric acid per year and there are thirty of these dumps - this particular kind of dumping has now been stopped (Kempe 1983).

There are numerous examples of acidic waste heaps where re-vegetation for agricultural or recreational use, or even just for cosmetic value, is severely hampered due to the acidic status of the material. In the U.S.A. there are extensive problems in the attempts to reclaim waste heaps and mined areas in the widespread Appalachian coalfields, for example, in south-western Pennsylvania and Western Virginia (Grube et al.1982). In Britain there are numerous coal waste heaps containing pyrite making their reclamation very difficult, for example, Gemmell (1973) cited pyritic sites in Lancashire, Pulford et al.(1982) studied pyritic spoils in Scotland and Costigan et al.(1982) studied pyritic sites in England and Wales.

1.3.2 Acid Sulphate Soils

Acid sulphate soils were formerly called cat clays from the Dutch 'Kattekli' which is what the farmers called the yellow mottled, infertile soils (Bloomfield and Coulter 1973). They can be defined as having a soil pH of less than 4 within 50 cm of the surface due to the oxidation of pyrite or occasionally other sulphides (van Breemen 1982). Potential acid sulphate soils are those soils which have a near neutral pH, but which are poorly drained and would become acidic upon drainage. Both these types of soils are found throughout the world especially in tropical areas. It has been estimated that there are 10 million hectares of land in recent coastal plains, mainly in the tropics, which have already developed or will develop, into acidic soils. Non-pyritic fluvial sediments or peat cover pyritic coastal sediments over an even larger area and in inland areas there are geologically older potential acid sulphate soils which were laid down in tidal areas (Pons et al.1982).

Moorman (1963) and Bloomfield and Coulter (1973) both summarise some of the occurrences of acid sulphate soils throughout the world - over a million hectares in Vietnam, 100,000 hectares in Sierra Leone, large areas in Pakistan, 200,000 hectares in West Malaysia. In Indonesia acid sulphate soils are found on the coastal areas of Sumatra and Borneo, in tropical Africa on both coasts of the continent and in South America, for example, in the Amazon delta. Acid sulphate soils occur to a much smaller extent in temperate lands, for example, Netherlands, Japan, United States (for example, Calvert and Ford 1973) and in Britain (Bloomfield 1972, Trafford et al.1973).

International conferences are held at intervals on the problems and possible solutions of acid sulphate soils (Dost 1973, Dost and Breemen) and in the 1973 papers there is an extensive bibliography of all aspects of acid sulphate soils from 1863 to 1973. The main problems of acid sulphate soils are high acidity, possible iron, manganese and aluminium toxicity problems, low fertility and poor physical soil conditions. Due to the widespread occurrence of these soils it is obviously vitally important to find a solution to these problems so that they can be successfully used for agriculture.

1.3.3 Treatment of Acidic Waste Heaps and Acid Mine Drainage

Lime is often used to treat both of these problems. In drainage problems it is normally used in conjunction with sedimentation techniques to remove the high content of iron solids formed upon neutralisation which can then be disposed of easily, leaving a neutral drainage (although it will contain a high content of dissolved salts, especially sulphates - Bilharz 1949, Bosman 1983, Glover 1983). Liming has been used on acidic waste heaps to neutralise the acidity. However there are often problems of acid regeneration (James and Mrost 1965, Maclean and Dekker 1976, Costigan 1979). This will occur if the lime is leached out and unoxidised pyrite remains which can then oxidise to produce acidic conditions. Liming of pyritic heaps will be discussed in later chapters.

Various amendments have been added to spoil heaps to try to improve yields of plants. Power plant fly ash has been used because of its alkaline nature and the possibility of it improving soil conditions (Plass and Capp 1974). Nebgen and Engelmann (1981) used fly ash as well as other alkaline materials - blast furnace slag, Portland cement and cement kiln dust and succeeded in reducing the amount of acidity in the leachate of pyritic spoil over a period of thirty weeks. Surface mulches have been used to improve the status of acidic spoils - Berg and Vogel (1973) used hardwood chips to reduce surface evaporation and promote leaching to decrease the toxic conditions of the spoil. Top soil is used but tends to be an expensive treatment, and the use of a barrier layer as well has been suggested to stop the upward movement of toxic metals into the soil and to reduce the infiltration of oxygen into the underlying pyritic material (Williamson et al. 1982).

Anti-bacterial agents have also been suggested to stop the activity of T. ferrooxidans in the spoil or drainage (Williamson et al. 1982, Lovell 1983), Kleinmann (1980) reported the use of anionic detergents as a bactericide and the successful reduction of acid production over a limited period. However the method has not really been completely tested, so at present the extent of its possible application is not known.

The use of hydrophobic materials to prevent oxidation has also been tried (Peeler 1963, Tyco 1971), although this method has not been widely used. It has been suggested that the silica gels used in this method are actually inhibiting the oxidation of pyrite by precipitating iron. Phosphate has also been suggested to precipitate iron (Lovell 1983). These kinds of methods will also be discussed in later chapters.

Other methods to prevent acidity developing include sealing old mines (Lovell 1983), infilling old mines, for example, with fly ash (Funke 1983), rapid dewatering of mines to prevent the formation of acidic drainage (Funke 1983) and flooding of mines and preventing the water escaping thus stopping further oxidation of pyrite (Glover 1983).

Sometimes locally occurring materials can help to reduce the acidity of the drainage - Infanger and Hood (1980) found placing limestone above pyritic spoil improved leachate quality and even placing a slightly alkaline shale over the pyrite improved the quality - presumably by maintaining a high pH in the water entering the pyritic spoil. Obviously if there are naturally occurring alkaline materials that are moved at the time of mining it is sensible to bury the pyrite under them. Often there will be alkaline strata below the pyritic strata and water from both of these can be mixed in underground pools and sumps to neutralise the acidic water (Glover 1983). If weathered and unweathered pyritic strata are removed during mining then the placement of the weathered rock over the unweathered rock can prevent the oxidation of the unweathered pyrite and a reasonable soil can sometimes be developed (Singh et al.1982).

1.3.4 Treatment of Acid Sulphate Soils

Acid sulphate soils are often kept in a flooded state to prevent pyrite oxidation and used for growing rice, but this is obviously not a very acceptable solution. This idea has been adapted where the pyrite horizon is not at the surface - the watertable level is raised by blocking drains to keep the pyritic horizon flooded. Acidification can occur during the dry season due to a lowering of the watertable, but the acid can be quickly leached out by unblocking the drains at the beginning of the wet season (Yin and Chin 1982). Also if the pyrite occurs at some depth shallow rooting crops can be grown (Coulter 1973).

Intensive leaching and draining has been attempted to try to oxidise all the pyrite and leach the oxidation products, but this method has failed, as a large amount of pyrite remained in the soil (Yin and Chin 1982). It was estimated that it would take about 13 years to completely oxidise and leach a pyritic soil (pyritic sulphur content 0.9%) from South East England, under optimum laboratory conditions (Bloomfield 1973, Trafford et al. 1973). Even if all the pyrite was oxidised there would be a considerable depth of very acidic soil left.

Liming is used extensively to raise the pH of the soil, to inhibit the pyrite oxidation and to combat metal toxicity problems. Trafford and co workers (1973) found decreased sulphate and iron levels in the leachate and the soil, after liming the pyritic soil and leaching it for one year, i.e. a decrease in pyrite oxidation. However, regular liming would be needed to keep the soil at a reasonable pH.

Ponnamperuma and Solivas (1982) found that the addition of manganese dioxide improved yields of rice on an acid sulphate soil, probably by counteracting iron toxicity physiologically.

Although some of these methods do work to a limited extent, there has not been a particularly satisfactory method developed to combat pyrite oxidation and the consequent problems in either pyritic mine wastes or acid sulphate soils.

1.4 Aims of Project

From the foregoing discussion it can be seen that pyrite oxidation, particularly in pyritic mine waste and acid sulphate soils, can create severe problems, preventing the establishment of vegetation. At present, most studies attempt to treat the consequences of pyrite oxidation, but this project concentrated on attempting to inhibit the pyrite oxidation, thus overcoming the need to treat the problems encountered due to pyrite oxidation. Various other points were also developed during the research, i.e. various points concerning the liming of pyritic spoils, and studies on the differences in the reactivity of different pyrite samples.

The project was laboratory based as it was hoped that an understanding of the chemistry involved in the oxidation of pyrite would lead to possible methods of inhibiting the pyrite oxidation. However, the results of field studies on pyritic colliery spoil were taken into account when discussing the results.

Although the studies were mainly on pyrite from colliery spoil it was hoped that any positive results could be adapted for use in other areas where pyrite oxidation causes problems, i.e. other types of mining operations and acid sulphate soils.

CHAPTER 2

Chemical Studies on the Oxidation of Pyrite and its Inhibition

2.1 Introduction

The oxidation of pyrite causes agricultural and environmental problems, as outlined in the last chapter. The various treatments of these problems succeed to various extents, but no universal relatively cheap method has been developed to combat the problems. Obviously an alternative method would be to prevent the oxidation of pyrite in the first place and thus stop the cause of the problems. This has been tried, mainly using methods which prevent air reaching the pyrite - in the mining industry by sealing old mines and in acid sulphate soils by flooding them and using the flooded soils for growing rice. However this is not very viable - neither of these methods works particularly well and it would be much better if the soils could be developed for agricultural use without being flooded.

In order to effectively stop the oxidation of pyrite, it is necessary to understand the main processes involved in the oxidation, especially that which causes the relatively rapid increase in acid. As discussed in the first chapter the oxidation of pyrite by oxygen alone is quite slow and it is thought that it is the oxidation of pyrite by ferric iron (and perhaps a bacterial oxidation of pyrite) which causes the increase in the acid production rate. Therefore if a method could be found to stop this oxidation pathway, then the rate of acid production would be significantly decreased. The slow acid production caused by the oxidation of pyrite by oxygen alone could probably be coped with by natural leaching of the acid or by the addition of small amounts of lime.

Therefore the initial aim of the study was to establish whether the ferric iron oxidation was important, so that possible methods of inhibiting the oxidation could be studied.

2.1.1 Pyrite Samples

The pyrite used throughout the project was from three locations. The majority of the studies concentrated on pyrite collected from Baads bing in West Lothian. Other samples came from Durham and Ballachulish. Baads and Durham pyrite were both reactive types of pyrite, shown by the fact that a white coating of sulphate formed on leaving the samples uncovered in a warm room. The Ballachulish sample was not so reactive and will only be referred to in the last chapter, where the properties of the three samples of pyrite will be compared.

The pyritic samples from Baads and Durham contained high percentages of pyrite, up to 75% FeS_2. Lumps of the pyritic material could easily be found in the field, the pyrite being visible as thin veins in the material. These pyritic lumps were ground up in a ball-mill to a size of less than 150 μm. Different lumps of material were ground up for different experiments, so the pyrite concentration was not the same for all the experiments. For some of the studies the finely ground up pyritic Baads material was 'diluted' by adding other spoil material (size less than 2 mm), also collected from Baads bing. The laboratory studies all used the pyritic material in flasks of water. This is obviously a totally artificial situation, but it was hoped that the results could be applied to subsequent pot experiments. The flasks containing the pyritic material were covered with paper to stop contamination but to allow the easy access of air, and the flasks were periodically shaken. In some experiments a series of replicate flasks were made up and a certain number of flasks were destroyed on each sampling date. In other experiments either duplicate or triplicate flasks were made up and some of the solution removed at each sampling date and replaced by deionised water. The first method is obviously more accurate, as in the second method the solution is diluted at each sampling date, but the second method was normally used when flasks with various different additions were needed, as the first method would have entailed a great number of flasks. The precise details for each experiment will be given in the appropriate section.

2.1.2 Analytical Techniques

The same analytical techniques were used throughout the project and are listed below, with only a brief summary of the method as they are standard chemical methods. The possible products of pyrite oxidation are ferrous ion, ferric ion, sulphate ion, elemental sulphur and acid which can all be determined relatively easily.

Determination of Pyrite - differential iron method using sequential HCl/HNO_3 extractions (Dacey and Colbourn 1979).

Duplicate 1 g samples (accurately weighed) were refluxed for thirty minutes with 50 cm^3 2M HCl. The extract was filtered through Whatmans number 1 filter paper and the residue washed thoroughly with deionised water. The residue plus filter paper were returned to the flask and again refluxed for thirty minutes with 50 cm^3 2M HCl. After again filtering the residue and washing thoroughly with deionised water, it was returned to the flask with the filter paper and refluxed for one hour with 50 cm^3 2M HNO_3. The extract was filtered into a volumetric flask, well washed with deionised water and the volume of the filtrate and washings made up to 1 litre. The iron in solution was determined by atomic absorption spectrophotometry. The concentration of pyrite was determined using the following equation:

$$\%FeS_2 (w/w) = \frac{F \times V}{W} \times 0.2148$$

F = conc of Fe (mgl^{-1})

V = vol (1)

W = spoil dry weight (g)

(This method will be discussed in Chapter 5)

Ferrous Iron - colormetric method (Hesse 1971)

Reagents - Buffer solution. 272 g sodium acetate trihydrate ($CH_3COONa3H_2O$) were dissolved in deionised water (about 1 litre) in a 2 litre volumetric flask. 120 cm^3 glacial acetic acid were added and the solution made up to 2 litres to give a buffer solution of pH 4.5.

0.1% 1, 10 phenanthroline ($C_{12}H_8N_2H_2O$, approx 5 X 10^{-3}M)

Ferrous ammonium sulphate ($(NH_4)_2SO_4.FeSO_4.6H_2O$) used for ferrous standards.

Method. 10 cm^3 of 1,10 phenanthroline solution and 10 cm^3 of buffer were added to standards or samples in 100 cm^3 volumetric flasks and the solutions made up to volume with deionised water. These were left for one hour and the absorbance read at 506 nm using a Bausch and Lomb colorimeter. Six ferrous standards were used in the range 0.0-2.5 $mgFe^{2+}l^{-1}$.

Ferric Iron - colorimetric method

The ferric iron was reduced to ferrous iron by the addition of 1.5 cm^3 10% hydroxylamine hydrochloride ($NH_2OH.HCl$, approx 1.4M) to the samples which were allowed to stand for ten minutes. The procedure for ferrous iron determination was then followed. This gave the concentration of total iron and ferric iron concentration could be found by subtracting ferrous iron concentration (determined as above).

Total Iron in Solution - atomic absorption spectrophotometry

Total iron in solution was determined by atomic absorption spectrophotometry using an air/acetylene flame and could be used as an alternative method to the above colormetric method.

Sulphate in Solution - gravimetric method (Hesse 1971)

5 cm^3 of solution were pipetted into a centrifuge tube (10 cm^3) of known dry weight. 1 cm^3 of 2M HCl was added and the tube placed in a boiling water bath for ten minutes, the mouth of the tube being covered. 2 cm^3 of 5% $BaCl_2$ solution (approx. 0.2m) were added dropwise to the tube with shaking. The tube was kept in the boiling water bath for thirty minutes. After cooling, the tube was centrifuged at 3000 rpm for fifteen minutes, the supernatant decanted and the precipitate was washed with ethanol. The tube was again centrifuged and the supernatant decanted. The tube was dried in an oven overnight at 105 °C. The tube was then cooled in a desiccator, and weighed. The amount of sulphate in the original solution could then be calculated from the weight of barium sulphate precipitated.

Sulphur - turbidimetric method (Hart 1961)

The contents of the flask containing the pyritic material were centrifuged and the supernatant used for the other determinations. A portion of the solid was weighed and dried overnight in 105 °C oven, cooled and reweighed to obtain the oven dry weight conversion value. The centrifuge tube and the rest of the sample was weighed and 25 cm^3 of acetone added. The tube was stoppered and shaken for five minutes and then centrifuged at 2000 rpm for fifteen minutes. An aliquot of the supernatant was pipetted into 80 cm^3 of deionised water (where the aliquot contained 100 - 700 μg S). Colloidal sulphur immediately formed and the solution was made up to 100 cm^3. After three hours the optical density was measured at 420 nm. Standards containing 1 - 8 mgS l^{-1} were prepared in the same way. The concentration of sulphur in acetone had to be less than 200 mg l^{-1} for the extraction to be complete, otherwise less soil had to be used. The concentration of sulphur in the soil could then be calculated.

Aluminium, Manganese, Calcium, Silicon in Solution

These elements were all determined by atomic absorption spectrophotometry. Manganese and calcium were determined using an air/acetylene flame (as was iron). Lanthanum was added to the standards and samples when determining calcium, to overcome any interference effects of phosphate (phosphate combines with lanthanum more readily than with calcium thus releasing the calcium). A nitrous oxide/ acetylene flame was used to determine silicon and aluminium in order to break up the oxides formed by these compounds. An excess of potassium was added to the standards and samples when aluminium was being determined, so as to minimise the ionisation of aluminium.

Acid Concentration - pH and titratable acidity

The acid concentration was determined using a pH meter. This only recorded the free acid and therefore titratable acidity was also used. The solution was titrated with standardised sodium hydroxide using phenolphthalein as the indicator. However the colour produced due to the presence of ferrous and ferric iron which was hydrolysed and precipitated tended to mask the colour change and so a pH meter was substituted to show the end point. Aluminium and iron both contributed to the concealed acidity in these experiments.

Acid Digest for Organic Materials

A small sample of organic material (approx 1 g) was accurately weighed into a 250 cm^3 conical flask and 10 cm^3 of nitric acid added. It was heated on a hot plate at 120 °C until brown fumes had stopped evolving (fifteen minutes - one hour). The cooled flask then had 10 cm^3 of perchloric acid added. This was heated to approximately 200 °C and left until dense white fumes appeared. The contents of the flask were then cooled and filtered, the filtrate volume being made up to 100 cm^3. This acid digest could then be analysed for various elements.

2.2 Oxidation of Pyrite

The initial experiments were performed to determine the oxidation pathway of pyrite. This was done by studying the release of the products of the oxidation and then by inhibiting various reactions to try to clarify the actual pathway.

2.2.1 Products of Pyrite Oxidation

A series of flasks was prepared, each flask containing approximately 1 g of finely ground Baads pyrite (52% FeS_2) and 50 cm^3 of deionised water. These flasks were kept at 24 °C. Initially every two days and then twice weekly, three flasks were removed, the contents of the flask filtered and the filtrate analysed for ferrous iron, ferric iron, sulphate ion, elemental sulphur and acidity (by measuring the pH and the titratable acidity).

The full results are presented in Table A.1 in the Appendix and some of the results are represented graphically in Figs 2.1 (a-c).

Sulphur and Sulphate Production

The method to determine sulphur seemed rather inaccurate, there being great variability between the three replicate flasks (up to 10 $mgSg^{-1}$) whereas the results for the other products were much more consistent. This sulphur determination method has been previously criticised as giving excessively large values (Bloomfield 1972). It can be seen that much larger quantities of sulphate compared to sulphur were found so presumably any sulphur that is produced is oxidised relatively quickly to sulphate. Le Roux et al. (1973) also concluded that any sulphur produced would be oxidised to sulphate. Due to the inadequacy of the sulphur determination method and the greater quantity of sulphate produced, it was decided that in further studies only sulphate would be determined. The sulphate level increased steadily over the period, with an overall increase of approximately 100%.

Ferrous and Ferric Iron

The concentration of ferric iron in solution was negligible compared to the concentration of ferrous iron throughout the period.

Fig 2.1 Release of Oxidation Products from Baads Pyrite.

Fig 2.1.a Comparison of Sulphur and Sulphate Concentrations in Solution.

Fig 2.1.b Comparison of Ferrous and Ferric Iron Concentrations in Solution.

Fig 2.1.c Release of Acid.

Fig 2.1.a.

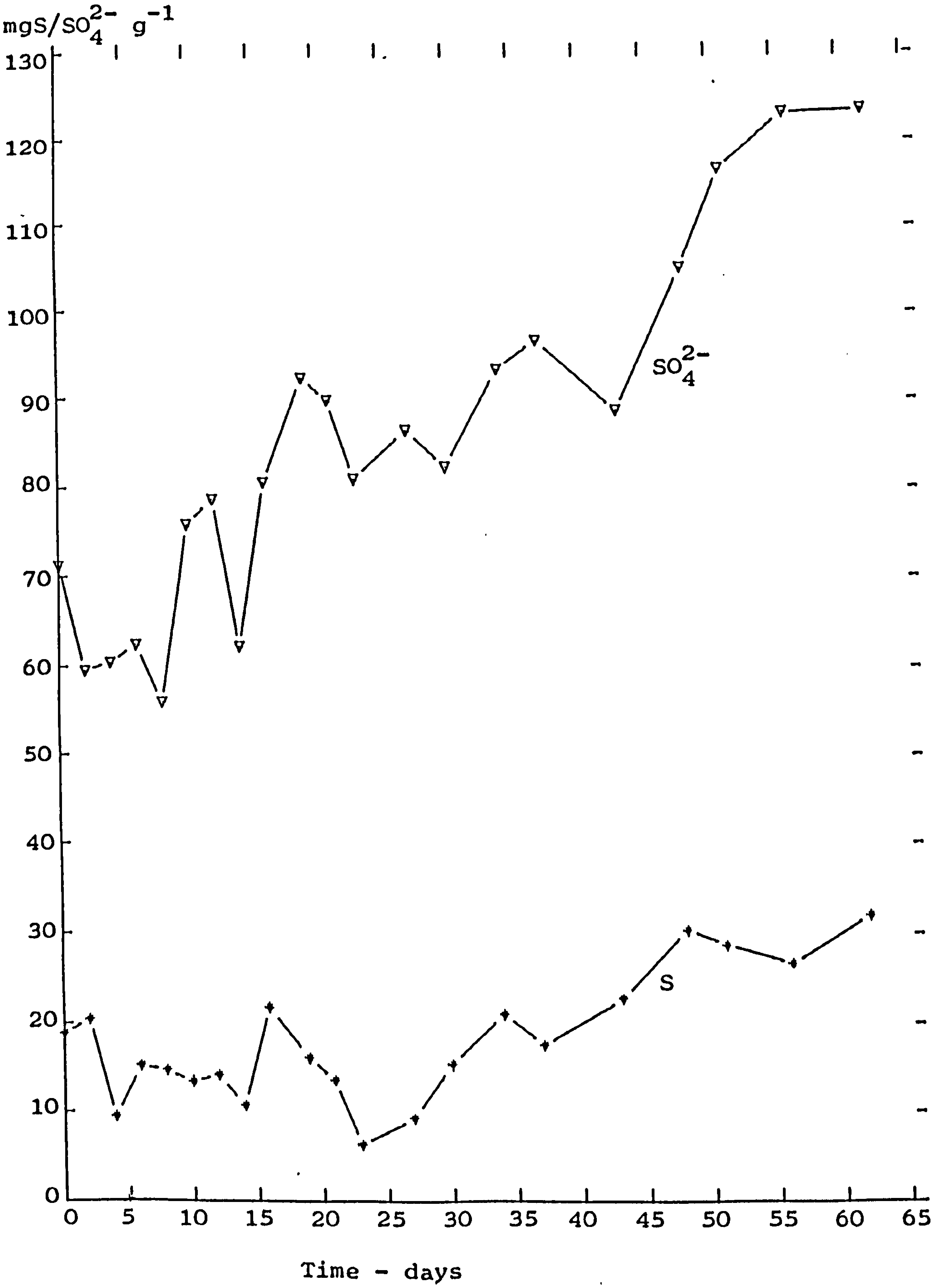

mgS/SO$_4^{2-}$ g^{-1}
130
120
110
100
90
80
70
60
50
40
30
20
10
0
SO$_4^{2-}$
S
0
5
10
15
20
25
30
35
40
45
50
55
60
65
Time - days

Fig 2.1.b.

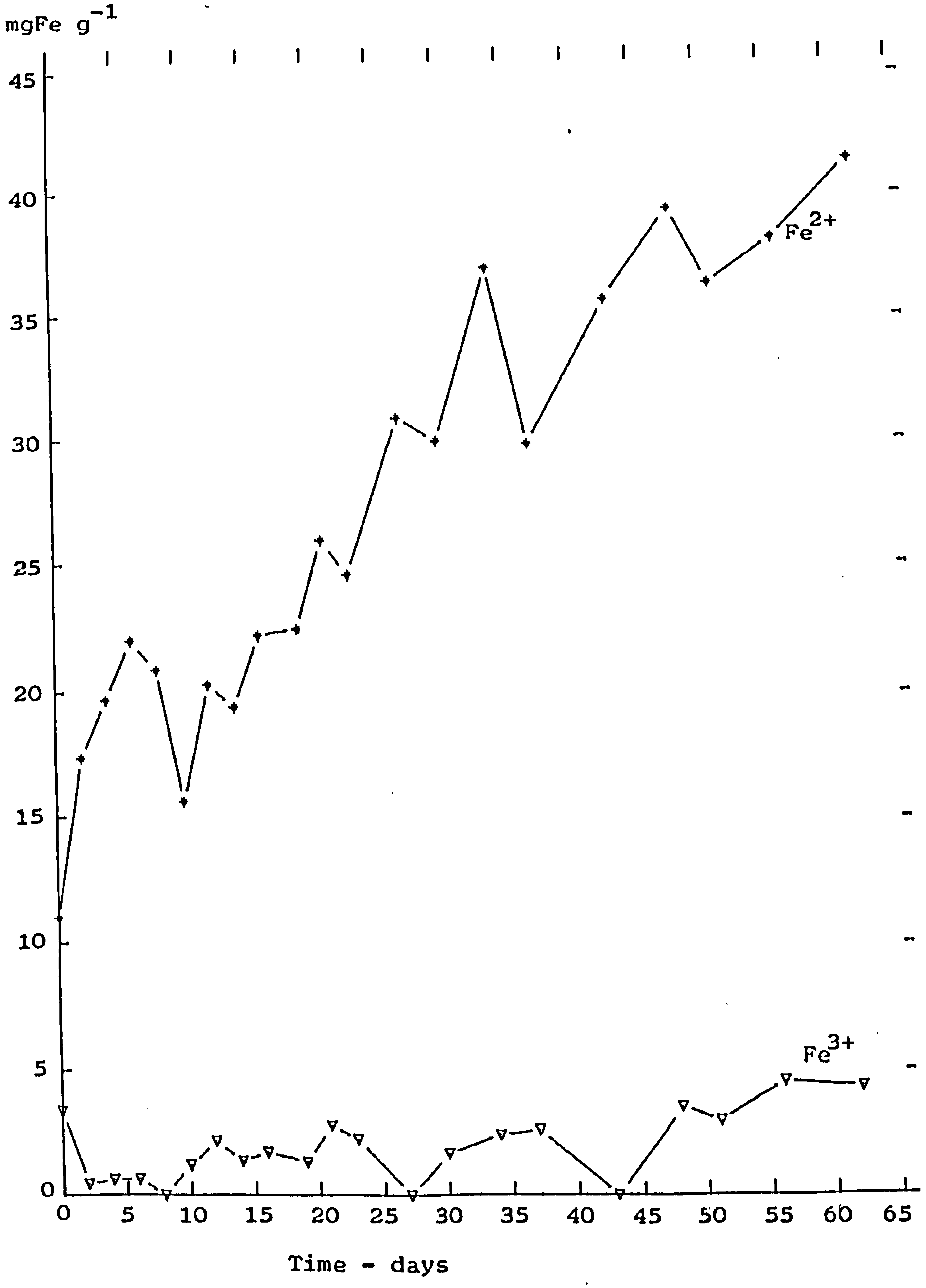
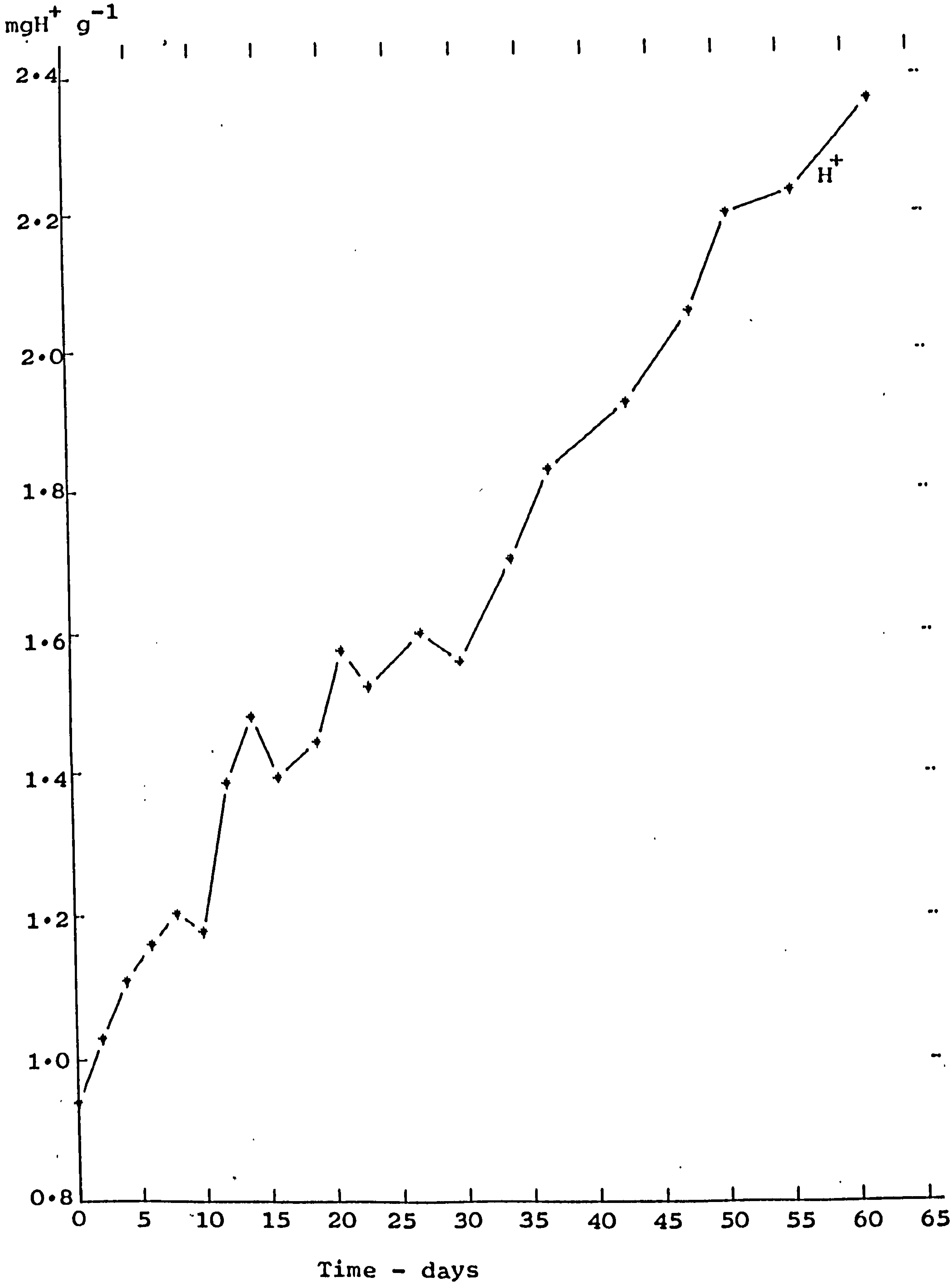

mgFe g^{-1}
45
40
35
30
25
20
15
10
5
0
Fe^{2+}
Fe^{3+}
0
5
10
15
20
25
30
35
40
45
50
55
60
65
Time - days

Fig 2.1.c.


mgH$^+$ g^{-1}
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0
5
10
15
20
25
30
35
40
45
50
55
60
65
Time - days
H$^+$

Acidity

The pH of the solutions decreased from 2.8 to 2.0 over the sixty two days, whilst titratable acidity increased steadily over the whole period. The titratable acidity obviously included the acid released upon the hydrolysis and precipitation of iron due to the addition of the alkali during the titration, which is present as hidden acid and not reflected in the pH.

Table 2.1 shows that the best correlations are for sulphate, ferrous iron, titratable acidity with time and between each other. This corresponds with these being the main oxidation products and with these increasing steadily with time.

Thus ferrous iron and sulphate are the main products in this case of pyrite oxidation, with sulphur and ferric iron only being present in minor quantities. However these results do not show whether

	TIME	pH	SULPHUR	SULPHATE	FERROUS	FERRIC
pH	-0.831					
SULPHUR	0.699	-0.602				
SULPHATE	0.926	-0.743	0.703			
FERROUS	0.949	-0.819	0.645	0.829		
FERRIC	0.589	-0.420	0.581	0.743	0.442	
ACIDITY	0.988	-0.817	0.671	0.917	0.933	0.592

Table 2.1 Correlation Coefficients for the Products of Pyrite Oxidation and Time

ferric iron takes part in the reaction pathway. The high concentration of pyrite may mean that the oxidation of ferrous to ferric iron is rate limiting (van Breemen 1973) and thus ferric iron will not be detectable in solution upon the oxidation of ferrous iron as it will be immediately reduced to ferrous iron by oxidising more pyrite. Therefore it was necessary to use a method which would be able to determine the role of ferric iron.

2.2.2 Effect of Altering Ferrous and Ferric Iron Concentrations

If it is assumed that the ferrous iron produced upon the oxidation of pyrite is itself oxidised to ferric iron which can then oxidise more pyrite, then prevention of the oxidation of ferrous iron should inhibit the oxidation of pyrite and therefore decrease the concentration of the products of pyrite oxidation. An increase in the ferric iron concentration would likewise be expected to increase the oxidation of pyrite. An experiment was set up to test this idea. Ortho-phenanthroline (1,10-phenanthroline) complexes ferrous iron (ferroin is the sulphate salt of this complex and is used as an indicator in redox reactions). O-phenanthroline was therefore used to stop the oxidation of ferrous iron by complexing it. Panacide (2,2'-dihydroxy-5,5'dichloro-diphenymethane) is a general bactericide and fungicide and therefore should be capable of stopping the bacterial oxidation of ferrous iron. Ferric chloride was added to some flasks to increase the ferric iron concentration.

A series of flasks containing approximately 5 g of finely ground up pyrite in 200 cm^3 of deionised water was set up. To different flasks the following additions were made, each treatment being replicated three times:

1. zero-control

2. 0.2 g o-phenanthroline (equivalent to 5 X 10^{-3}M)
3. 0.1 cm^3 panacide (equivalent to 0.5 mgl^{-1})
4. 0.5 g ferric chloride dissolved in 10 cm^3 of 0.4M HCl, only 190 cm^3 of deionised water was used in these flasks. (1.8 X 10^{-3}M Fe^{3+})
5. 5 g ferric chloride in 10 cm^3 of 4M HCl, only 190 cm^3 of deionised water used. (9 X 10^{-3}M Fe^{3+})

These flasks were prepared using both finely ground Baads pyrite (72% FeS_2) and Durham pyrite (approximately 62% FeS_2). Initially 10 cm^3 of the solution was removed and replaced by 10 cm^3 deionised water and the solution tested for pH, titratable acidity and sulphate. In later tests, 15 cm^3 were removed and replaced by water, and the solution tested for total iron (by atomic absorption spectrophotometry) as well as the other products.

The results are presented in Tables A2 and A3 in the Appendix and graphically in Figs 2.2-2.5. Some of the results for ferric chloride flasks have been separated from the other results as they needed a totally different scale. The results for Baads pyrite and Durham pyrite show the same trends but are of a different order of magnitude, due to the differences in the samples. The differences between the two samples will be discussed in Chapter 5.

O-phenanthroline Flasks

The o-phenanthroline initially added to the flasks was not adequate to complex all the iron present by day 19 (calculated from control and o-phenanthroline flasks, one mole of iron needs three moles of o-phenanthroline to complex it. Excess o-phenanthroline was then added to the flasks. This obviously affected the pH and titratable acidity (Fig 2.2(a,b) and 2.3(a,b). On the last sampling date the ferrous iron concentration of these flasks was measured. The concentration in each flask was measured with and without added extra o-phenanthroline. For the Durham flasks there was no difference in the absorbance between the two samples, (both sets were diluted 500 times and both showed absorbances of 0.14 units equivalent to 0.6 mgFe^{2+} l^{-1}). However the Baads flasks showed a greater concentration of ferrous iron on the addition of extra o-phenanthroline (those samples without extra o-phenanthroline had absorbances after dilution by 500 times, of 0.16 equivalent to 0.7 mgFe^{2+}l^{-1}, whereas the samples with extra o-phenanthroline had absorbances, after dilution by 500 times, of 0.26 equivalent to 1.1 mgFe^{2+}l^{-1}). Therefore it was only in the Durham flasks that all the ferrous iron was being complexed, whereas in the Baads flasks there was free ferrous iron. O-phenanthroline is a mono-acid base and in acid solutions ferrous iron can be replaced by hydrogen ion (Lea et al 1948):

$$\mathrm{Fe(Ph)_3^{2+} + 3H^+ \longrightarrow Fe^{2+} + 3PhH^+}$$

Ph = o-phenanthroline

The instability of the complex in acid solution explained the fact that the complex decomposed to a greater extent in the Baads case than in the Durham case where the solution was not so acidic. Also there was not so much iron present in the Durham case to be complexed.

However, the total iron and sulphate concentrations were considerably reduced compared to the control case and, considering that the flasks were effectively diluted at each sampling date so the effect of the initial neutralisation of the acid would be diminished, the reduction in the pyrite oxidation rate was probably not due to the raising of the pH, but actually due to the complexing of the ferrous iron.

Panacide Flasks

Panacide, like o-phenanthroline is also a basic compound, but its neutralisation effect was negligible shown by the rapid fall in pH in the Durham case (Fig 2.2.b). In the Durham flasks the acidity actually increased much more than in the Baads flasks (although it was always less than in the Baads case). In the Durham flasks the acidity, sulphate and iron levels all increased in the panacide flasks, although maintaining lower concentrations than in the control flasks, whereas in the Baads flasks they remained roughly constant. The initial higher pH of the Durham control flasks compared to the Baads flasks suggested that at least initially oxidation by oxygen alone was important in these flasks, as the pH was too high for the acidophilic bacteria to be active, and the ferric iron oxidation of pyrite only operates at lower pH values. The inhibition of pyrite oxidation by panacide is in agreement with that found by Le Roux et al.(1973).

Ferric Chloride Flasks

The addition of ferric chloride in the hydrochloric acid to the flasks obviously affected the pH and titratable acidity, as well as the iron concentration. Over the period the titratable acidity and iron concentration both decreased, probably due to the dilution of the flasks at each sampling date. The concentration of added iron and acid (ferric chloride plus hydrochloric acid) was much greater than that produced by pyrite oxidation in the control flasks (Figs 2.3 and 2.5), so the production of any iron and acid in the ferric chloride flasks due to pyrite oxidation would have been masked - the sampling method would just cause a gradual decrease in the iron and acid concentrations. The sulphate concentration in these flasks did increase - initially it was greater than in the control flasks, but by the end of

Figs 2.2-2.5 The Effect of Altering the Ferrous or Ferric Iron Concentration on the Release of the Oxidation Products of Pyrite.

Fig 2.2 Effect on pH

a. Baads Pyrite
b. Durham Pyrite

Fig 2.3 Effect on Titratable Acidity

a. Baads Pyrite - 1, 2 and 3 only (see key)
b. Durham Pyrite - 1, 2 and 3 only
c. Baads Pyrite - 4 and 5 only
d. Durham Pyrite - 4 and 5 only

Fig 2.4 Effect on Sulphate Concentration

a. Baads Pyrite
b. Durham Pyrite

Fig 2.5 Effect on Total Iron in Solution (not measured until day 19)

a. Baads Pyrite - 1, 2 and 3 only
b. Durham Pyrite - 1, 2 and 3 only
c. Baads Pyrite
d. Durham Pyrite

KEY

1 control
2 o-phenanthroline
3 panacide
4 0.5 g $FeCl_3$
5 2.5 g $FeCl_3$

Fig 2.2.a.

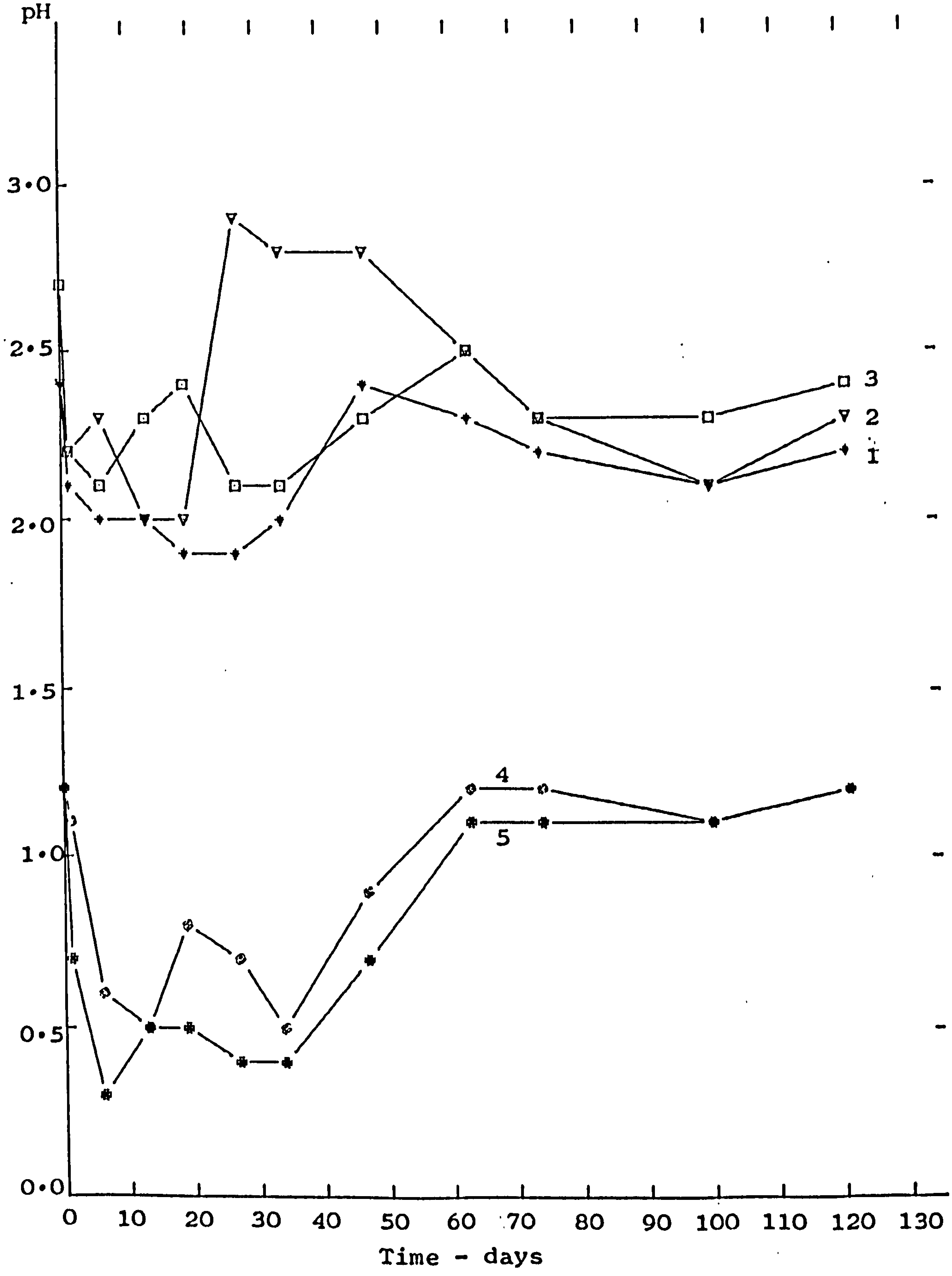

pH
3·0
2·5
2·0
1·5
1·0
0·5
0·0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
Time - days
3
2
1
4
5

Fig 2.2.b.

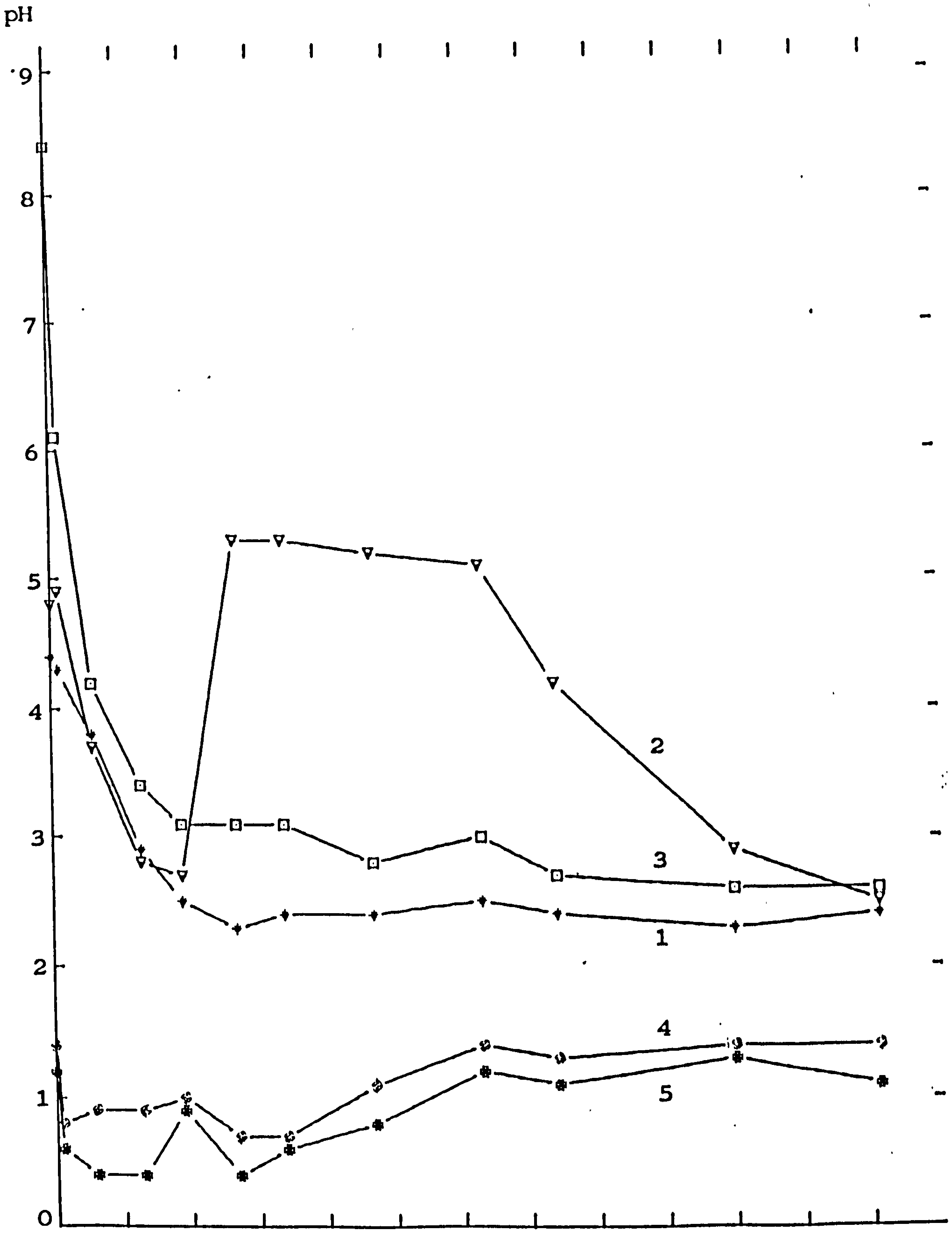
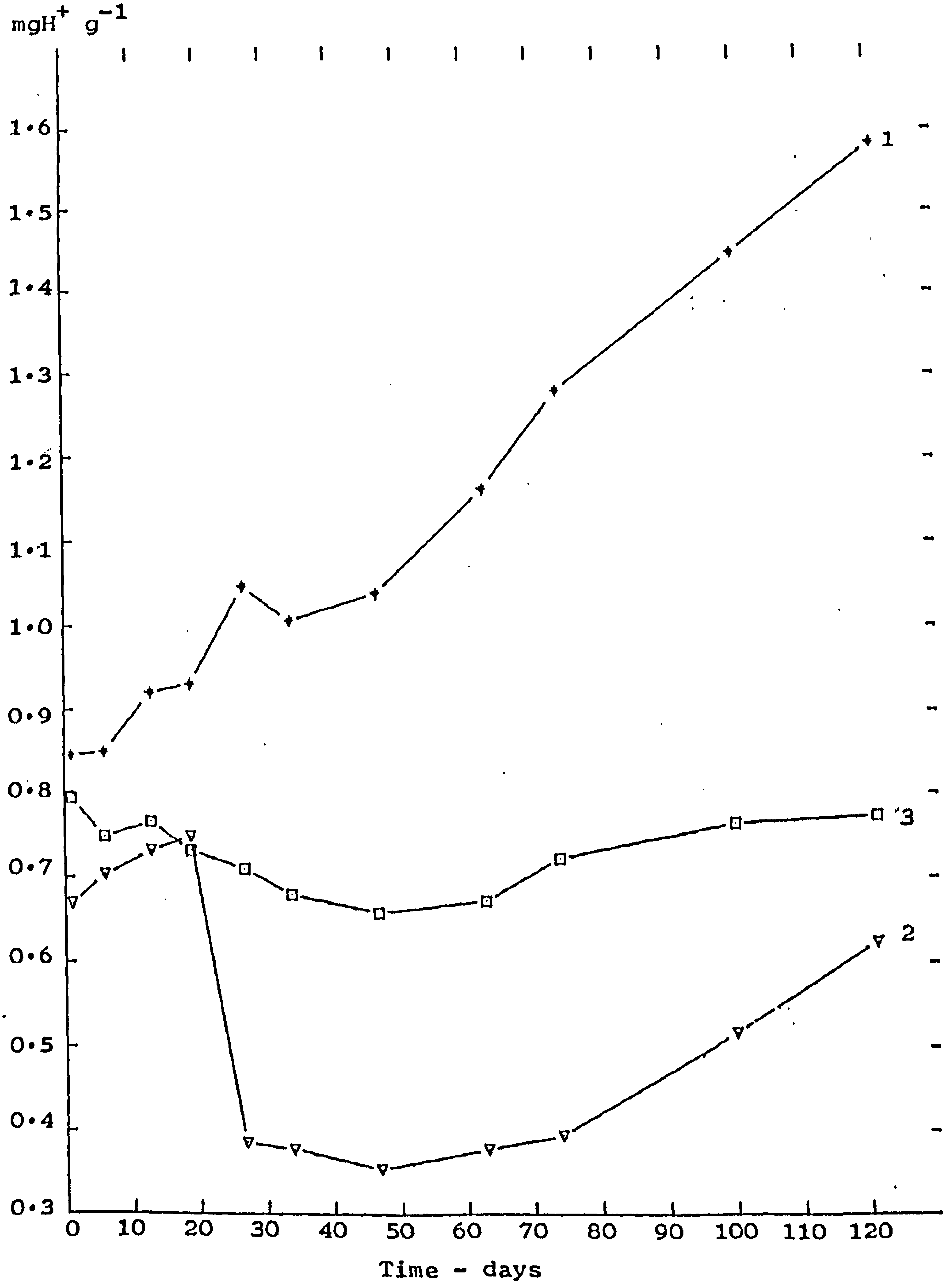

pH
9
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
Time - days
1
2
3
4
5

Fig 2.3.a.



mgH⁺ g⁻¹
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0
10
20
30
40
50
60
70
80
90
100
110
120
Time - days
1
2
3

Fig 2.3.b.

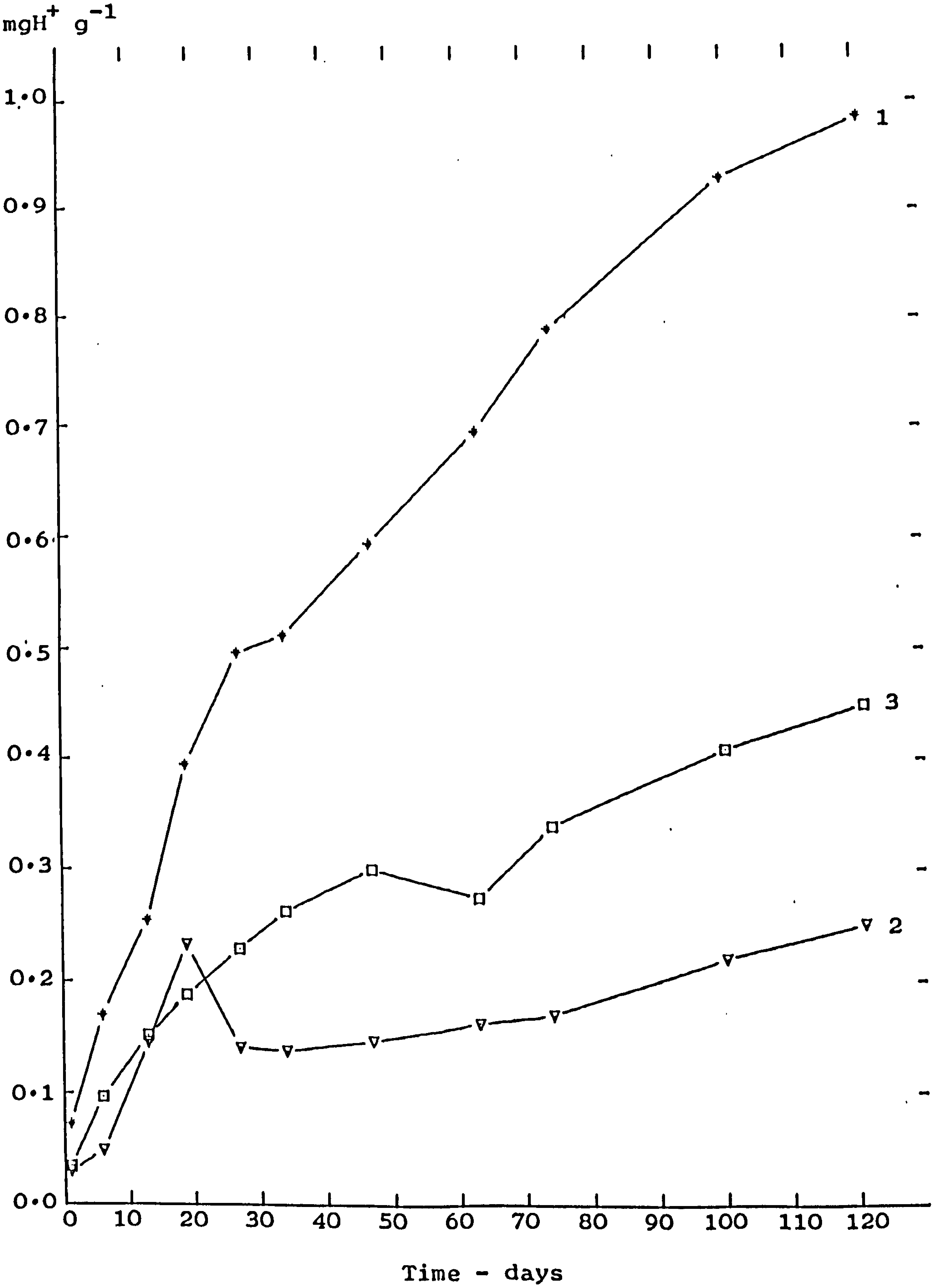

mgH$^+$ g^{-1}
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
0
10
20
30
40
50
60
70
80
90
100
110
120
Time - days
1
3
2

Fig 2.3.c.

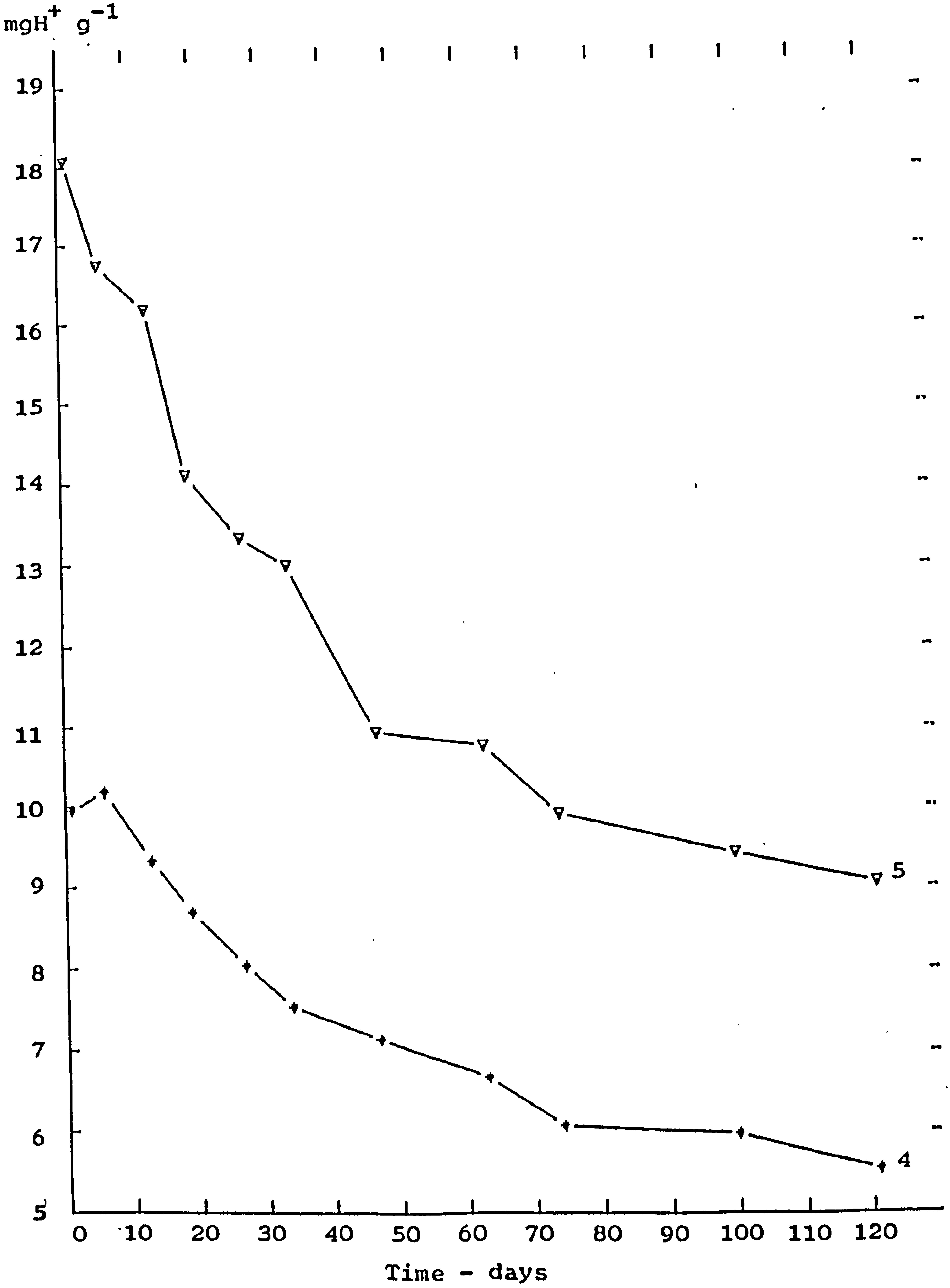

mgH$^+$ g^{-1}
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
0
10
20
30
40
50
60
70
80
90
100
110
120
Time - days
5
4

Fig 2.3.d.

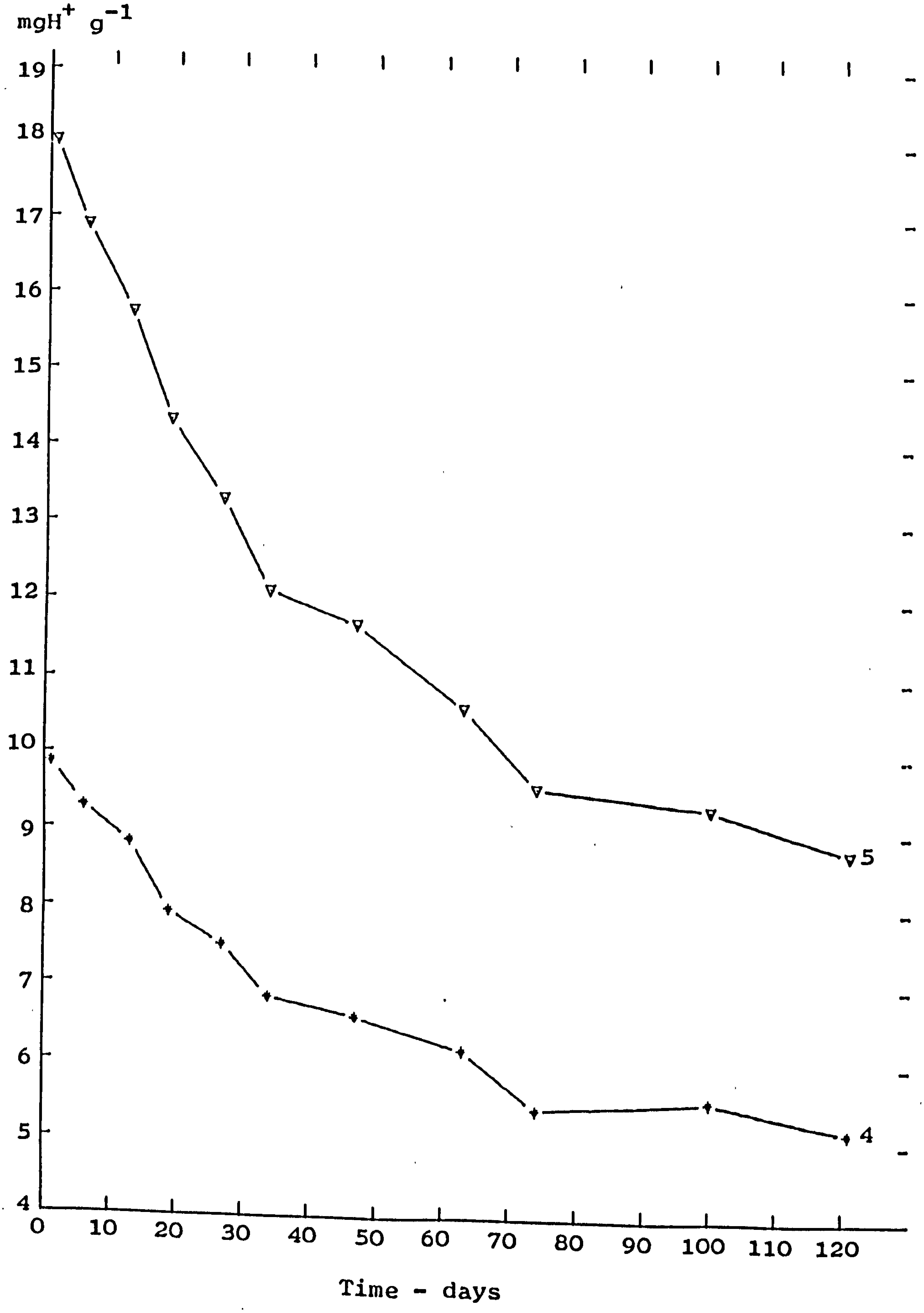

mgH$^+$ g^{-1}
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
0
10
20
30
40
50
60
70
80
90
100
110
120
Time - days
5
4

Fig 2.4.a.

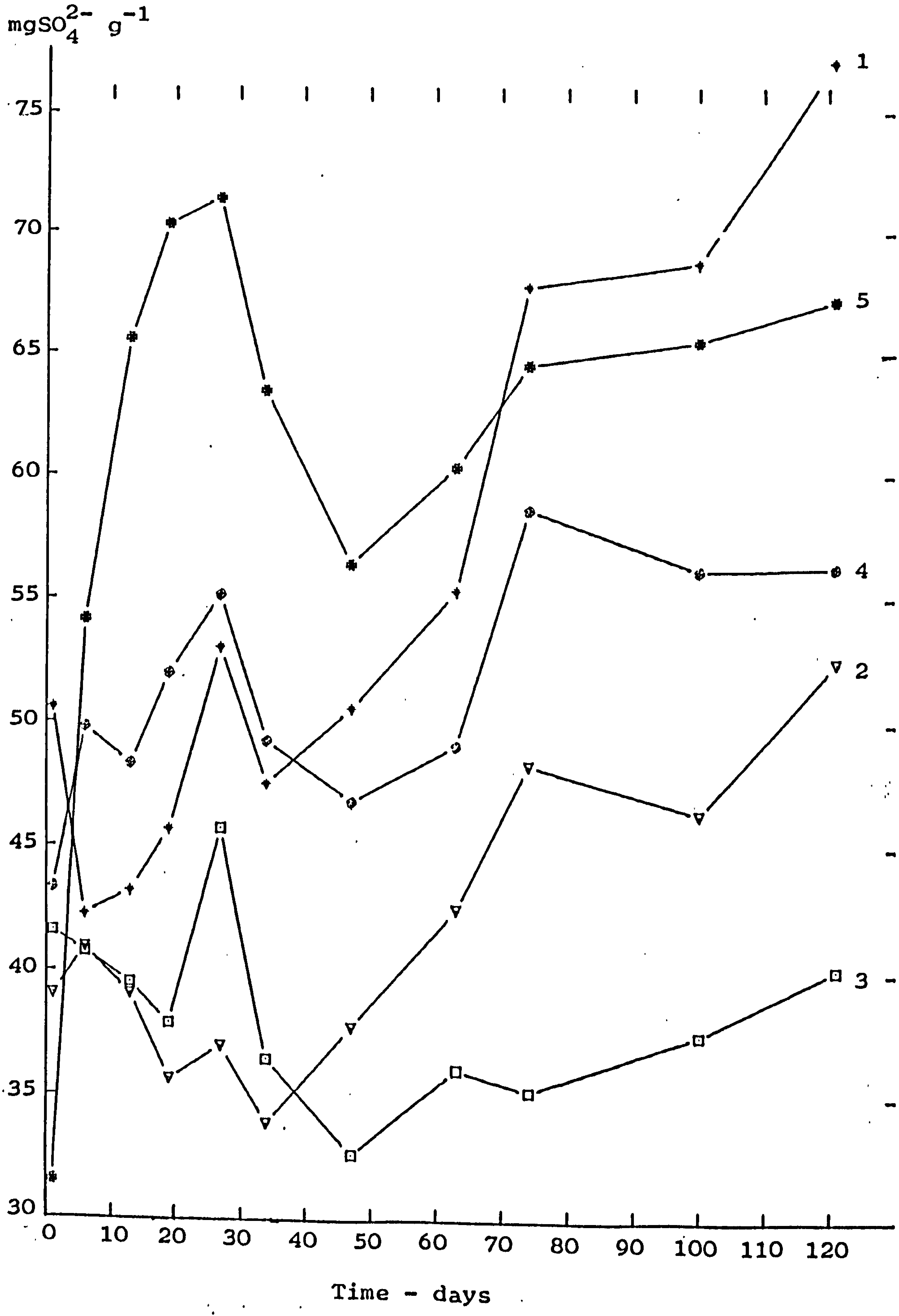

$mgSO_4^{2-}\ g^{-1}$
75
70
65
60
55
50
45
40
35
30
0
10
20
30
40
50
60
70
80
90
100
110
120
Time - days
1
5
4
2
3

Fig 2.4.b.

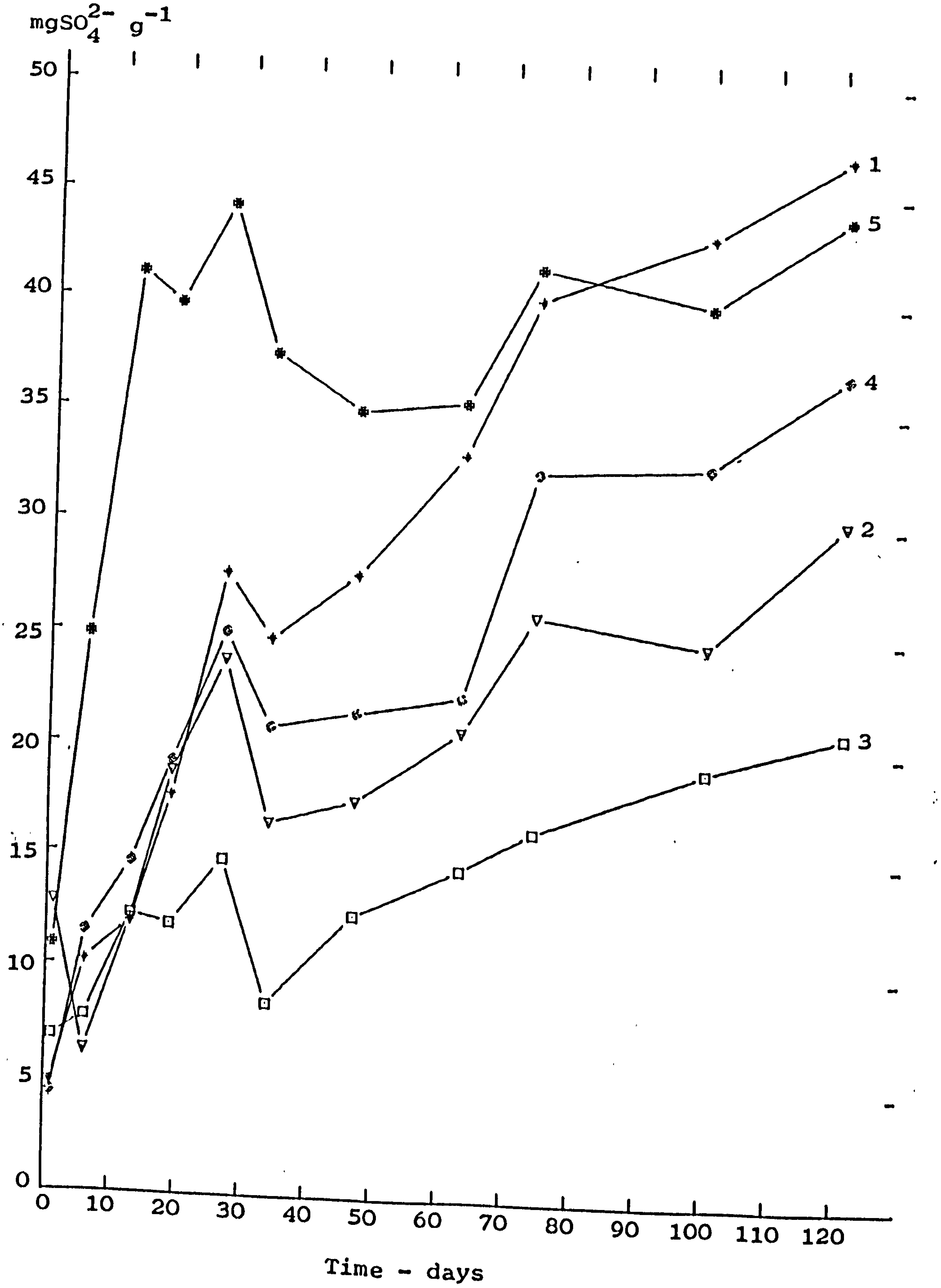

$mgSO_4^{2-}\ g^{-1}$
50
45
40
35
30
25
20
15
10
5
0
0
10
20
30
40
50
60
70
80
90
100
110
120
Time - days
1
5
4
2
3

Fig 2.5.a.

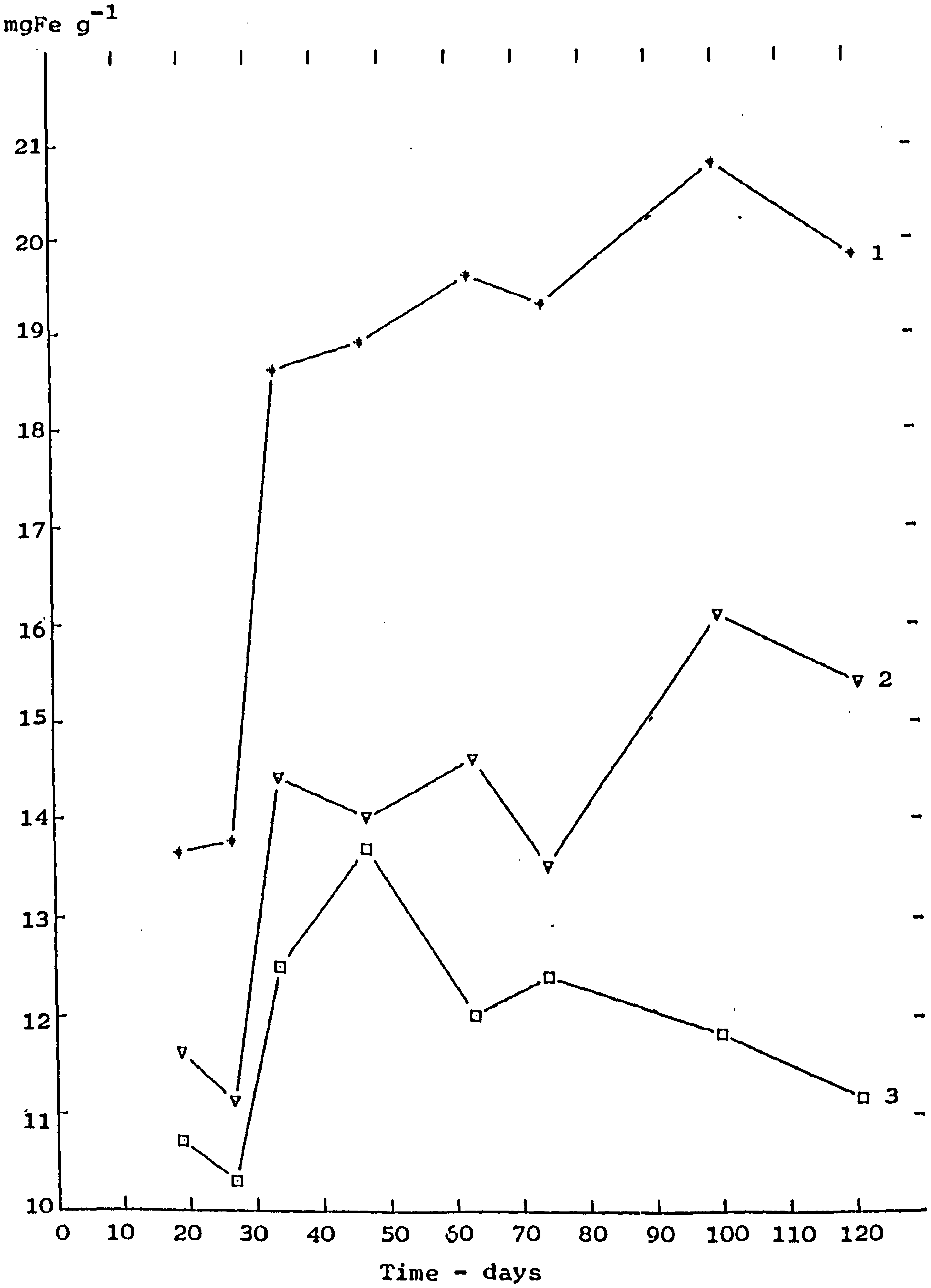

mgFe g^{-1}
21
20
19
18
17
16
15
14
13
12
11
10
0
10
20
30
40
50
60
70
80
90
100
110
120
Time - days
1
2
3

Fig 2.5.b.

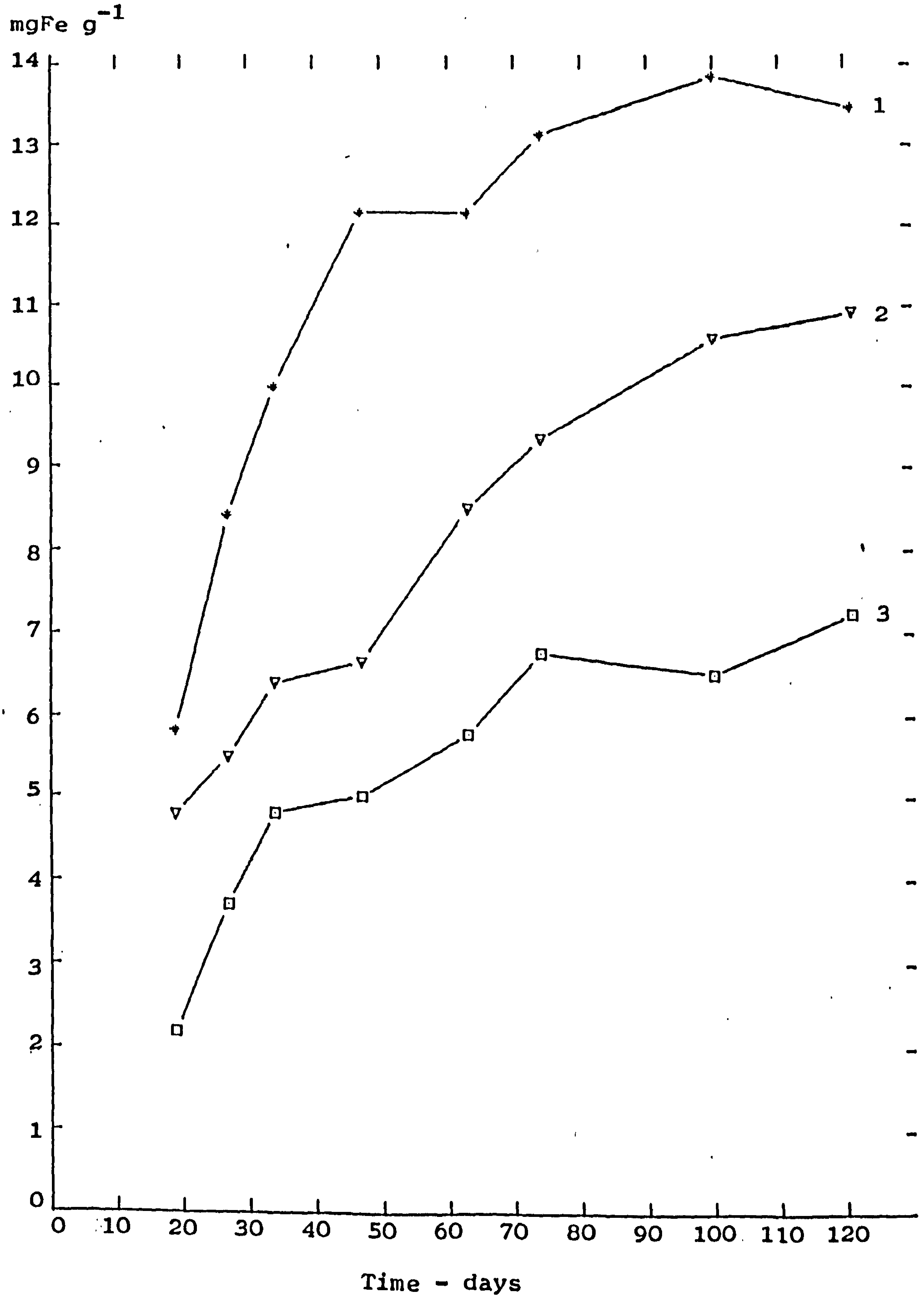

mgFe g^{-1}
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
Time - days
1
2
3

Fig 2.5.c.

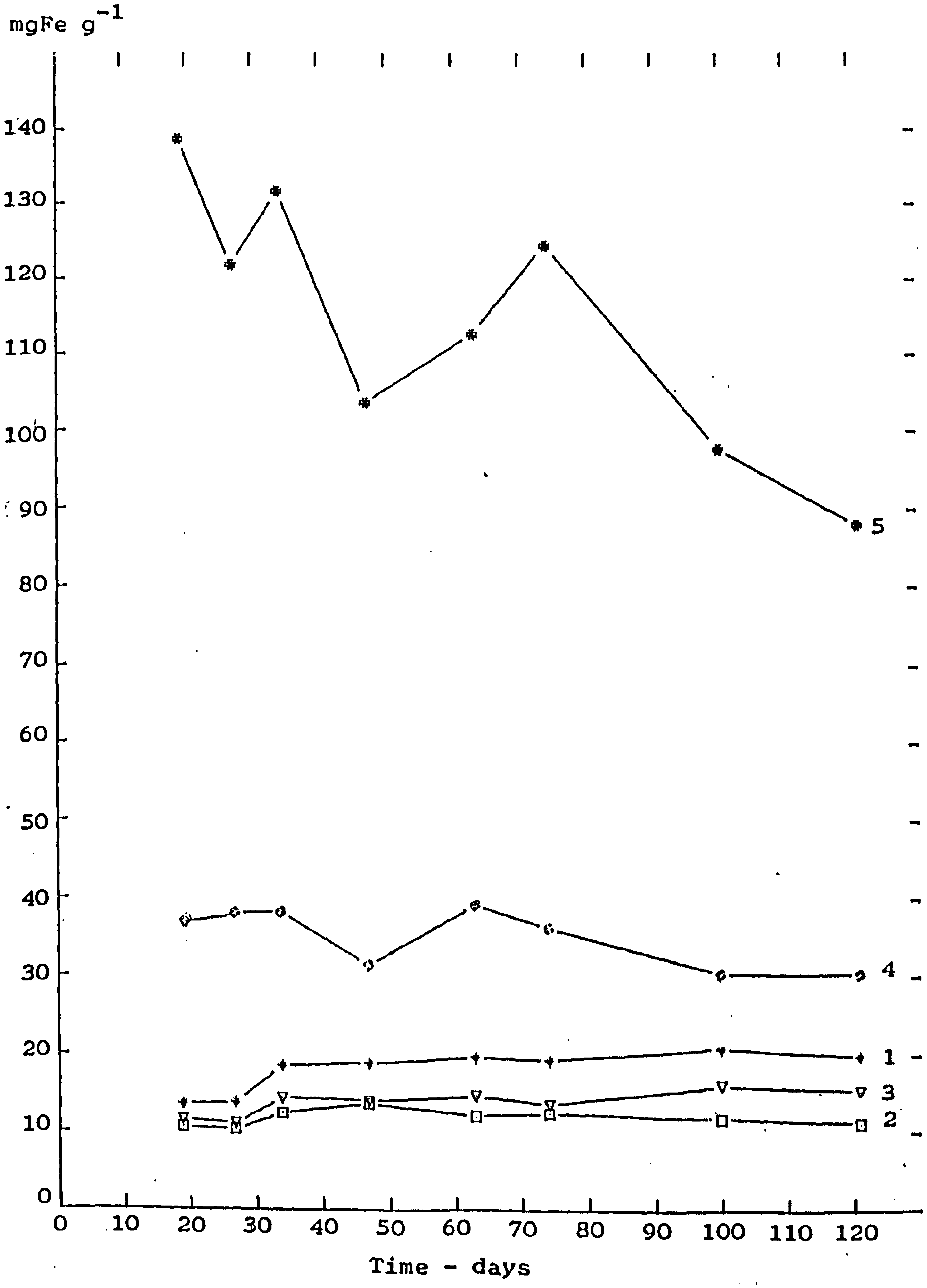
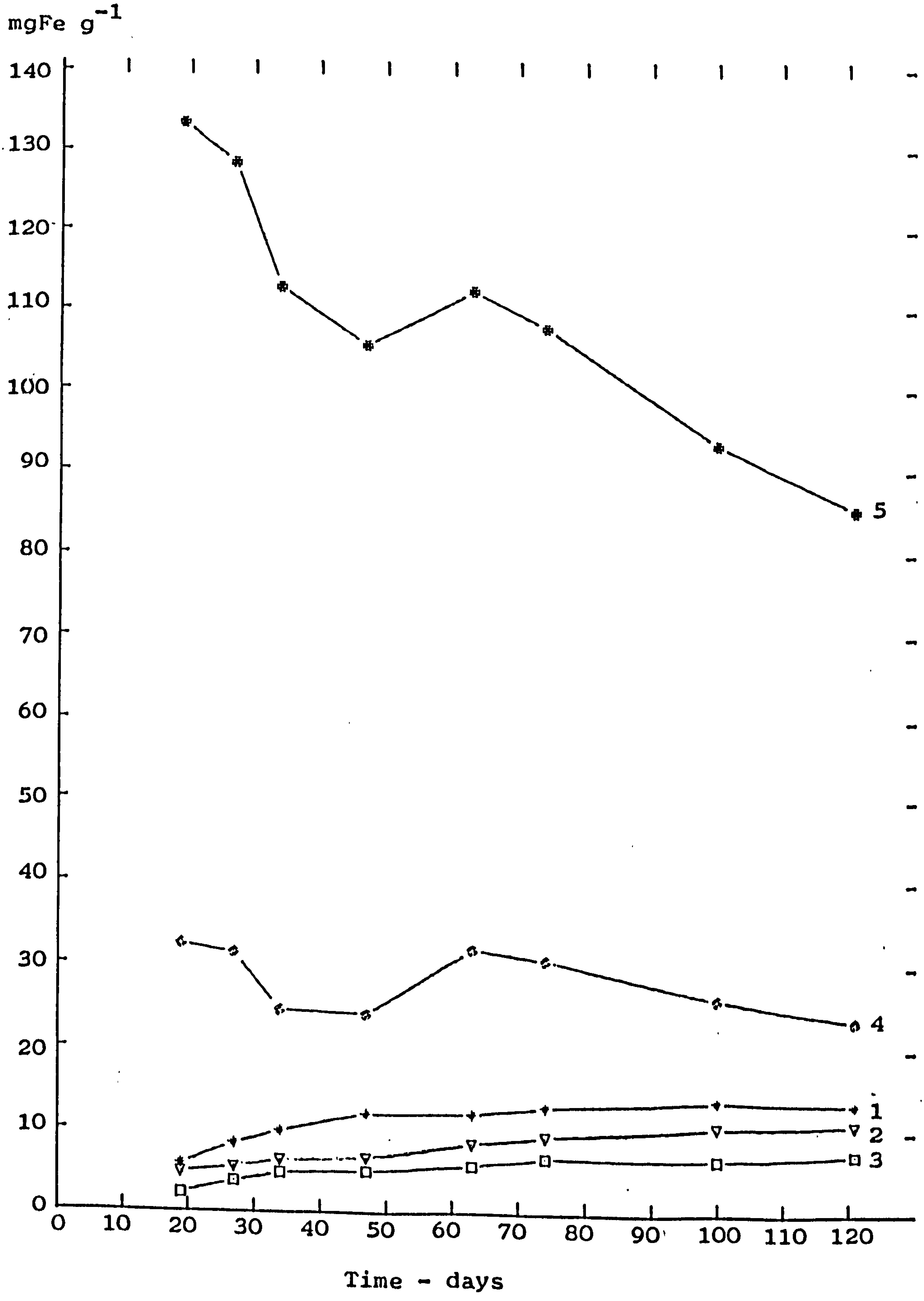

mgFe g^{-1}
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
110
120
Time - days
5
4
1
3
2

Fig 2.5.d.


mgFe g^{-1}
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
110
120
Time - days
5
4
1
2
3

the period it was less than in the control flasks.

Obviously the results from these flasks were rather confusing and it was difficult to ascertain the effect of added ferric iron on pyrite oxidation. However the conditions in the flasks may have had adverse effects on the oxidation. At these very low pH's, bacterial activity would probably be inhibited, stopping the oxidation of ferrous iron to ferric iron. Also the rate of pyrite oxidation is thought to be proportional to the pyrite surface area covered by ferric ions (Garrels and Thompson 1960) and at these high ferric ion concentrations the whole surface would be expected to be covered by ferric ions (the proportion of surface covered being proportional to the ratio of ferric to ferrous ions in solution). Therefore no increase in the rate would be expected. Le Roux et al.(1973) found a decrease in the rate of pyrite oxidation on increasing the iron content above 6 gl^{-1}. The concentration of iron was lower in these experiments than in those of Le Roux et al, but different concentrations of pyrite and totally different conditions were being used. Therefore, it is rather difficult to draw any direct conclusions from the addition of ferric chloride in these flasks.

Both panacide and o-phenanthroline decreased the rate of pyrite oxidation. The addition of ferric iron did not seem to increase the rate of pyrite oxidation. The panacide would have stopped the bacterial oxidation of ferrous to ferric iron and would have also stopped any bacterial oxidation of the pyrite itself, whilst the o-phenanthroline would have stopped the oxidation of ferrous to ferric iron by complexing the ferrous iron (to varying extents depending on the conditions). Therefore it was not clear whether the rate of pyrite oxidation was decreased due to the inhibition of the ferrous iron oxidation with the consequent reduction of pyrite oxidation by ferric iron, or whether it was also due to the inhibition of bacterial oxidation of the pyrite itself. Two further sets of experiments were performed to try to clarify the situation.

2.2.3 Effect of Different Concentrations of O-phenanthroline on the Oxidation of Pyrite

As shown in the last experiment, o-phenanthroline did not effectively reduce the rate of pyrite oxidation over a long period. If this is due to the complex being unstable in acid solution, as previously explained, then increasing concentrations of o-phenanthroline would be expected to be more effective at reducing the pyrite oxidation rate. A series of flasks was set up containing 0.5 g finely ground pyrite in 100 cm^3 of deionised water. The following quantities of o-phenanthroline were added to the flasks, each quantity being added to a quarter of the flasks: 0.05 g, 1 g and 2 g. The other flasks acted as the controls. This was done for both Baads and Durham pyrite. On each sampling date two flasks of each concentration of o-phenanthroline for both Baads and Durham were destroyed and the solution tested for acid, sulphate, ferrous and ferric iron. This overcame any possible dilution factor problems as encountered in the last experiment.

The results for both sets of flasks are presented in Tables A4 and A5 in the Appendix, but only the results for Baads are presented graphically, as the two sets of results showed similar trends. (Figs 2.6 (a, b, c)). Only ferrous iron results are presented as negligible amounts of ferric iron were detected. Ferrous iron was measured in the normal way even though there was o-phenanthroline already present. This may have affected the results slightly as the standards would not have had the excess o-phenanthroline present, but the results should not be too inaccurate for the present purposes. The amount of o-phenanthroline that would be needed to complex all the iron detected at any particular sampling time for both set of flasks is shown in Table A6 in the Appendix. These figures show that in the Baads case there was only enough o-phenanthroline present in the 0.2 g flasks (apart from initially in the 0.1 g case) to complex all the iron present and even this was not enough by the end of the period. For the Durham flasks the 0.2 g case was adequate throughout the study, 0.1 g was adequate for just under half the period and 0.05 g was adequate to complex all the iron present only initially. However, as already discussed, the ferrous - o-phenanthroline complex is unstable in acid conditions, so presumably the ferrous iron was not complexed completely for as long as these figures suggested. The amount of iron produced in the Baads flasks was very similar in all cases. Initially in the Durham flasks, the amount of iron produced in the flasks containing the o-phenanthroline was less than in the control flasks, but by the end of the period the iron concentrations in all the flasks were similar. This supports the fact that the complex formed was unstable in acid solutions, especially in the more acidic Baads flasks. The sulphate levels in the Baads flasks were reduced initially compared to the control case, suggesting that at least some of the ferrous iron was being complexed by the o-phenanthroline, thus slowing the rate of oxidation of the pyrite. In the Durham case the sulphate concentration is effectively reduced throughout the period. The titratable acidity is lowered in both Baads and Durham cases in the o-phenanthroline flasks compared to the control cases.

These results support the previous argument that the o-phenanthroline does reduce the rate of pyrite oxidation, presumably by slowing

Fig 2.6 Effect of Different Concentrations of O-phenanthroline on the Rate of Oxidation of Baads Pyrite.

Fig 2.6.a Production of Ferrous Iron.

Fig 2.6.b Production of Sulphate.

Fig 2.6.c Production of Acid.

KEY

1 control
2 0.05 g o-phenanthroline
3 0.1 g o-phenanthroline
4 0.2 g o-phenanthroline.

Fig 2.6.a.

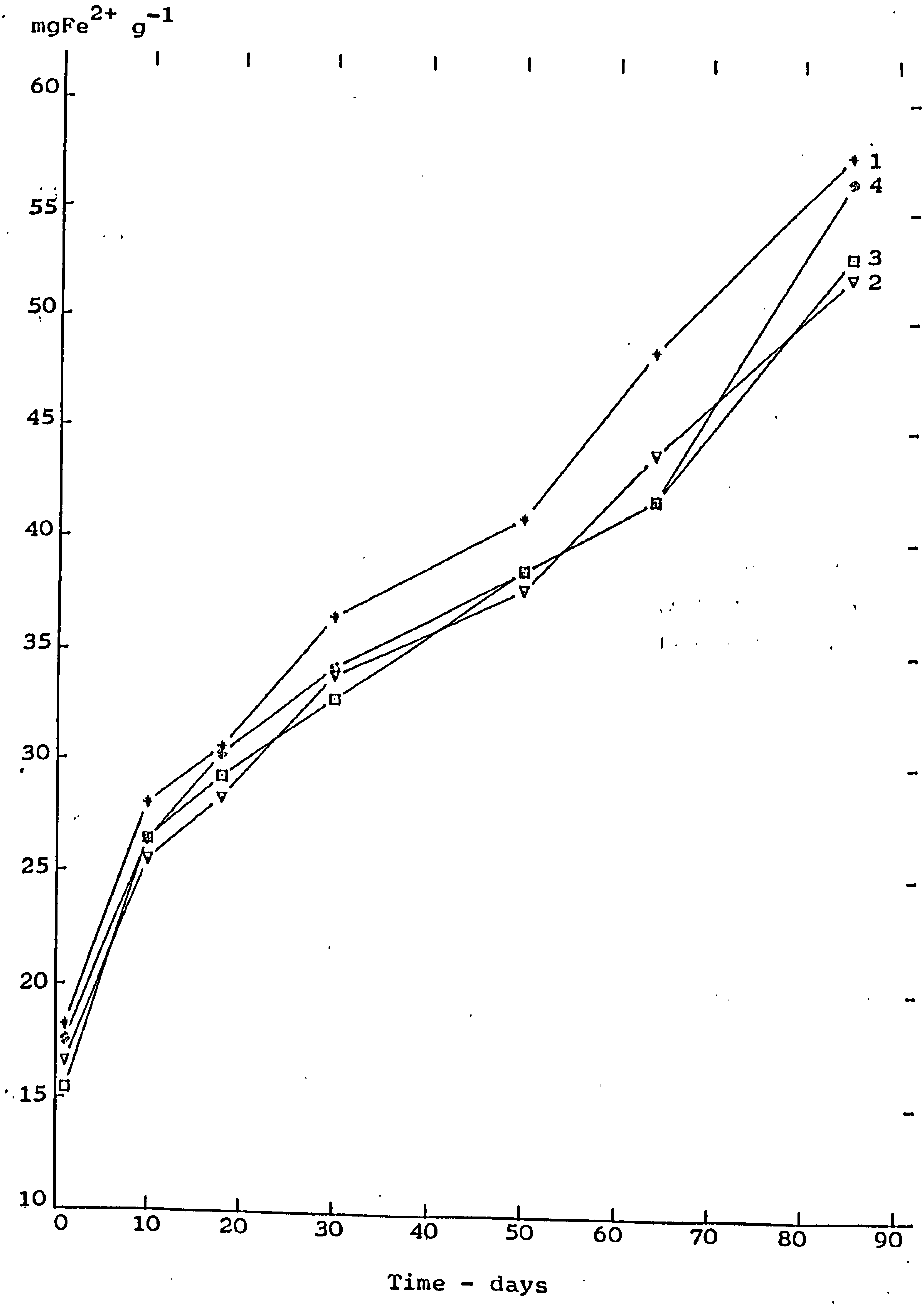

mgFe^{2+} g^{-1}
60
55
50
45
40
35
30
25
20
15
10
0
10
20
30
40
50
60
70
80
90
Time - days
1
4
3
2

Fig 2.6.b.

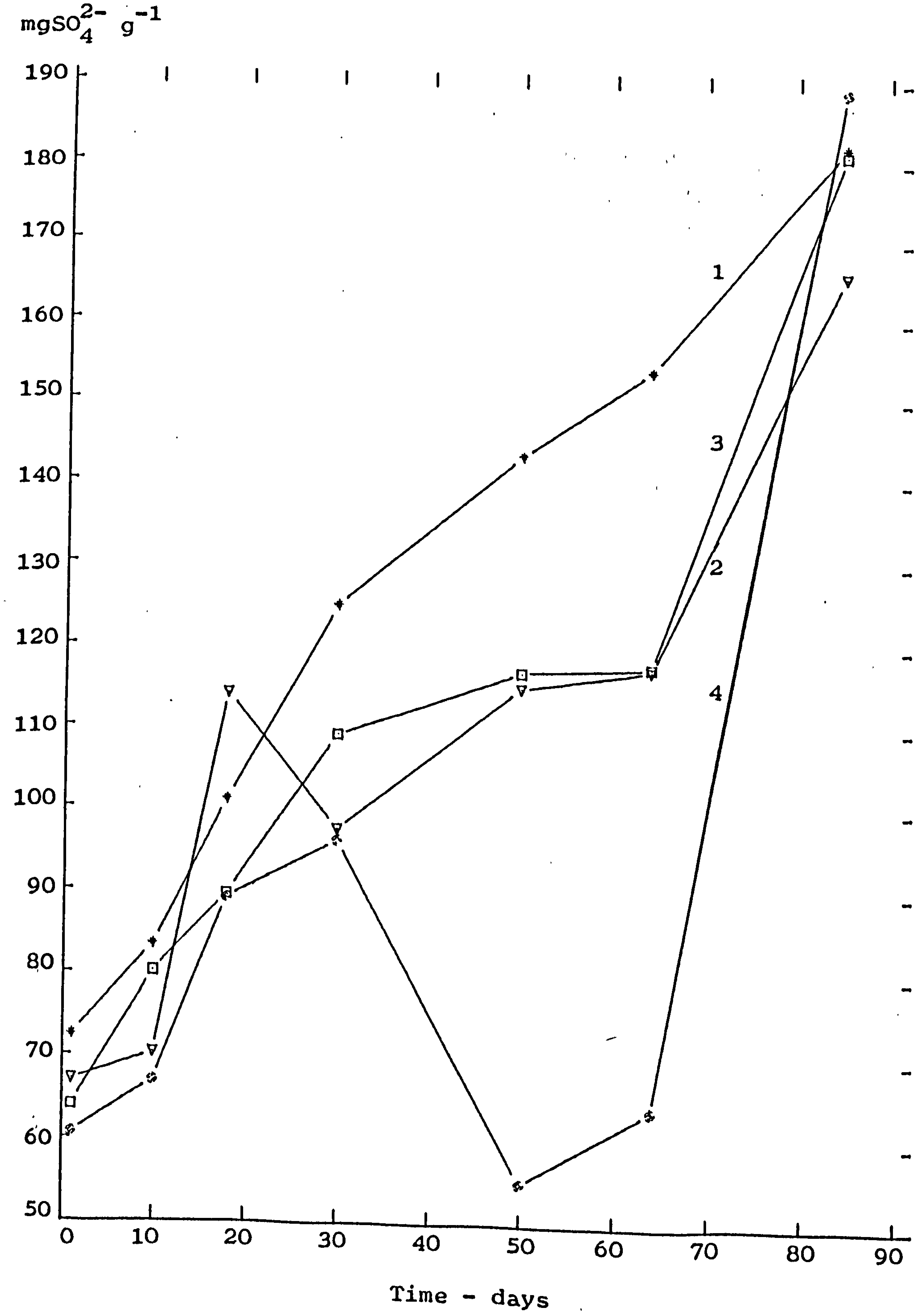
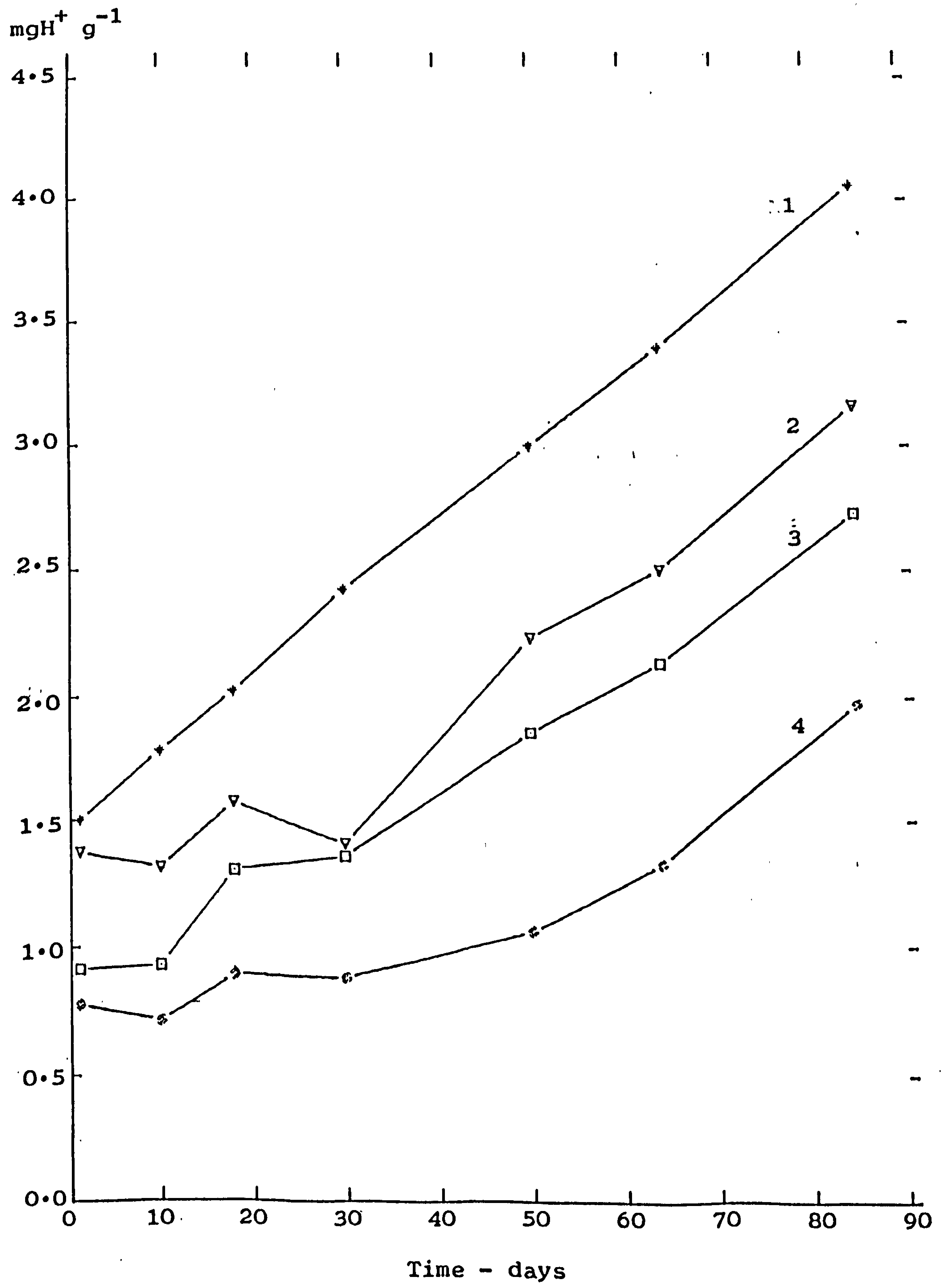

$mgSO_4^{2-}\ g^{-1}$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
0
10
20
30
40
50
60
70
80
90
Time - days
1
3
2
4

Fig 2.6.c.


mgH$^+$ g^{-1}
4·5
4·0
3·5
3·0
2·5
2·0
1·5
1·0
0·5
0·0
0
10
20
30
40
50
60
70
80
90
Time - days
1
2
3
4

down the rate of oxidation of the ferrous iron. However it is not very effective as its stability is decreased in acid solution.

2.2.4 Rate of Ferrous Iron Oxidation in Different Solutions

This experiment was performed to confirm the effect of o-phenanthroline and panacide on ferrous iron oxidation.

The first set of flasks consisted of solutions of ferrous ammonium sulphate (100 cm^3) , buffered at different pH's using acetic acid/sodium acetate and phthalic acid/potassium hydrogen phthalate buffers. The pH's used were 2.3, 2.6, 3.0, 3.4, 3.6, (phthalic acid/ phthalate) and 3.4, 4.0, 5.0, 5.8, (acetic acid/acetate). The solutions from the control flasks of the last experiments were also used. They were diluted and the rate of ferrous iron oxidation noted. The pH of the Baads solution was 2.9 and that of the Durham solution was 3.4. Each flask was duplicated.

The second set of flasks also consisted of solutions isolated from the control flasks of the previous experiment. They were diluted to give concentrations of 90 and 50 $mgFe^{2+}l^{-1}$ for Baads and Durham solutions respectively. To duplicate flasks of the Baads and Durham solutions (50 cm^3), 0.1 g o-phenanthroline was added (this would have been adequate to complex all the ferrous iron present), and to other duplicate flasks for both solutions 0.025 cm^3 of panacide was added. The initial pH of these solutions was for Baads, 4.9 (o-phenanthroline), 3.0 (panacide) and 2.8 (control) and for Durham solutions was 5.6 (o-phenanthroline), 4.5 (panacide) and 3.0 (control).

A selection of the results are shown in Figs 2.7 (a, b), the full results being in Tables A7 and A8 in the Appendix.

Below pH 3, ferrous iron in sterile solution did not oxidise, Fig 2.7 Rate of Ferrous Iron Oxidation

Fig 2.7.a Oxidation of Ferrous Iron Solutions Buffered to Different pH's Compared to that of Ferrous Iron Solutions Isolated from Baads Pyrite and Durham Pyrite (pH 2.9 and 3.4 respectively).

KEY

1 Baads solution

2 Durham solution

3 ferrous iron solution buffered to pH 3.0

4 ferrous iron solution buffered to pH 4.0

5 ferrous iron solution buffered to pH 5.0

Fig 2.7.b Effect of O-phenanthroline and Panacide on Oxidation of Ferrous Iron Solutions Isolated from Baads and Durham Pyrite.

KEY

1 Baads solution - control

1P Baads solution + o-phenanthroline and Baads solution + panacide

2 Durham solution - control

2P Durham solution + o-phenanthroline and Durham solution + panacide.

Fig 2.7.a.

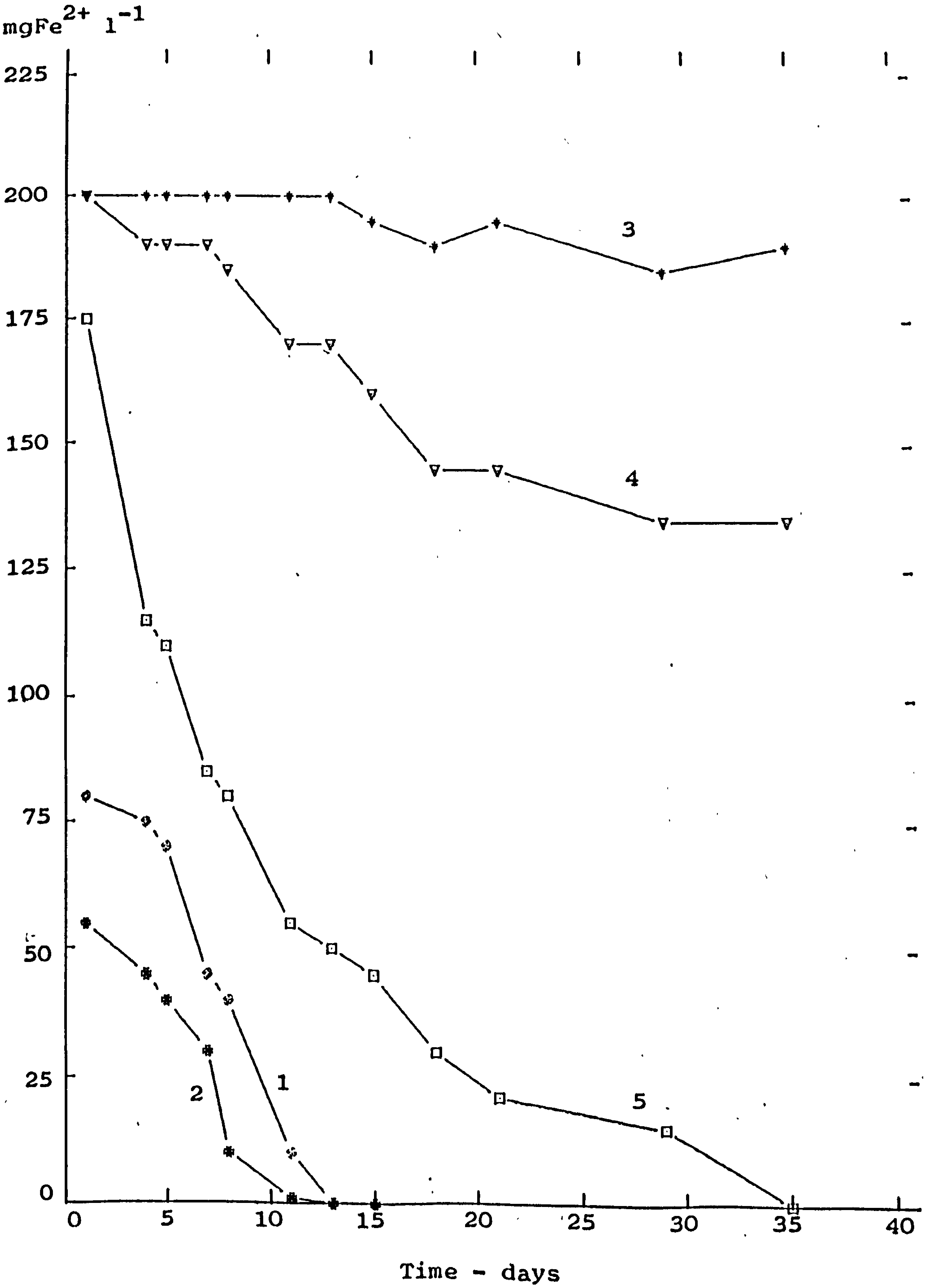
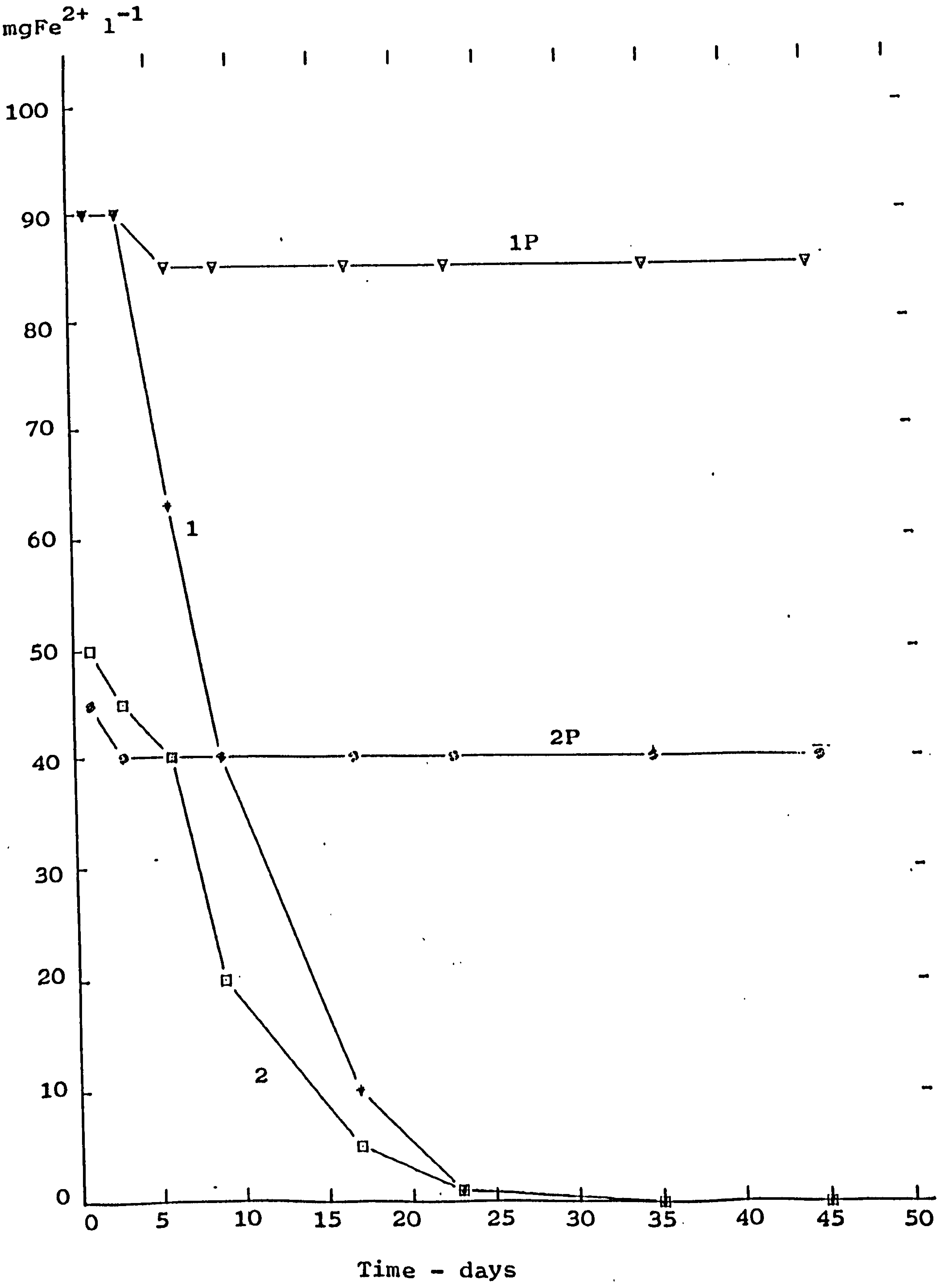

mgFe^{2+} l^{-1}
225
200
175
150
125
100
75
50
25
0
0
5
10
15
20
25
30
35
40
Time - days
1
2
3
4
5

Fig 2.7.b.


mgFe^{2+} l^{-1}
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
40
45
50
Time - days
1P
1
2P
2

at pH 4 it oxidised quite slowly, whereas at pH 5 it oxidised rapidly (Fig 2.7.a). The results for the intermediate pH's fitted into this scheme. This is in agreement with previous work (Singer and Stumm 1970). However the ferrous iron isolated from the pyrite flasks oxidised rapidly, which showed that it must be catalysed bacterially, presumably by Thiobacillus ferrooxidans. The second set of flasks show that both panacide and o-phenanthroline were capable of stopping the bacterial oxidation of ferrous iron (Fig 2.7.b).

From all the results presented so far various conclusions can be drawn. The ferrous iron produced during the oxidation of pyrite must be oxidised to ferric iron which then rapidly oxidises more pyrite, the bacterial oxidation of the ferrous iron being slower than the oxidation of the pyrite by ferric iron, which explains the negligible amounts of ferric iron in solution. Other studies have found ferric iron in solution when lower concentrations of pyrite are used (for example, Bloomfield 1972) and this will also be demonstrated in the next experiment. Slowing the oxidation of the ferrous iron reduced the rate of pyrite oxidation, as demonstrated by the effect of o-phenanthroline and panacide. It could be argued that the panacide is also stopping the bacterial oxidation of pyrite itself, and this cannot be conclusively disproved. However as ferric iron will obviously be produced in solution due to the oxidation of the ferrous iron, then the ferric ion must be oxidising more pyrite to explain its disappearance (the pH of the solutions is too low to allow precipitation of ferric iron). It would seem probable that the oxidation by ferric iron is more important than any possible bacterial pyrite oxidation.

2.2.5 Amount of Acid, Iron and Sulphate Produced by Pyrite Oxidation

In this study the amounts of acid, iron and sulphate produced from different samples and concentrations of pyrite were compared. The ratio of the different products was then compared to the theoretical ratios.

Three different sets of flasks were compared - one set contained Baads pyrite (71% FeS_2), another set Durham pyrite (64% FeS_2) (size less than 150 µm, approx 0.5 g accurately weighed for each flask) and the other set contained Baads pyrite (less than 150 µm) mixed with spoil (less than 2 mm) to give approximately 3.5% FeS_2 (these flasks contained 5 g of material). Each flask had 50 cm^3 of deionised water added to it. At intervals (approx. every three months) four of each set of flasks were destroyed and the solutions tested for acid, total iron, ferrous iron and sulphate concentrations.

Only the final set of results are presented as the results for each testing date showed the same trends. The ratio of mmoles produced for SO_4^{2-} : H^+ : Fe (Table 2.2) corresponded quite closely to 2:4:1 as predicted by the equation:

$$FeS_2 + 15/4\ O_2(aq) + H_2O(l) \longrightarrow Fe(OH)_3(s) + 2H_2SO_4(aq)$$

In these flasks the pH of the solution was too low to allow the precipitation of the ferric ion, calculated from the solubility product of:

$$[Fe][OH^-]^3 = 6.0 \times 10^{-38}$$

The addition of alkali to measure the titratable acidity obviously caused the precipitation of the ferric ion and therefore these results did not reflect the situation in the flasks, where the iron was still

	Flask	Total mmoles Produced			Ratio of mmoles Produced			pH of Solution	mmoles H^+ (from pH)	$gFeS_2$ Oxidised (from Fe in solution)
		SO_4^{2-}	H^+	Fe	SO_4^{2-}	H^+	Fe			
Baads Pyrite	1	4.14	8.6	2.23	1.4	3.8	1.0	1.8	0.79	0.268
	2	4.12	9.4	2.39	1.7	3.9	1.0	1.8	0.74	0.287
	3	2.96	7.8	2.08	1.9	3.8	1.0	1.8	0.84	0.250
	4	4.25	7.8	2.09	2.0	3.7	1.0	1.8	0.95	0.251
Durham Pyrite	1	3.48	6.4	1.70	2.0	3.8	1.0	1.9	0.63	0.204
	2	3.50	7.1	1.64	2.1	4.3	1.0	1.9	0.58	0.197
	3	3.49	6.8	1.57	2.2	4.3	1.0	1.9	0.55	0.188
	4	3.15	6.1	1.64	1.9	3.7	1.0	1.9	0.64	0.197
Baads Spoil	1	2.68	6.6	1.45	1.8	4.6	1.0	1.8	0.46	0.174
	2	2.83	6.5	1.44	2.0	4.5	1.0	1.8	0.55	0.173
	3	2.90	6.8	1.58	1.8	4.3	1.0	1.8	0.54	0.190
	4	3.45	7.7	1.69	2.0	4.6	1.0	1.8	0.60	0.203

mmoles H^+ calculated from the pH is different for flasks with the same pH as the total amount of solution in each flask varied slightly by this final sampling date.

Baads Pyrite	Initial concentration 71% FeS_2	16 month incubation
Durham Pyrite	Initial concentration 64% FeS_2	16 month incubation
Baads Spoil	Initial concentration 3.5%FeS_2	8 month incubation

Table 2.2 Production of Acid, Iron and Sulphate from Three Pyrite Samples

in solution. Most of the acid present is hidden acid - the production of the acid occurring upon the precipitation of ferric iron. This explains the vast discrepancy between mmoles H^+ calculated from the pH of the solution and that calculated from the titration of the solution with sodium hydroxide. If the oxidation of pyrite occurs by ferric iron thus:

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

then 16 moles of H^+ are produced per mole of pyrite oxidised. However the oxidation of the ferrous iron consumes acid:

$$Fe^{2+} + 1/2\ O_2 + H^+ \longrightarrow Fe^{3+} + 1/2\ H_2O$$

If the above two reactions are combined then only 1 mole of acid is produced per mole of pyrite oxidised (assuming that all the ferrous iron is reoxidised to ferric iron). It is only upon the precipitation of ferric iron that greater quantities of acid are produced:

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+$$

This ultimately produces 4 moles of acid per mole of pyrite oxidised. The same kind of argument can be applied to the oxidation of pyrite by oxygen alone, but as already explained this is a much slower reaction, so that the amount of acid produced in a specific time will be much less than when the ferric iron oxidation of pyrite predominates.

In the higher concentration Baads and Durham pyrite flasks the iron was initially present as ferrous iron, but by the end of the period there was more ferric iron than ferrous iron present. In the lower concentration Baads pyrite flasks the iron was present predominantly as ferric iron throughout the period (apart from the initial sampling)- Fig 2.8. This confirmed that the bacterial

Fig 2.8 Fraction of Iron Present as Ferrous Iron in Long-Term Incubation Experiment.

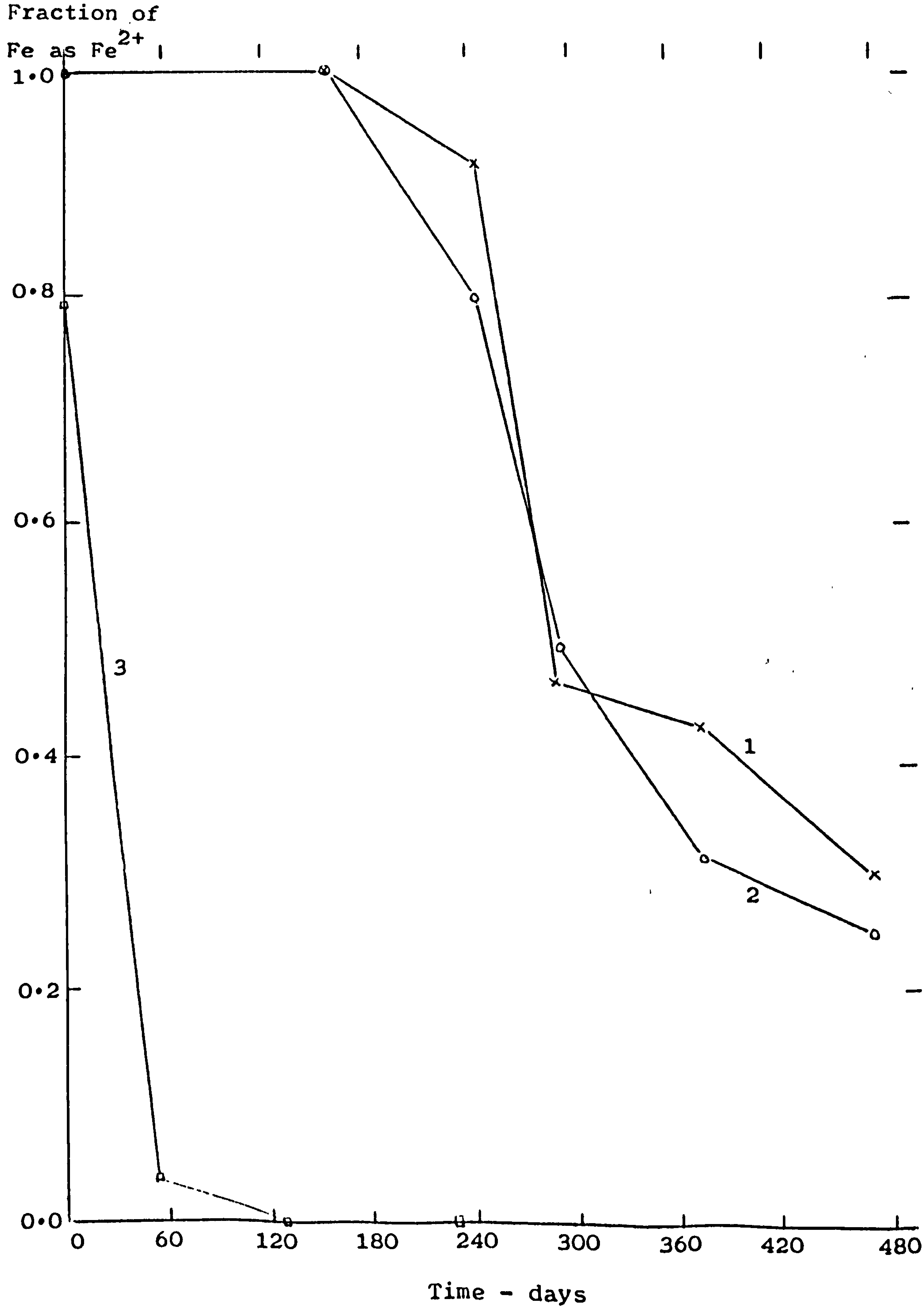
KEY

1 Baads pyrite - initial concentration 71% FeS_2

2 Durham pyrite - initial concentration 64% FeS_2

3 Baads pyrite - initial concentration 3.5% FeS_2

Fig 2.8.


Fraction of
Fe as Fe^{2+}
1·0
0·8
0·6
0·4
0·2
0·0
0
60
120
180
240
300
360
420
480
Time - days
1
2
3

oxidation of ferrous iron to ferric iron was faster than the rate of oxidation of pyrite by ferric iron, except at high pyrite concentrations (van Breemen 1973). Obviously in a field situation precipitation of some of the ferric iron would occur, especially if the iron was leached away from the immediate zone of pyrite oxidation to an area of higher pH.

Although pyrite determinations were done on the flasks when they were destroyed, the calculated amount was not accurate as the weight of sample used in the calculation was the original weight, which was obviously greater than the weight of sample left in the flask. Therefore, as none of the iron had precipitated, the weight of pyrite oxidised was calculated from the iron concentration in the flasks. In the last six months of the sixteen month period there was very little change in the amount of products in the high concentration pyrite (Baads and Durham) flasks. The amount of oxidation products in the lower concentration pyrite Baads flasks increased throughout the period, but these flasks were only kept for eight months in all. Le Roux et al. (1973) found no increase in the iron concentration above certain iron concentrations (6 g l^{-1}), and it would seem that this also happened in the high concentration Baads and Durham pyrite flasks in this experiment with no appreciable pyrite oxidation occurring after the first ten months. The amount of pyrite oxidised was greatest in the high concentration Baads pyrite flasks and lowest in the lowest concentration Baads pyrite flasks. This indicates that the amount of pyrite oxidised in a certain period depends on the initial concentration of pyrite.

These results can be combined with the previous results to give the overall picture of pyrite oxidation. If the pH is high enough for the iron to precipitate, 4 moles of acid are produced per mole of pyrite oxidised. This will tend to be the normal situation in the field. The ferric iron oxidation of pyrite appears to be the most important pathway:

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

The oxidation of ferrous iron to ferric iron must be mediated by bacteria, due to the low pH's found in areas where pyrite oxidation is occurring.

2.3 Inhibition of Pyrite Oxidation

If the ferric iron oxidation of pyrite can be stopped, then the amount of acid produced can be reduced as the air oxidation of pyrite is very slow. The acid produced by this reaction could be coped with relatively easily, either by natural leaching or by small additions of lime. It has already been shown that it is possible to inhibit the pyrite oxidation by interfering with the role of ferric iron in the oxidation.

Lime is traditionally used to treat the spoil or soil where pyrite oxidation has occurred. The addition of lime obviously causes an increase in the pH, which would stop the ferric iron oxidation of pyrite, but the pH does tend to decrease leading to consequent acid regression problems (Doubleday 1974, Costigan et al. 1981). In this project lime was used in conjunction with other materials to treat pyritic spoil - the aim was that the lime would increase the pH, whilst the amendments would hopefully inhibit the ferric iron oxidation of pyrite, leading to a pH maintained at a reasonable level for a longer period than when lime is used alone. The effect of two different rates of lime was studied (that required to raise the pH of the spoil to 6.0

and half this amount) in conjunction with the amendments as well as the effect of the amendments alone.

2.3.1 Limed Flasks

Baads pyrite (less than 150 µm) was mixed with spoil (less than 2 mm) to give a pyrite content of about 4%. 10 g of this was used with 200 cm^3 of deionised water for each flask. The lime requirement was calculated by shaking different amounts of lime water with the spoil mixture. No account was taken of the potential acidity due to the presence of the pyrite. The amount of lime required to raise the pH to 6.0 was used as the highest liming rate, half this rate was used and a control set of zero lime flasks was also used. Panacide and o-phenanthroline were used (as in the previous flask experiments). Phosphate was also used, being added in a neutral form as well as an acid form - phosphate should precipitate ferric iron. Citrate was also used, to complex ferric iron. The amount of these substances used was estimated in the absence of a better method, by calculating the amount of each chemical that would be required to complex or precipitate the iron that would be released upon the oxidation of a certain percentage of the pyrite. The additions used are listed below, each liming rate being used with each addition, each treatment being duplicated:

Lime

Full rate 0.8 g hydrated $Ca(OH)_2$ per 100 g of spoil

Half rate 0.4 g hydrated $Ca(OH)_2$ per 100 g of spoil

Zero rate

Additions (per flask)

Zero (control)

o.5 g o-phenanthroline

0.1 cm^3 panacide

0.5 g $NaH_2PO_42H_2O$ sodium dihydrogen phosphate

0.5 g Na_2HPO_4 disodium hydrogen phosphate

0.1 g $Na_3C_6H_5O_72H_2O$ trisodium citrate

The full results are in Table A9 in the Appendix. Only the results for the zero and full lime cases are presented graphically (Figs 2.9 and 2.10) as the half lime results tended to be intermediate between the two. The citrate flasks were not sampled on the first day as the solution was too cloudy to obtain a sample.

Zero Lime Flasks (Fig 2.9)

In the zero lime flasks the effectiveness of o-phenanthroline at reducing the iron, acid and sulphate concentrations decreased with time, as found before. The panacide was again more effective at reducing the pyrite oxidation rate. Sodium dihydrogen phosphate initially increased the acid concentration due to its own acidity, but this then decreased with time. Although the sulphate concentration increased with time in these flasks (although it was always less than the control case) the iron concentration was negligible. The other phosphate flasks and the citrate flasks had a considerably increased pH (they are both alkaline materials). This by itself will obviously affect the pyrite oxidation rate so it was difficult in these flasks to distinguish between the effect of increased pH and the effect of the added chemicals on the pyrite oxidation rate.

Full Lime Flasks (Fig 2.10)

Lime by itself did not succeed in maintaining the pH, whereas the addition of o-phenanthroline and panacide did maintain the pH (o-phenanthroline was effective until the last sampling date). Very little iron was produced in the panacide flasks, but the iron concentration in the o-phenanthroline was greater than in the control case which is not the result that would be expected. The sulphate contentrations are all too closely grouped to make any clear distinction between them. Even though the addition of the sodium dihydrogen phosphate caused an initial decrease in the pH, the final pH was higher than in the control case and the titratable acidity steadily decreased over the period. The iron was virtually zero. The other two additions again had such an overwhelming effect on the pH that the reduction in the iron and acid production could not be separated from a purely pH effect.

Half Lime Flasks

The effects of lime itself on iron and sulphate concentrations without any additions is shown (Figs 2.11 (a, b)). The effect on the iron concentration (as well as pH and titratable acidity not presented as figures) was as expected. The effect on the sulphate concentration was unexpected, with the half lime case causing an increase in the sulphate concentration compared to the control case (except for the last sampling date). The reason for this is unclear and the pattern is reflected in the other flasks to varying extents (it may be due to increased sulphur to sulphate oxidation at this pH). The half lime results for the other products for all the additions is between the zero lime and full lime cases. Only disodium hydrogen phosphate and tri-sodium citrate maintained a pH above 6 at the half lime rate.

Fig 2.9-2.11 Effect of Various Amendments, With and Without Lime on Rate of Oxidation of Baads Pyrite.

Fig 2.9 Zero Lime Flasks

a. effect on pH

b. titratable acidity

c. total iron in solution

d. sulphate concentration

Fig 2.10 Full Lime Flasks

a. effect on pH

b. titratable acidity

c. total iron in solution

d. sulphate concentration

KEY for Figs 2.9 and 2.10

1 control

2 o-phenanthroline

3 panacide

4 sodium dihydrogen phosphate

5 disodium hydrogen phosphate

6 trisodium citrate

Fig 2.11 Effect of Lime on Iron and Sulphate Concentrations

a. total iron in solution

b. sulphate concentration

KEY for Fig 2.11

1 zero lime

2 half lime

3 full lime

Fig 2.9.a.

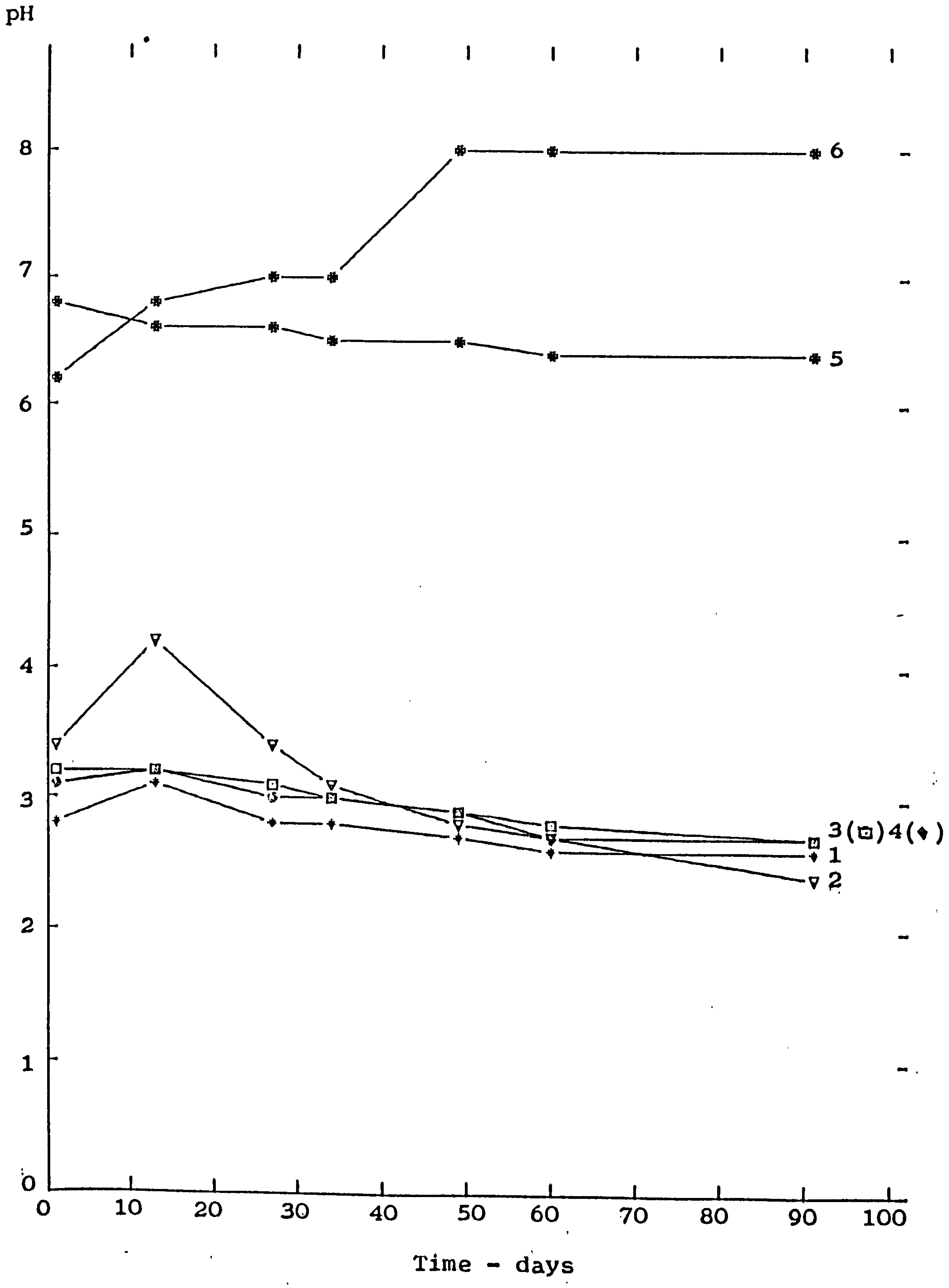


Fig 2.9.b.

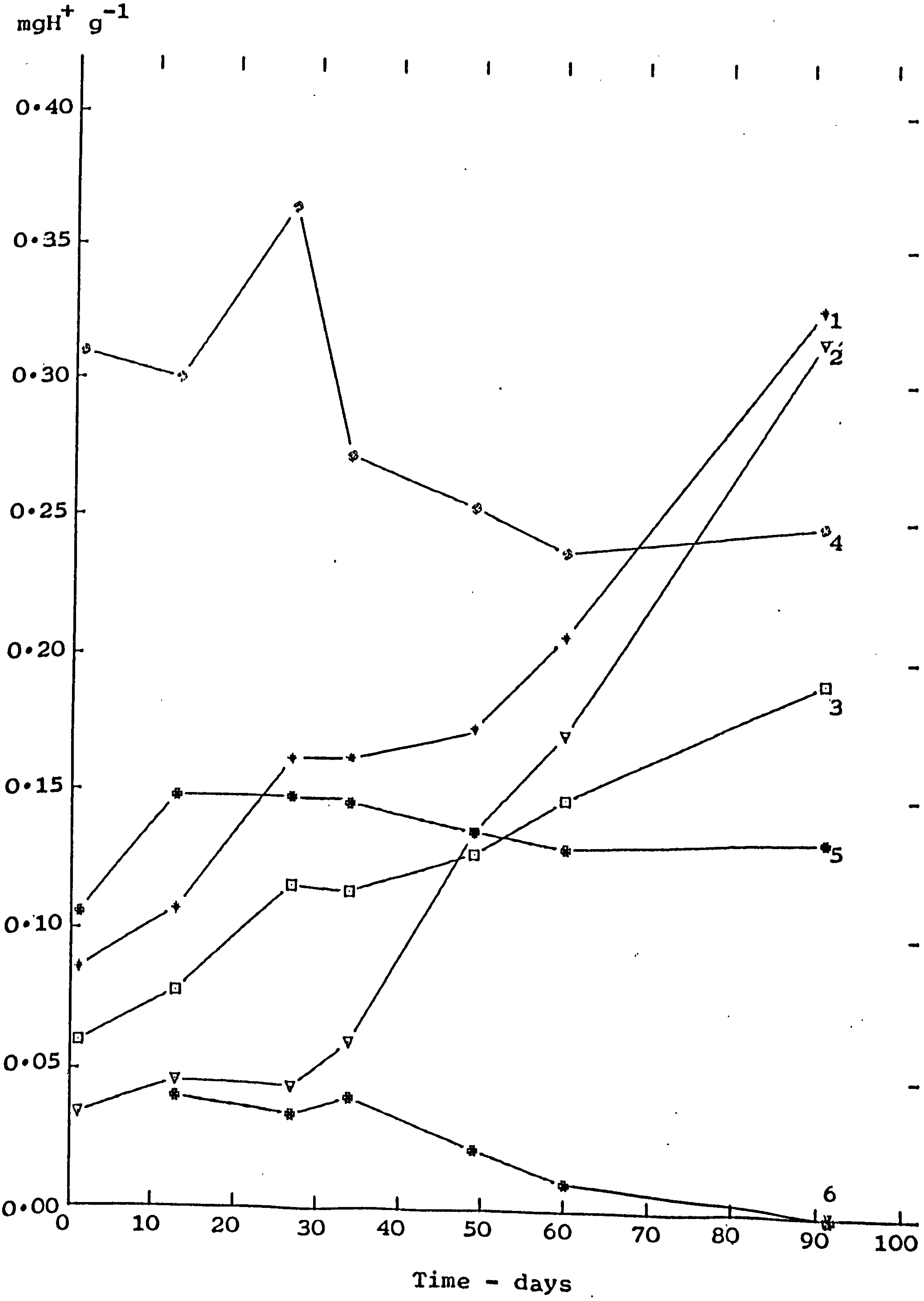

mgH$^+$ g^{-1}
0·40
0·35
0·30
0·25
0·20
0·15
0·10
0·05
0·00
0
10
20
30
40
50
60
70
80
90
100
Time - days
1
2
4
3
5
6

Fig 2.9.c.

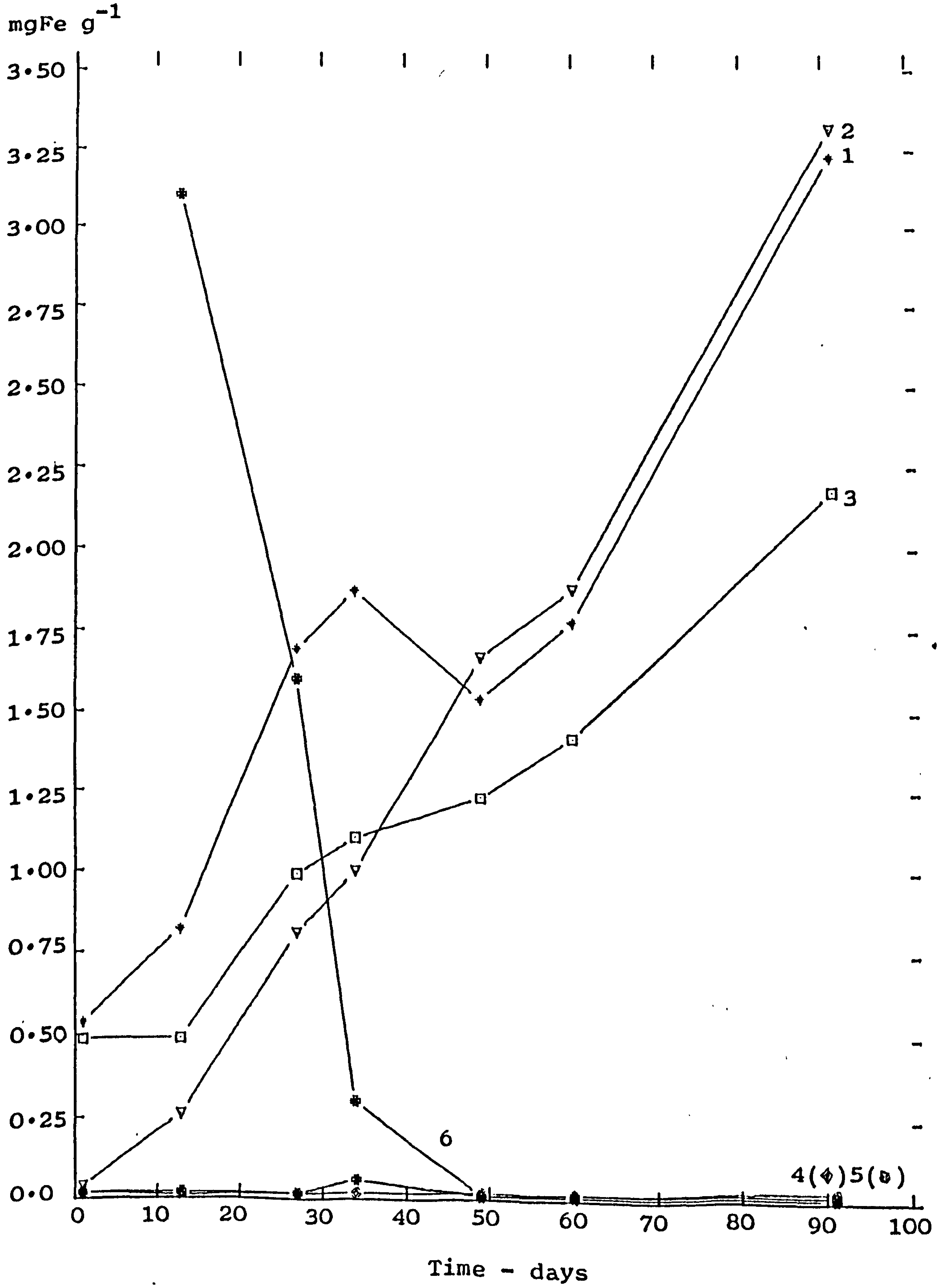

mgFe g^{-1}
3·50
3·25
3·00
2·75
2·50
2·25
2·00
1·75
1·50
1·25
1·00
0·75
0·50
0·25
0·0
0
10
20
30
40
50
60
70
80
90
100
Time – days
2
1
3
6
4(◈)5(◘)

Fig 2.9.d.

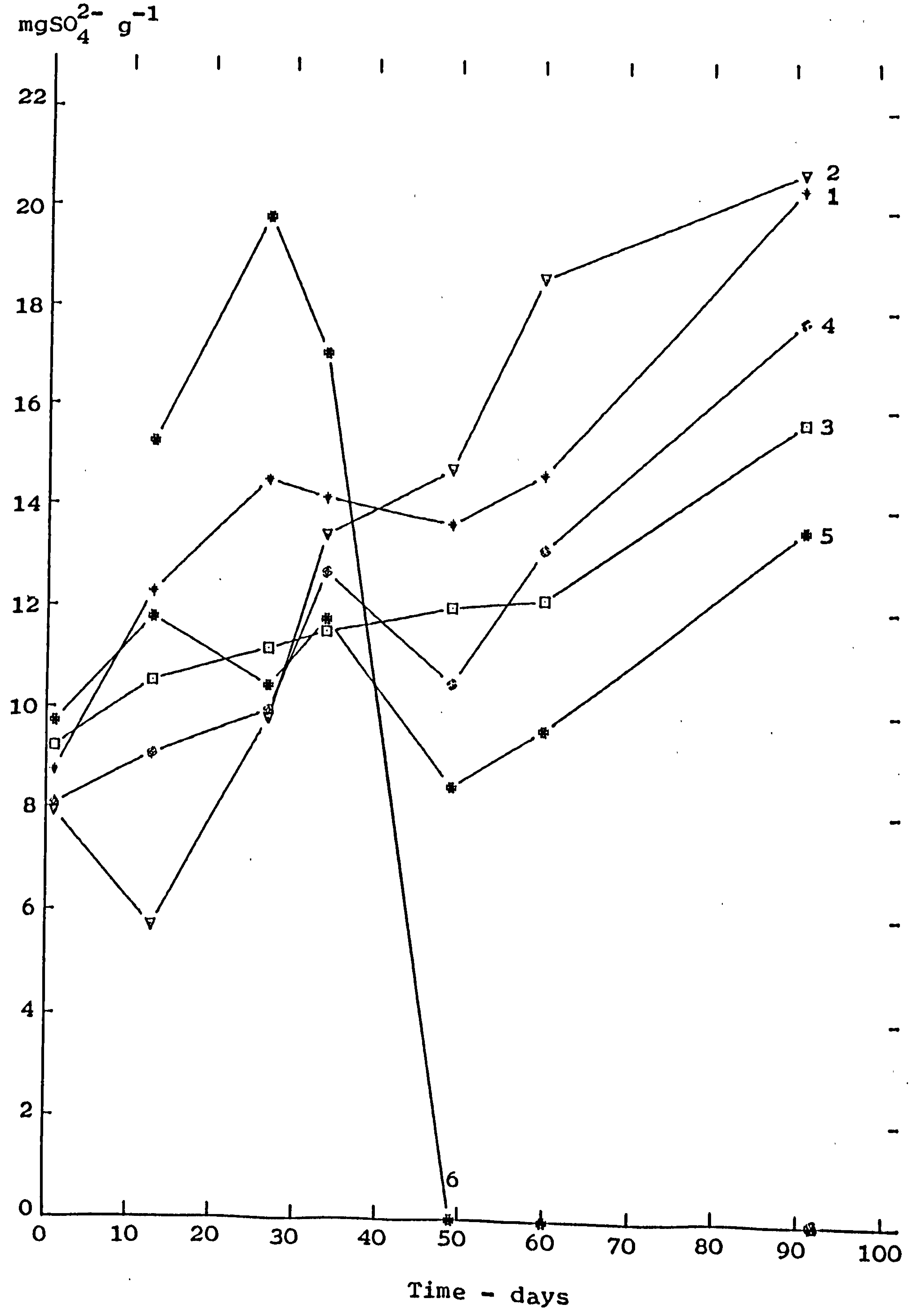

mgSO$_4^{2-}$ g^{-1}
22
20
18
16
14
12
10
8
6
4
2
0
0
10
20
30
40
50
60
70
80
90
100
Time - days
2
1
4
3
5
6

Fig 2.10.a.

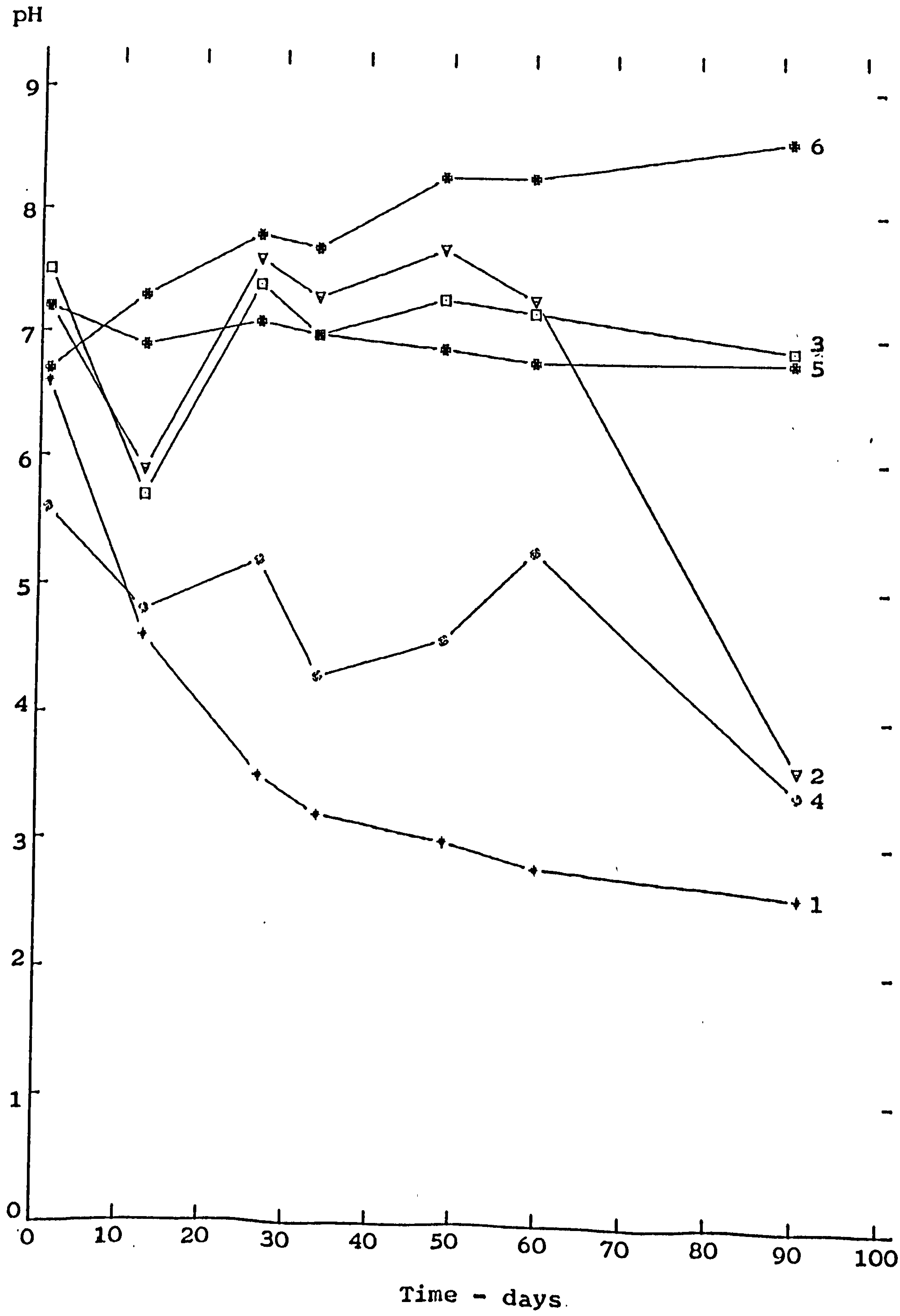


Fig 2.10.b.

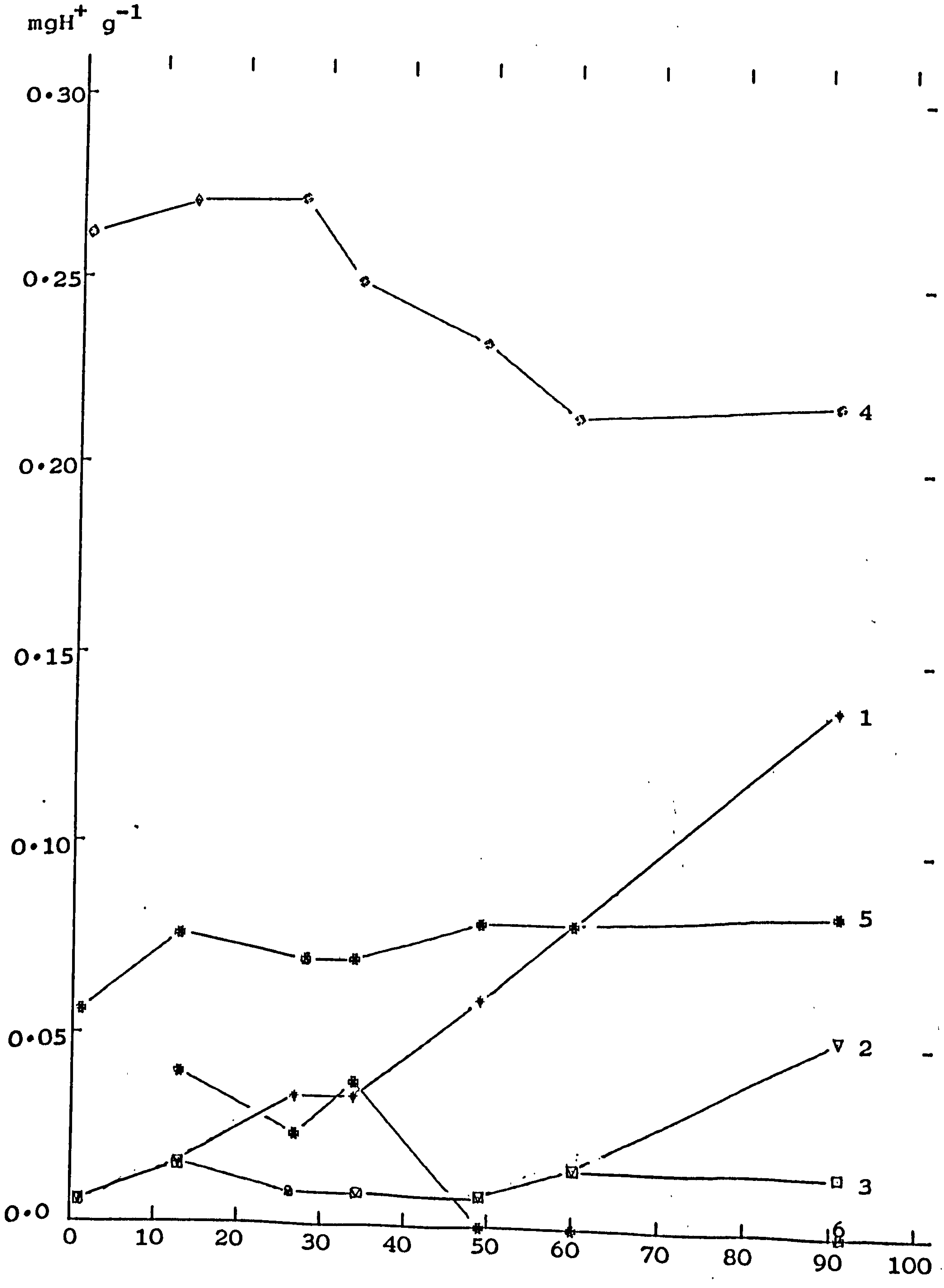

mgH$^+$ g^{-1}
0·30
0·25
0·20
0·15
0·10
0·05
0·0
0
10
20
30
40
50
60
70
80
90
100
Time - days
4
1
5
2
3
6

Fig 2.10.c.

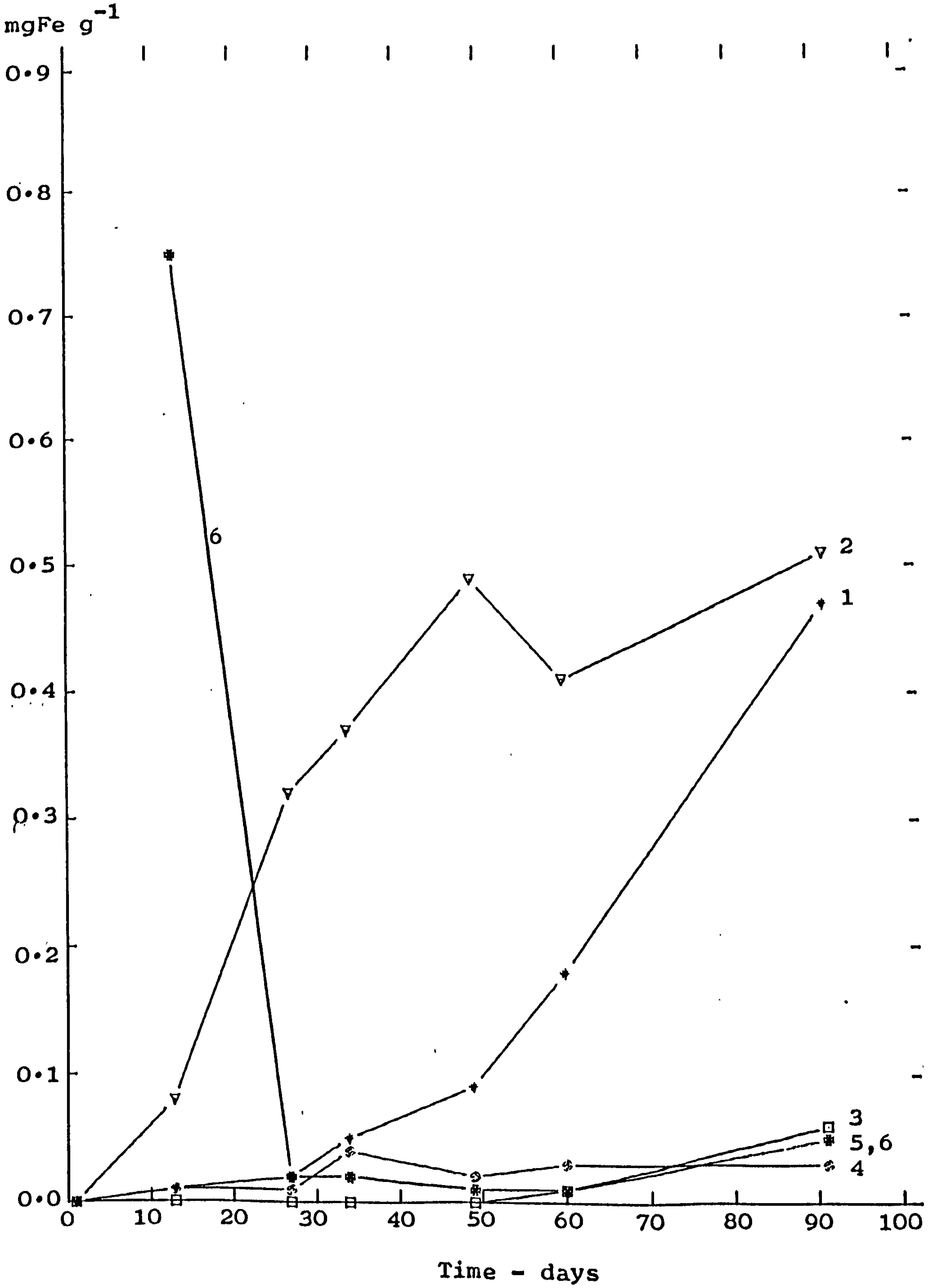
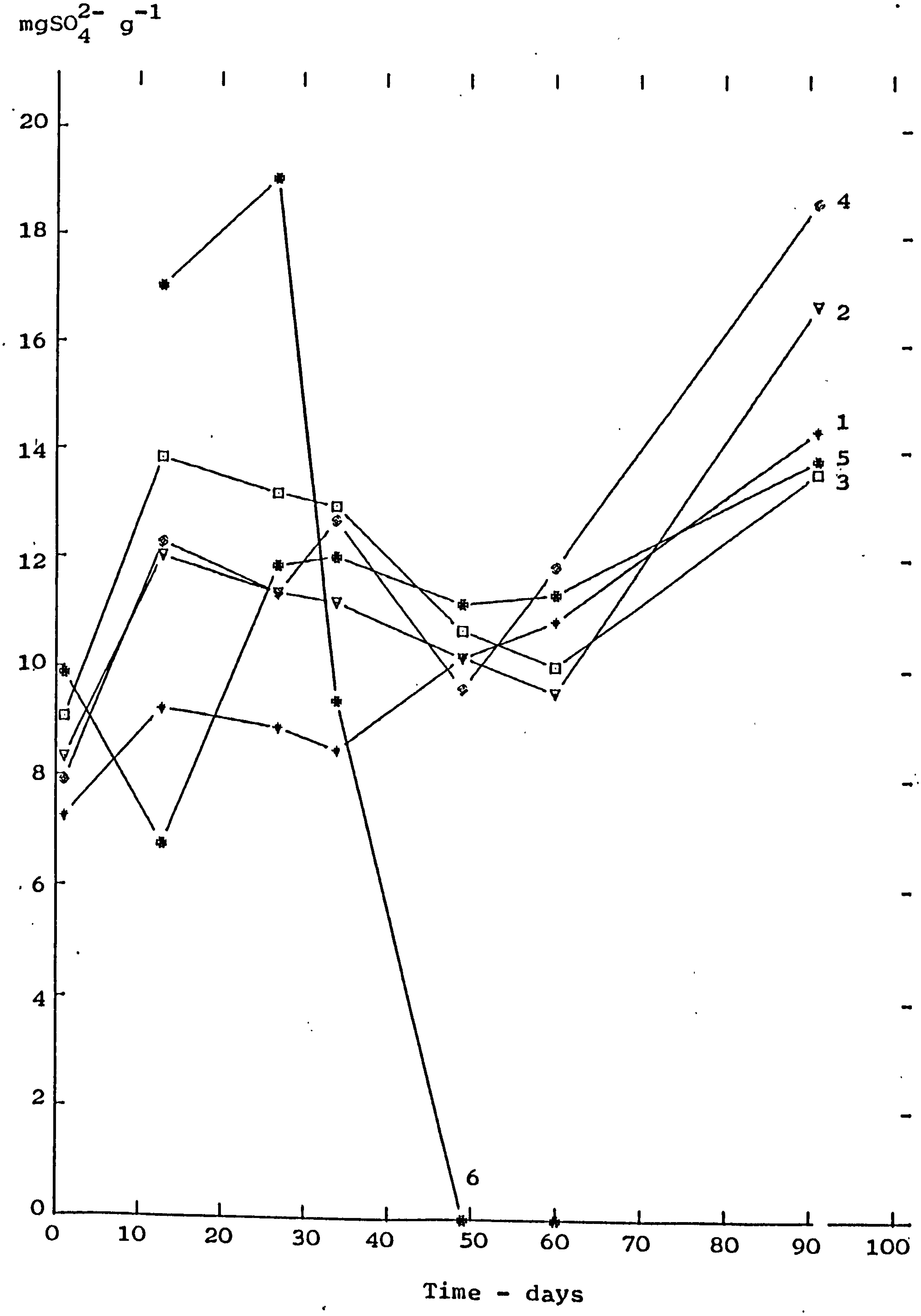

mgFe g^{-1}
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
0
10
20
30
40
50
60
70
80
90
100
Time - days
6
2
1
3
5,6
4

Fig 2.10.d.



mgSO$_4^{2-}$ g^{-1}
20
18
16
14
12
10
8
6
4
2
0
0
10
20
30
40
50
60
70
80
90
100
Time - days
4
2
1
5
3
6

Fig 2.11.a.

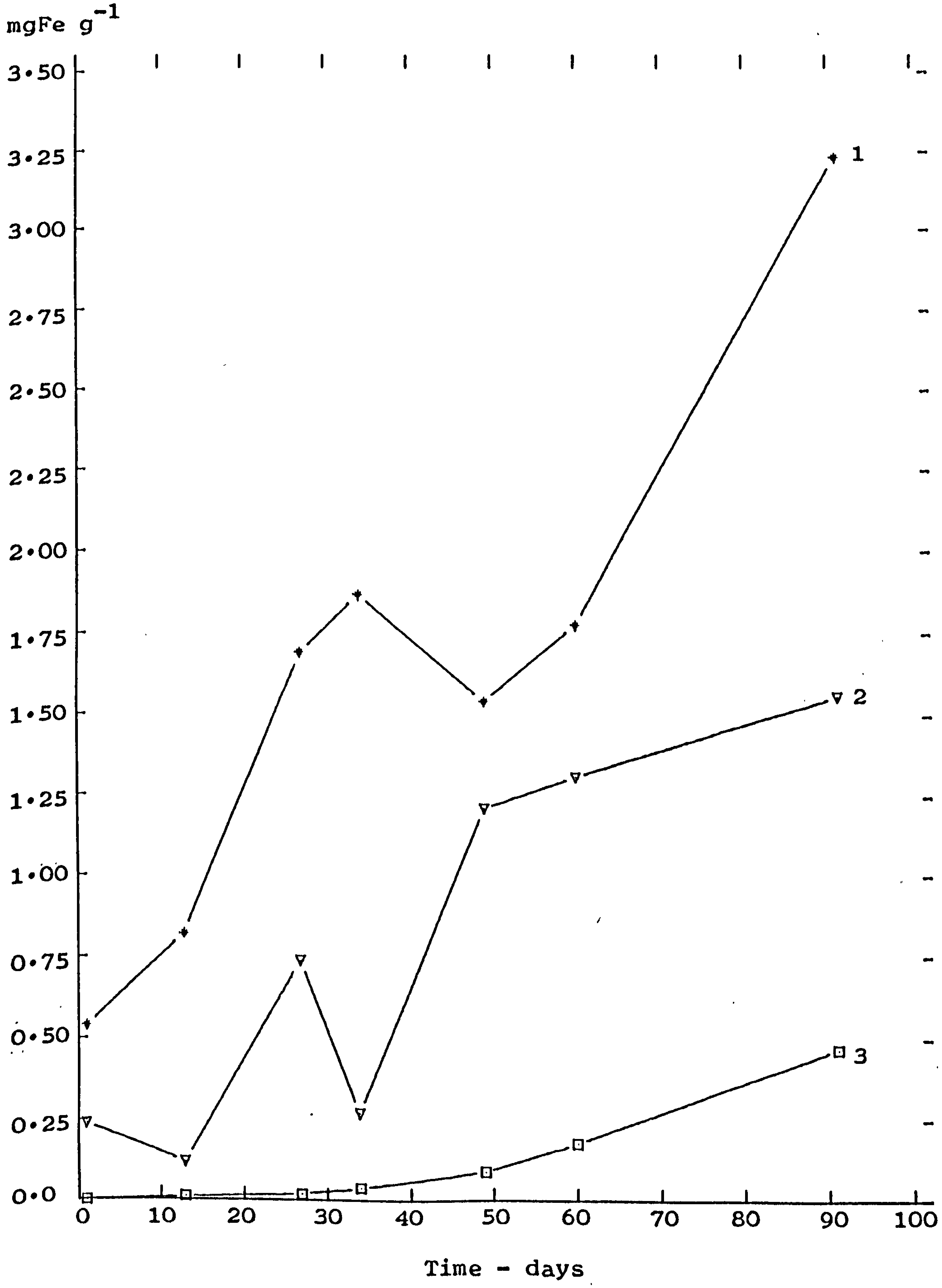
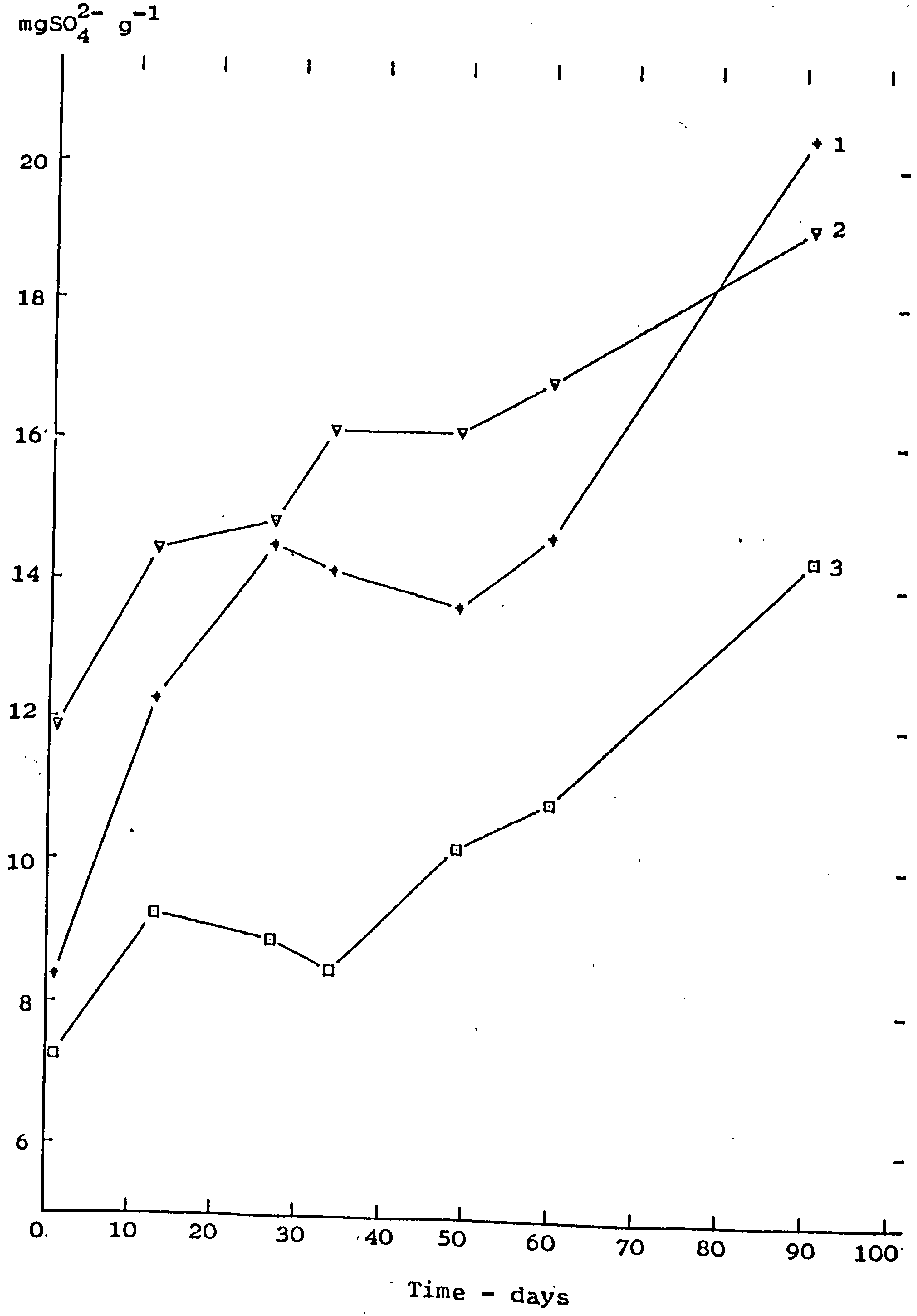

mgFe g^{-1}
3·50
3·25
3·00
2·75
2·50
2·25
2·00
1·75
1·50
1·25
1·00
0·75
0·50
0·25
0·0
0
10
20
30
40
50
60
70
80
90
100
Time - days
1
2
3

Fig 2.11.b.


$mgSO_4^{2-}\ g^{-1}$
20
18
16
14
12
10
8
6
0
10
20
30
40
50
60
70
80
90
100
Time - days
1
2
3

These results showed that the addition of certain chemicals could inhibit pyrite oxidation and thus maintain a reasonable pH for a longer period than the addition of lime alone. The effect in the full lime case of these chemicals was obviously greater than the effect in the zero lime case, due to the initial higher pH. The effect of tri-sodium citrate and disodium hydrogen phosphate could not be conclusively assigned to the complexing or precipitating of the iron and could be attributed to the increased pH only.

2.3.2 Complexation and Precipitation of Iron

The zero lime part of the previous experiment was repeated, with some variations to try to clarify the actual role of the added chemicals.

1 g of pyrite (Baads, less than 150 µm, 57% FeS_2) was used in 100 cm^3 of deionised water. A series of flasks were made up and no additions were made until day 9 so that pyrite oxidation would have started in all the flasks. The following additions were then made to duplicate flasks:

Zero (control)

0.5 g o-phenanthroline

0.05 cm^3 panacide

0.15 sodium dihydrogen phosphate

0.15 g disodium hydrogen phosphate

0.3 g trisodium citrate

The full results are in Table A10 in the Appendix and some graphically in Figs 2.12 (a, b, c).

The effect on the pH due to the addition of the various chemicals was not so great as to inhibit the oxidation of the pyrite

Fig 2.12 Production of Acid and Iron from Baads Pyrite, as Affected by Various Amendments, Added After Second Sampling.

Fig 2.12.a Production of Acid

Fig 2.12.b & c Comparison of Ferrous and Total Iron Concentrations in Solution (where only total iron is presented, the difference between ferrous and total iron concentrations was negligible)

KEY

1 control
2 o-phenanthroline
3 panacide
4 sodium dihydrogen phosphate
5 disodium hydrogen phosphate
6 trisodium citrate

Fig 2.12.a.

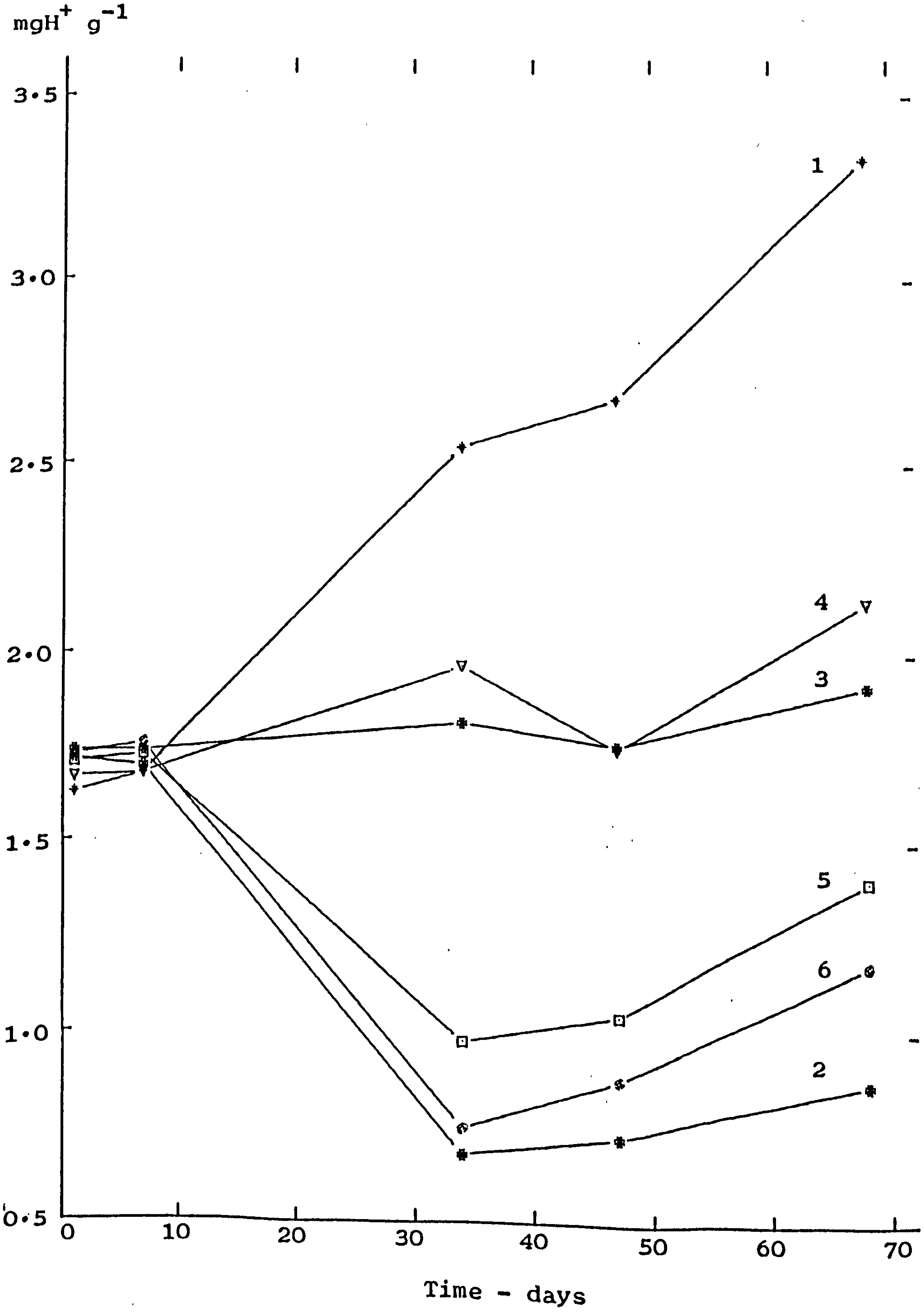


Fig 2.12.b.

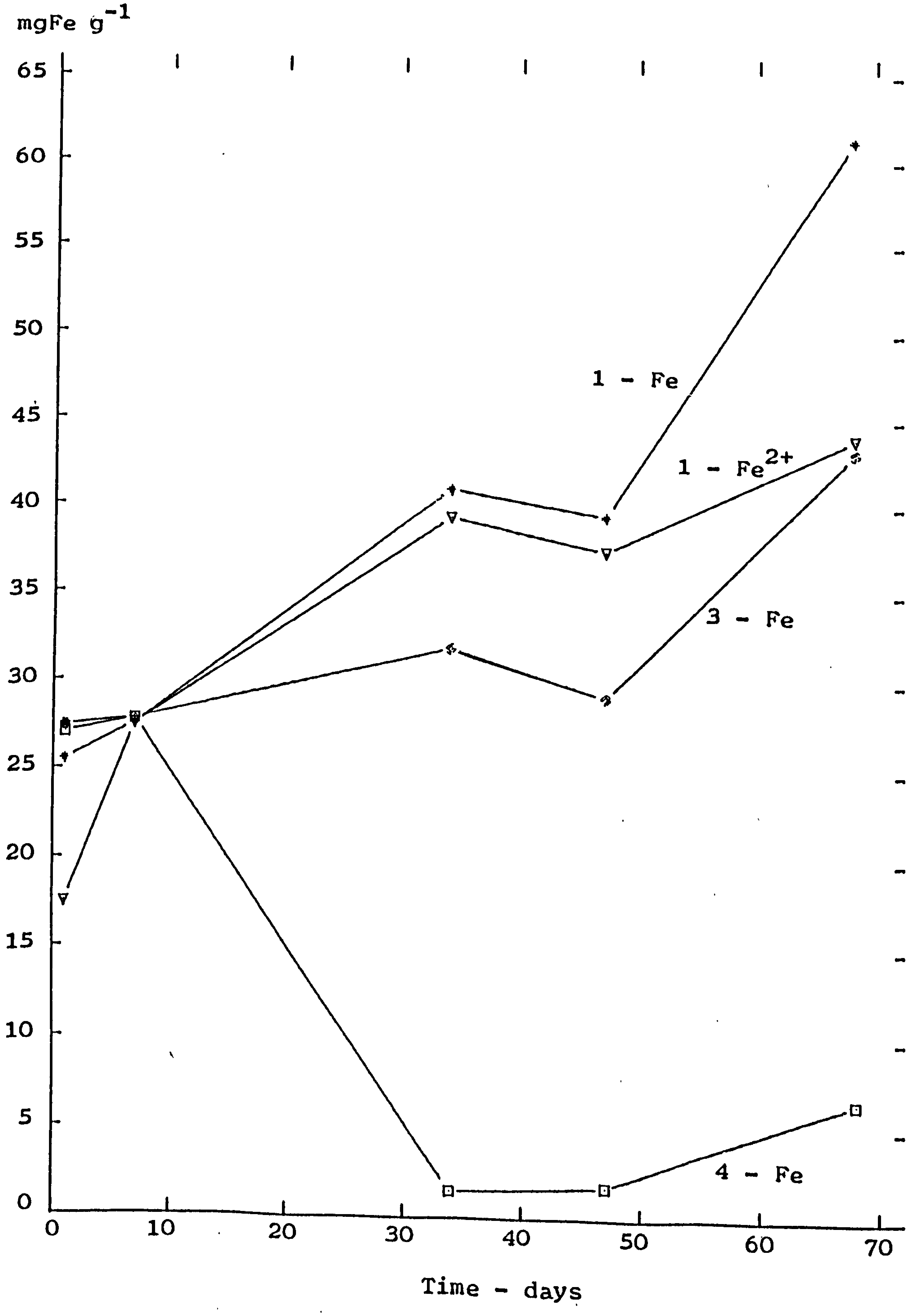
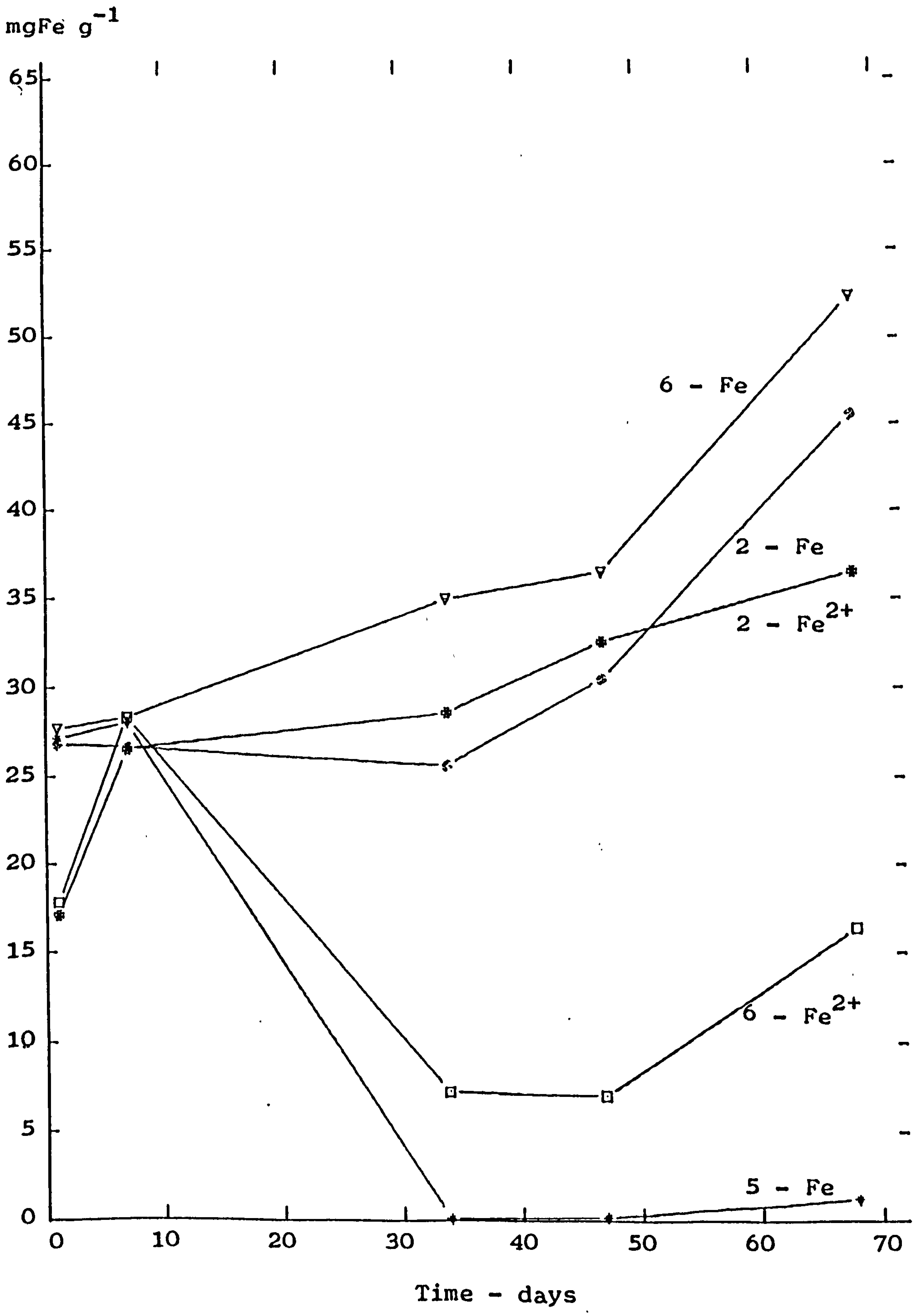

mgFe g^{-1}
65
60
55
50
45
40
35
30
25
20
15
10
5
0
0
10
20
30
40
50
60
70
Time - days
1 - Fe
1 - Fe^{2+}
3 - Fe
4 - Fe

Fig 2.12.c.


mgFe g^{-1}
65
60
55
50
45
40
35
30
25
20
15
10
5
0
0
10
20
30
40
50
60
70
Time - days
6 - Fe
2 - Fe
2 - Fe^{2+}
6 - Fe^{2+}
5 - Fe

by a purely pH effect. The tiratable acidity was decreased by the addition of the more alkaline materials as would be expected and it then gradually increased. The other two chemicals (panacide and sodium dihydrogen phosphate) caused the acidity to be kept much lower than in the control case. Figs 2.12 (b and c) show ferrous and total iron concentration. Where only total iron is shown for particular flasks the difference between ferrous and total iron was negligible after the addition of the amendment. These figures show the effect of the various chemicals on the iron and its oxidation state. In the control flasks some of the iron was present as ferric iron and the relative concentration of this increased with time. The panacide reduced the iron concentration and kept it in the ferrous state. In the o-phenanthroline case the recorded value for the total iron was actually less than the ferrous iron value on two dates, but this slight discrepancy was due to the two different measurement methods being used (colorimetric for ferrous iron and atomic absorption spectrophotometry for total iron). By the last date the total iron was significantly higher than the ferrous iron, showing that the o-phenanthroline was effective initially but did not sustain the effect. In the phosphate flasks virtually all the iron disappeared, consistent with ferric phosphate being precipitated. In the citrate flasks the majority of the iron was kept in solution as ferric iron (the ratio of ferric to ferrous iron being over 3:1). This shows that probably a ferric-citrate complex was being formed, effectively 'tying-up' the ferric iron. All the sulphate levels were reduced compared to the control case.

The different additions obviously successfully inhibited the oxidation of pyrite by stopping the ferric iron participating in the reaction, either by precipitating it (phosphate), complexing it (citrate) or by stopping its formation (panacide and o-phenanthroline). Any oxidation that did take place could be attributed mainly to oxidation by oxygen, which is much slower than the oxidation of pyrite by ferric iron.

2.4 Complexation of Ferrous and Ferric Iron

Various different compounds will chelate or complex ferrous or ferric iron, which could therefore be used to inhibit pyrite oxidation.

Ferrous ion has the electron configuration of d^6 whilst ferric ion is d^5 and therefore the chemistry of the two ions will obviously differ. Both the species form mainly octahedral compounds. Ferric ion tends to form high spin compounds, except with ligands such as CN^-, 2,2'-bipyridal and o-phenanthroline which have ligand fields strong enough to cause spin pairing. Other amine compounds do not form stable complexes with ferric ion. Anionic ligands especially those chelating by oxygen can form very stable compounds with ferric ion, for example, phosphate, citrate, oxalate and E.D.T.A. Ferrous ion is a good π donor and can be stabilised by π acceptor ligands. Ligands such as 2,2'bipyridal and o-phenanthroline have low lying π^* orbitals which can accept charge and thus help to stabilise compounds formed with ferrous ion. Ferric ion however is a poor π donor, mainly because of its higher charge.

Thus ferrous and ferric iron will be stabilised by various different ligands. Complex organic materials containing many different chemical groups would be expected to complex iron in these two oxidation states. Two such waste materials are chicken manure and woodwastes and these were therefore used in the next experiment to 'tie up' either ferrous or ferric iron. E.D.P.H.A. (ethylenediamine-di(o-hydroxyphenyl acetic acid)) is a specific chelator for ferric iron and this was also used. Florisil which is activated magnesium silicate was used as a source of silicate to complex ferric iron.

The idea of using silicate as a complexor of ferric iron was extended in another set of flask experiments when P.F.A. (pulverised fuel ash) and sodium silicate solution were also used.

2.4.1 Inhibition of Pyrite Oxidation by Waste Materials and Specific Chemicals

A series of flasks was set up containing 10 g spoil (Baads spoil with finely ground pyrite to give 4% FeS_2) in 200 cm^3 deionised water. After twelve days the flasks were tested for acid ferrous iron, total iron and sulphate. Various additions were then made to each flask, each treatment being added to duplicate flasks:

1. zero - control
2. 20 g woodwaste
3. 5 g chicken manure
4. 0.5 g E.D.P.H.A.
5. 1.5 g florisil

The results are presented as concentrations, as during the course of the experiment evaporation from the flasks occurred at different rates, and this was not corrected accurately so that all the flasks contained different amounts of solution. The use of the concentration negated the necessity of knowing the amount of solution.

The results are presented in Table A11 in the Appendix and Figs 2.13 (a, b). Ferrous iron was not measured after day 39, as the

Fig 2.13 Inhibition of Pyrite Oxidation by Waste Materials and Specific Chemicals - additions made on day 13.

Fig 2.13.a Titratable Acidity

Fig 2.13.b Total Iron in Solution

KEY

1 control
2 woodwaste
3 chicken manure
4 E.D.P.H.A.
5 Florisil

Fig 2.13.a.

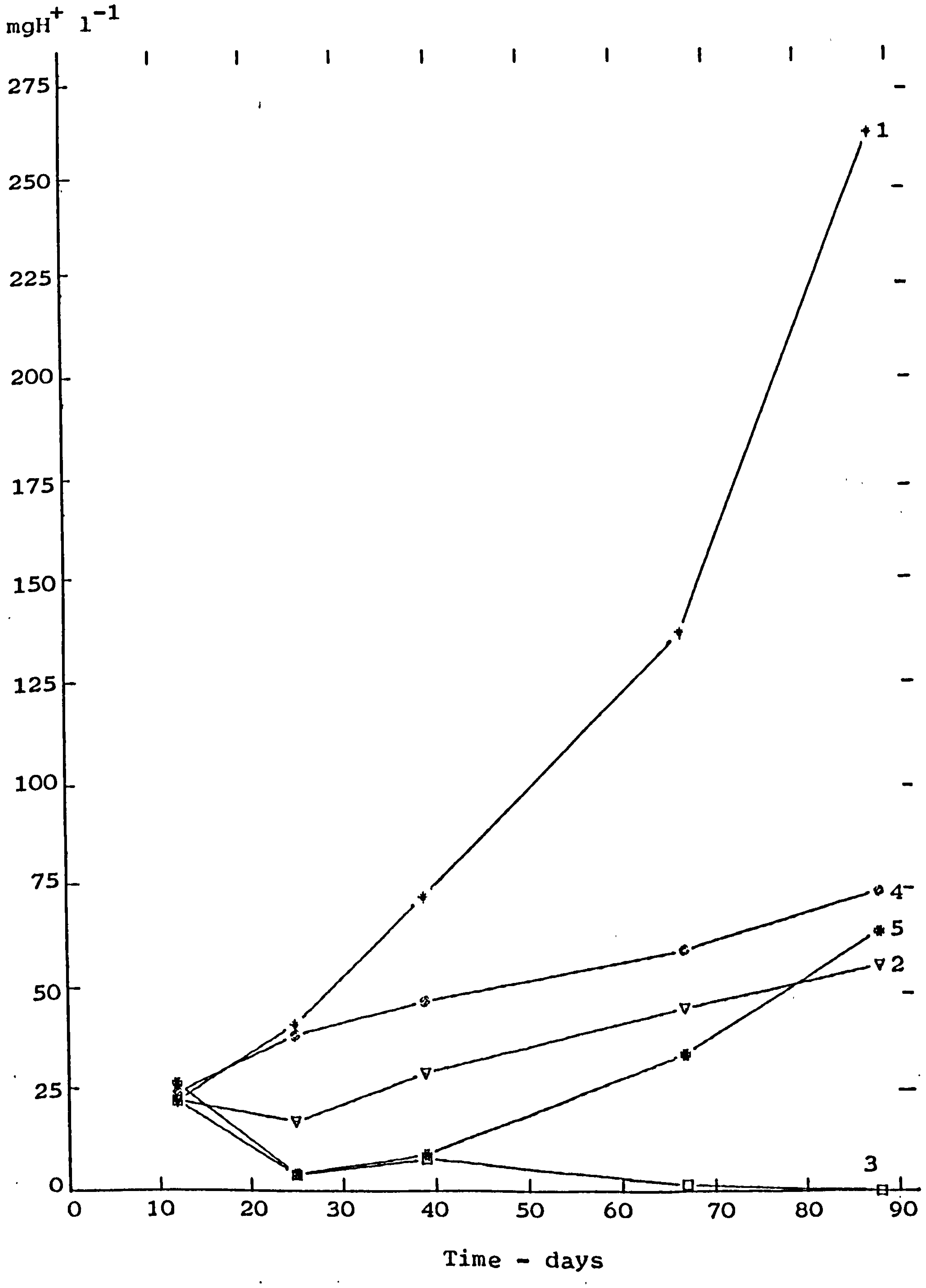
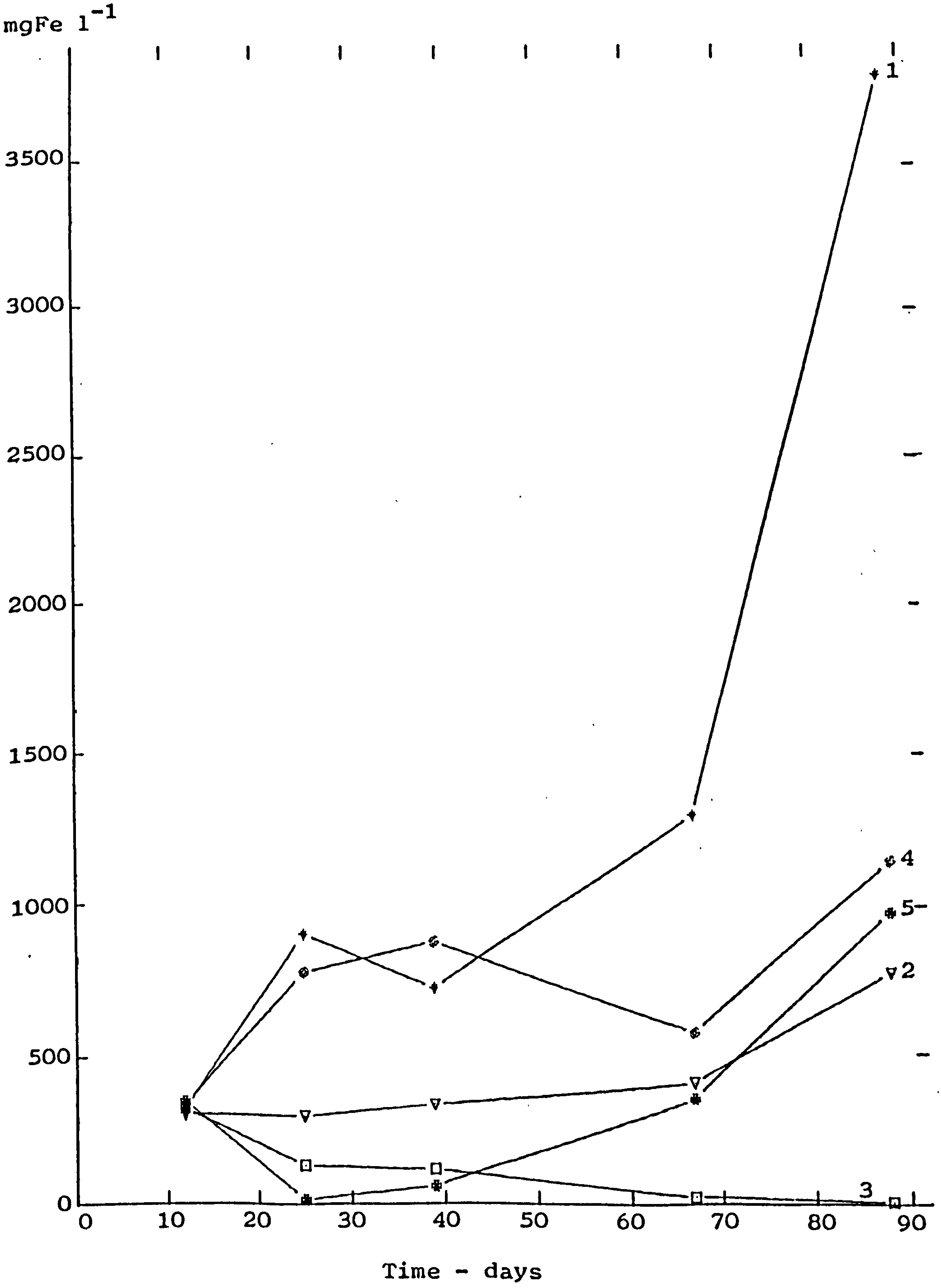

mgH+ l-1
275
250
225
200
175
150
125
100
75
50
25
0
0
10
20
30
40
50
60
70
80
90
1
4
5
2
3
Time - days

Fig 2.13.b.


mgFe l^{-1}
3500
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
60
70
80
90
Time - days
1
4
5
2
3

results between duplicate flasks varied greatly, probably due to the influence of the different additions on the colour of the solutions.

E.D.P.H.A. Flasks

The addition of E.D.P.H.A. did not lower the titratable acidity as much as the other additions, but as can be seen from the pH, E.D.P.H.A. slightly lowered the pH compared to the control whilst all the other additions raised the pH, thus explaining the different ability to affect the titratable acidity. Iron and sulphate in these flasks was also lowered compared to the control. The solution in these flasks was red and therefore the ferrous iron test could not be done.

Florisil Flasks

The addition of the florisil caused a yellow precipitate to form, presumably a ferric iron precipitate. Over the time the iron in solution did increase showing that not all the iron was precipitated.

Woodwaste Flasks

Woodwaste was very effective at reducing the levels of acid, iron and sulphate over the whole period.

Chicken Manure Flasks

Chicken manure reduced the acid sulphate and iron levels to virtually zero. The pH was maintained about 7 throughout the whole period. The diminishment of the acid, iron and sulphate concentrations was more than just a dilution effect of removing 15 cm^3 of solution at each sampling date and replacing by 15 cm^3 of deionised water, and therefore chicken manure was obviously very successful at inhibiting the pyrite oxidation.

2.4.1.a Further Studies on Chicken Manure and Woodwaste

Different concentrations of ferrous and ferric iron solutions were shaken with chicken manure or woodwaste. The solutions were made up in different concentrations of hydrochloric acid, as well as water, to study the effect of the pH. These studies showed that chicken manure complexed 50 mgFe g^{-1} (45 mgFe g^{-1} oven dry weight) and that woodwaste complexed 16 mgFe g^{-1} (5 mgFe g^{-1} oven dry weight). The results were the same for ferrous and ferric iron and the same for all pH's in the range 2-7. Below pH 2 the amount of iron complexed was greatly reduced.

Infra-red absorption spectra were also obtained for the chicken manure and woodwaste before and after shaking with the iron solutions. Those for the chicken manure showed different peaks after having been shaken with the iron solutions, whereas there was no change in the spectrum of the woodwaste. Therefore the actual solid of the chicken manure complexed the iron whereas in the woodwaste case it must be a soluble constituent of the woodwaste which complexed the iron. Probably soluble as well as insoluble constituents of chicken manure complexed iron. The actual classification of the components of chicken manure and woodwaste which complexed iron was not attempted.

2.4.2 Silicate Flasks

Finely ground Baads pyrite (less than 150 µm) was mixed with Baads spoil (less than 2 mm) to give a pyrite content of 4% FeS_2, and 11 g used for each flask. To triplicate flasks the following additions were made:

1. 200 cm^3 deionised water (control)
2. 5 g P.F.A. in 200 cm^3 deionised water
3. 1.5 g florisil in 200 cm^3 deionised water
4. 200 cm^3 sodium silicate solution - Si conc 0.15% Si
5. 200 cm^3 sodium silicate solution - Si conc 0.015% Si

6. 200 cm^3 sodium silicate solution - Si conc 1.5% Si
7. 200 cm^3 sodium silicate solution - Si conc 0.75% Si

The original sodium silicate solution was 18% w/w Na_2O and 36% w/w SiO_2. The lowest concentration Si flasks (4 and 5) were set up after the other flasks, as it was only after the first sampling that it became apparent that the other sodium silicate flasks had an exceedingly high pH.

Silicon in solution was measured using atomic absorption spectrophotometry, as the high concentration of iron made the use of the colorimetric method (molybdate method) impossible. Although the measurement of silicon by atomic absorption spectrophotometry is not very accurate, it was adequate for the gross comparisons needed here. The two lowest Si concentrations used (0.15% Si and 0.015% Si) did not interfere with the measurement of iron by atomic absorption spectrophotometry (standard solutions of iron made up in these Si concentrations showed the same absorbance as control standard solutions).

The results for the first two sodium silicate flasks are not represented as figures due to the exceedingly high pH which would make the use of this concentration unrealistic. However the results are given in Table A12 in the Appendix. The solution in these flasks was red and during the course of the experiment the spoil material became expanded into a gelatinous mass, presumably due to the formation of silicate polymers. At these high pH's iron could only exist in solution if it was complexed, and the decrease with time of the iron and silica content concentrations could be due to the polymerisation of the iron-silicate complex. The sulphate test was not possible, a colloidal suspension being formed upon the addition of the hydrochloric acid.

The pH and iron and silica concentrations for sets of flasks 1-5 are shown in Figs 2.14 (a, b, c). The lowest concentration of sodium silicate solution used was not effective at reducing the acid, iron and sulphate production. However the 0.15% Si sodium silicate solution maintained a pH of 6-7, and negligible amounts of sulphate were produced. Both the iron and silicon concentrations gradually decreased. The solution in these flasks was red as was the solution in the flasks with higher silicate concentrations, but a gelatinous mass was not formed as before. The solution in the lowest concentrations silicate flasks was clear, and a slight yellow precipitate formed.

The flasks containing the P.F.A. had very low iron concentrations, whereas those containing florisil had higher iron concentrations (although less than that of the control flasks). The pH of both these sets of flasks was initially 7, which then decreased over the period and any inhibitory effect on pyrite oxidation of the additions could just be attributed to the increased pH. However, in the last set of flasks (2.4.1) when the florisil was added after pyrite oxidation had been established in the flasks, it did not have a very great effect on the pH, but still managed to inhibit pyrite oxidation. Therefore in this set of flasks the florisil and P.F.A. were probably inhibiting pyrite oxidation, and the reduction in the iron concentrations was not just due to the initially higher pH. Some pyrite oxidation was occurring, shown by the decrease in the pH but the levels of acid, iron and sulphate in the florisil and P.F.A. flasks were all reduced compared to the control flasks. Both these sets of flasks contained yellow precipitates, confirming that some iron was being precipitated. The silicon concentration was higher than in the control flasks showing that silica was being released into solution

Fig 2.14 Release of Acid, Iron and Silicon from Baads Pyrite Amended with Silicon - Containing Chemicals

Fig 2.14.a pH of solution

Fig 2.14.b Concentration of Total Iron in Solution

Fig 2.14.c Concentration of Silicon in Solution

KEY

1 control

2 P.F.A

3 florisil

4 0.15% Si sodium silicate solution

5 0.015% Si sodium silicate solution

Fig 2.14.a.

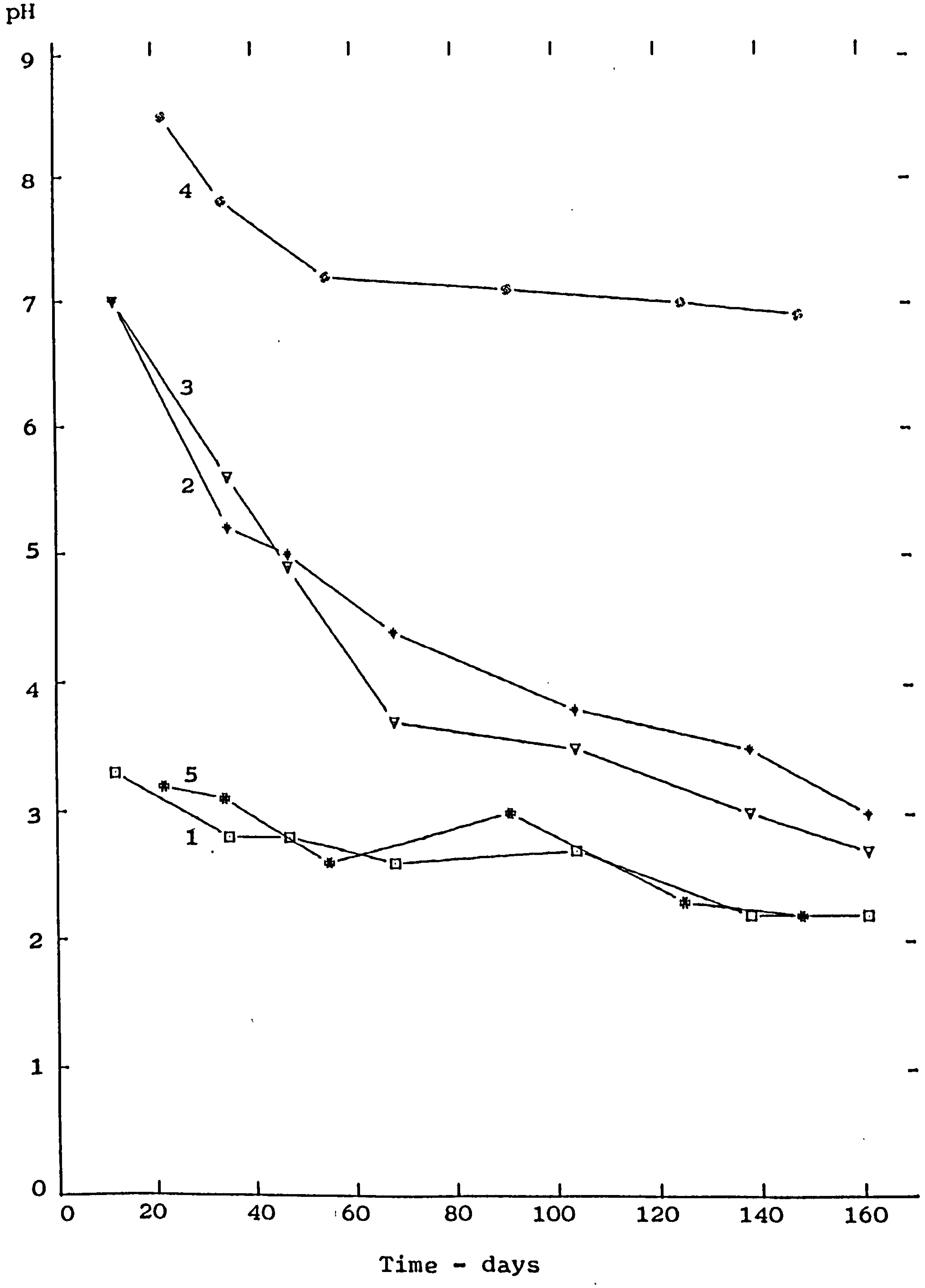


Fig 2.14.b.

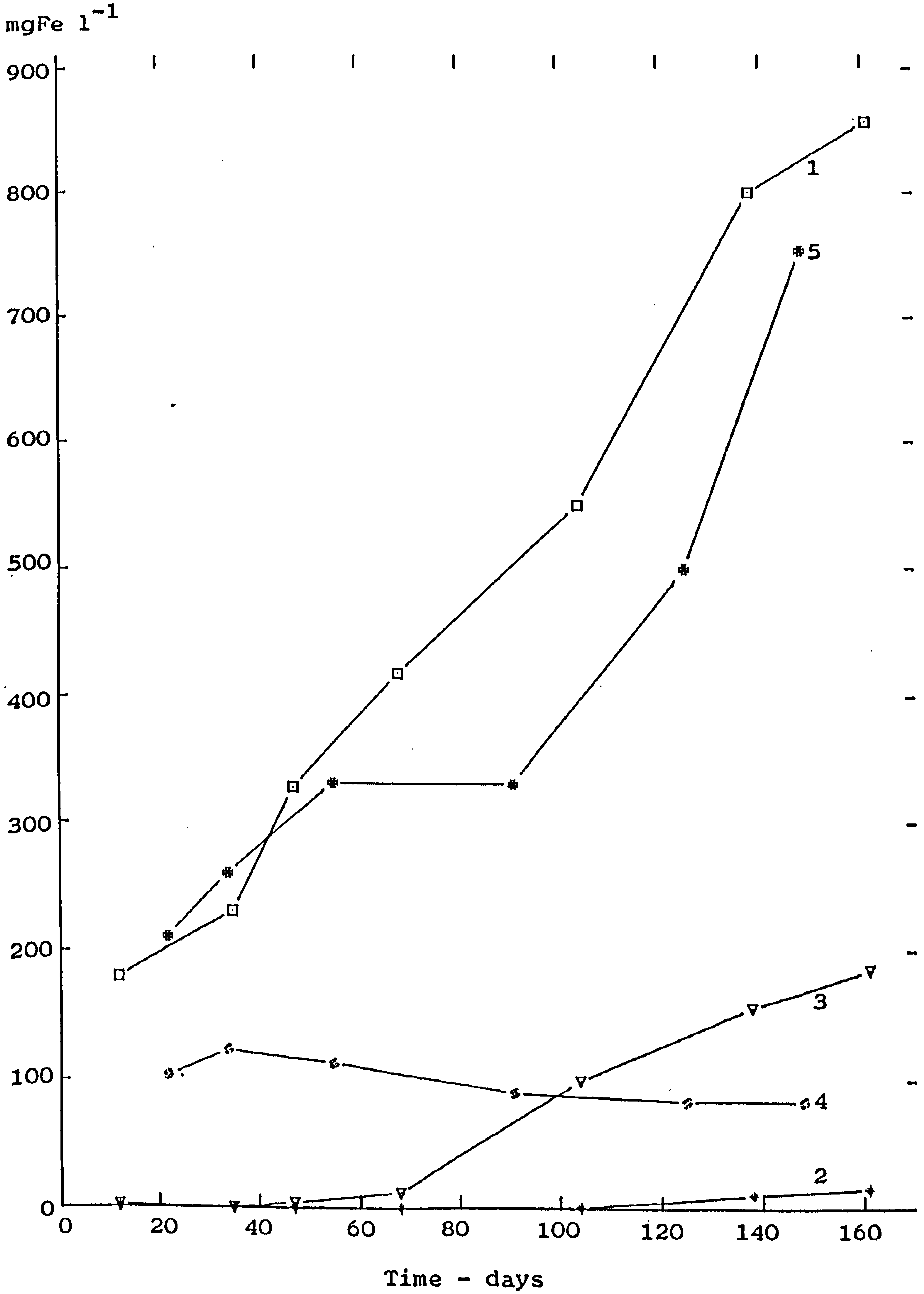
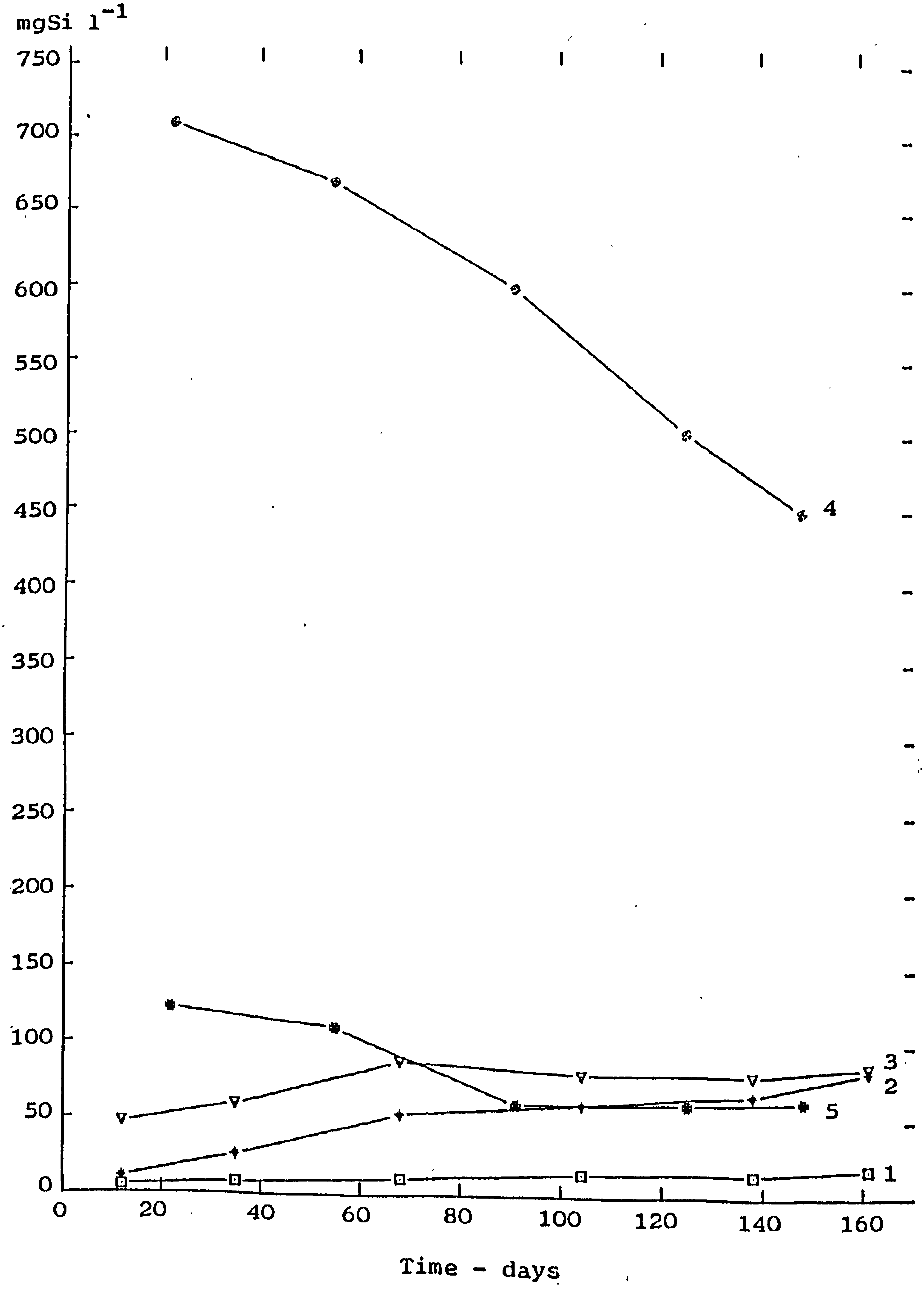

mgFe l^{-1}
900
800
700
600
500
400
300
200
100
0
0
20
40
60
80
100
120
140
160
Time - days
1
2
3
4
5

Fig 2.14.c.


mgSi l^{-1}
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700
650
600
550
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50
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Time - days
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from these additions. Therefore P.F.A., florisil and 0.15% sodium silicate solutions all reduced the pyrite oxidation rate.

2.4.2.a Reaction of Iron and Sodium Silicate Solution

The reaction of the sodium silicate solutions with iron was investigated. Ferrous and ferric iron solutions (using ferrous ammonium sulphate and ferric chloride, with no adjustment in the pH of the solutions) were added to the sodium silicate solution to give a final Si concentration of 0.15% and iron concentrations of 100 mg l^{-1}. These were then added to a solution of 1% cetab (cetyltrimethylammonium bromide) and a precipitate was formed. Sodium silicate solution by itself also formed a precipitate with cetab. The iron plus sodium silicate plus cetab solutions were filtered and the iron in solution measured by atomic absorption spectrophotometry. Only 5 mgl^{-1} was recorded in the case of the ferrous solution, and 0.5 mgl^{-1} for the ferric solution. Therefore the iron must have been complexed by the silicate solution, and this then formed a colloid with cetab.

2.4.3 Conclusion

The two last sets of flasks (section 2.4.1 and 2.4.2) confirmed the earlier results showing that it is possible to inhibit pyrite oxidation using specific chelators or precipitators of iron as well as using waste materials.

E.D.P.H.A. inhibited pyrite oxidation, presumably by complexing ferric iron, whilst florisil inhibited pyrite oxidation presumably by precipitating or complexing some of the iron, probably as ferric silicate.

Woodwaste and chicken manure both decreased the acid, iron and sulphate concentration, chicken manure being especially effective. It was shown that both these materials complexed ferrous and ferric iron and thus they would have inhibited the ferric iron oxidation of pyrite.

P.F.A., presumably acting as a source of silicate, and florisil both decreased the pyrite oxidation rate in the last set of flasks. The sodium silicate solutions with the two highest silica concentrations obviously caused such a drastic increase in the pH of the solution, that the use of silicate solutions equivalent to these concentrations in the field would be impractical. However, the 0.15% Si concentration managed to maintain the pH about 7 throughout the whole period and also showed an overall decrease in iron concentration, obviously very successfully inhibiting pyrite oxidation. The lowest silicate concentration did not very effectively reduce the acid, iron and sulphate concentrations.

The idea of inhibiting pyrite oxidation by precipitating or complexing ferrous or ferric iron was extended into pot studies to see the effectiveness of the various amendments in a more realistic situation than in the flask experiments. These studies are discussed in the next chapter.

CHAPTER 3

Inhibition of Pyrite Oxidation in Pot Experiments

3.1 Introduction

The flask experiments of the last chapter showed that it was possible to inhibit the oxidation of pyrite - by complexing either ferrous or ferric iron, by precipitating ferric iron or by stopping the bacterial oxidation of ferrous iron. This inhibited the ferric iron oxidation of pyrite, so that the main oxidant of pyrite became oxygen alone. The air oxidation of pyrite produces acid, iron and sulphate at a much slower rate than does the ferric iron oxidation of pyrite - at such a slow rate that it should not really create many problems in the field. Therefore the results from the last chapter were extended into pot studies to determine their effectiveness in a more realistic situation.

A bactericide had proved very successful in the flasks, (by inhibiting the bacterial oxidation of ferrous to ferric iron) but bactericides were not used in further studies due to the problems of obtaining a selective bactericide which would only attack the Thiobacilli and not the bacteria which are responsible for the establishment of a good soil, for example, Nitrosomonas and Nitrobacter. Bactericides have been used in other studies to prevent the oxidation of pyrite. Booth and Sefton (1970) suggested the use of 4-chloro-m-cresol, which could be placed in a museum case and the inhibition would be effected from the vapour phase. However this was specifically to preserve museum samples of pyrite and could not be applied in the field. Some studies have considered the use of anionic detergents, which act as a bactericide at low pH (Kleinmann 1980, Kleinmann et al. 1981, Dugan and Apel 1983). These workers reported that acid production was reduced using these detergents. Kleinmann et al (1981) reported the use of a slow release technique of anionic detergents in small scale field tests, the effectiveness of which lasted 2 to 5 years. However, this technique has not been tested adequately - either for a long enough period or on a large enough scale.

Both specific chemicals and waste materials as used in the flask experiments, were used in the pot experiments to compare their effectiveness at inhibiting pyrite oxidation.

Phosphate, citrate and E.D.P.H.A. were again used - phosphate to precipitate iron, and citrate and E.D.P.H.A. to complex iron (as shown in Chapter 2-2.3.2 and 2.4.1). These chemicals would not be particularly suitable for application on a large scale (although phosphate does tend to be applied on a relatively large scale as a fertilizer, for example, a typical rate used on a colliery spoil would be 50 kgPha^{-1}, whilst the amount of phosphate used in the pot experiments in this study was equivalent to about 200 kgPha^{-1}). However they were used in this study mainly to compare their effects with that of the waste materials. Florisil was also used in the first set of pots, as a source of silicate to complex iron, as the P.F.A. and sodium silicate solutions were not available until later in the study. Florisil would also obviously not be suitable for application on a large scale.

Chicken manure and woodwastes are both waste materials so the use of them in a field situation would obviously be ideal, as they would be relatively cheap and it would be an effective method of disposing of them. Different types of woodwastes have been investigated to determine their ability to help establish vegetation on mine spoils (Cunningham and Wittwer 1980, Koon and Graves 1980, Wittwer et al. 1980).

The general effects of these mulches on the spoil are to reduce the spoil temperature (the spoils have a high temperature due to their dark colour), increase the spoil moisture content, increase the organic matter content and to provide erosion control due to the weight and interlocking fibre characteristics of the woodwastes. Berg and Vogel (1973) found that hardwood chips used as a surface mulch on Kentucky acid spoils decreased the water soluble aluminium and slightly increased the pH, probably by reducing surface evaporation and promoting leaching. Chicken manure is often used as a slow release fertilizer due to its high phosphate, nitrogen and potassium content (Bradshaw et al.1973). The varying nitrogen, potassium and phosphate contents of different poultry manures are outlined in ADAS Advisory Leaflet 320. Chicken manure is generally rich in nitrogen and phosphorous, which tend to be the nutrients that are deficient in colliery spoil (Gemmell 1973). Bradshaw et al.(1973) suggested the use of chicken manure at about 12 tonnes ha^{-1} for fertilizing colliery spoil (in the pot experiments in this study it was used at about 5 tonnes ha^{-1}). Obviously the application of chicken manure or woodwaste to a spoil can improve either the chemical or physical properties of the spoil. In Chapter 2 (2.4.1) both these waste materials were shown to be capable of inhibiting pyrite oxidation, probably by complexing ferrous or ferric iron, and therefore either of these waste materials would be very suitable for applying to pyritic colliery spoil.

Another waste product is pulverised fuel ash (P.F.A.) - it is the waste product of coal-fired electricity generating stations. It was shown in the last chapter (2.4.2) that it also could inhibit pyrite oxidation so it was used in the following pot experiments. P.F.A. is sterile and contains negligible nitrogen but does contain most other nutrients. Vast quantities of this material are produced - in 1980

12 million tonnes of ash per year were being produced by the Central Electricity Generating Board (Snell and Brown 1980). It is often used as a filling for worked out gravel pits or for old brick pits, and can be used for building bricks or as a kind of cement, but this does not account for all the P.F.A. that is produced, and its disposal is a problem.

The main constituents of a typical Scottish P.F.A. are (Lawson and Nixon 1978):

SiO_2	44-55%	CaO	1.0-3.0%
Al_2O_3	30-35%	MgO	0.5-3.0%
Fe_2O_3	3- 9%	SO_3	0.1-0.5%

Other elements occurring in trace amounts include phosphorous, potassium, sodium, manganese, boron, zinc, chromium and molybdenum (Townsend and Gillham 1975). The interior of the ash particles is predominantly an aluminosilicate material. Some elements are present as part of this matrix whilst others are mainly present on the surface of the particle, and other elements are associated with both the matrix and the surface of the particles (Hanson and Fisher 1980). Greater than 95% of the P.F.A. can be of the fine sand (0.2-0.06 mm) and silt size (0.06-0.002 mm) range, which can lead to problems of compaction and cementation. The ash tends to be very alkaline, with a pH of about 11 before weathering, and about pH 8 after weathering, and is often used with acid peat for this reason. It can also be mixed with topsoil and reasonable plant growth can be obtained, especially if the ash has been previously weathered, which reduces the pH and reduces the possibility of boron being present in toxic amounts. Nitrogen and phosphorous also need to be added as fertilizers for successful plant growth - even though there is a reasonably high level of phosphorous in the ash it is unavailable for plants, probably because it is fixed by the aluminium present in the ash (Townsend and Gillham 1975).

P.F.A. has been used as an amendment for acidic colliery spoil mainly because of its alkaline properties. Jastrow et al.(1981) found that some plant tissues had greater concentrations of some elements - Co, V and Zn- when grown on P.F.A - amended acidic colliery spoil than when grown on lime-amended spoil, although the P.F.A.-amended spoil produced less Cd and Mn in the plant tissues than the lime-amended spoil. P.F.A. added to acidic colliery spoil can cause an increase in pH, increase in spoil porosity and an increase in percolation depth (Plass and Capp 1974, Plank et al.1975, Fail and Wochok 1977, Capp 1978). It has also been used to reduce copper toxicity - surface layers of P.F.A. were found to be more effective at establishing plant growth than sewage sludge or domestic refuse on copper smelter wastes (Goodman and Gemmell 1978).

The main constituent of P.F.A. is silica and it was used in this study as it was hoped that it could act as a source of silicate which could precipitate iron and thus inhibit the pyrite oxidation. However, Hanson and Fisher (1980) actually showed that the majority of the silica was released by hydrofluoric acid but not by hydrochloric acid, as the silica was present predominantly in the aluminosilicate matrix, so it was unclear as to the quantity of silica that would be released in these studies. In the last chapter (section 2.4.2) there was more silica present in the P.F.A. flasks than in the control flasks, showing that at least some silica can be released by P.F.A., but whether this could complex iron is unclear. However the P.F.A. did inhibit pyrite oxidation in the flasks and so was used in the pot studies.

Silicates have also been used to combat pyrite oxidation by being used to form a gel (Peeler 1963). Alkali metal silicates, such as sodium silicate, will react with the acid from the pyrite oxidation to form a silica gel, which will then act as a sealant and prevent further oxidation of pyrite by preventing contact with the air. Tyco (1971) investigated the use of sodium silicate to form a gel as well as the possible formation of ferrous or ferric silicates. The gel formation is based on the following:

$$Na_2SiO_3 + H_2SO_4 \longrightarrow (SiO_2)_n + Na_2SO_4 + H_2O$$

Silicic acid is formed when sodium silicate is neutralised below pH 10.7:

$$SiO_3^{2-} + 2H^+ \longrightarrow H_2SiO_3$$

Silicic acid is monomeric but on aging a three-dimensional structure of Si-O-Si bonds forms which sets into a gel. The pH, temperature and sodium silicate concentration will all affect the rate of these reactions (Tyco 1971).

Various soluble iron silicate complexes can be formed due to the interaction of ferric ions and monomeric silicic acid depending on the pH and the concentration of iron and silicic acid. At pH less than 3, and iron concentration less than 5 X 10^{-5}M, the mononuclear species $FeOSi(OH)_3^{2+}$ is formed. At higher pH polynuclear species will also be formed (Weber and Stumm 1965, Olson and O'Melia 1973). At higher iron concentrations, it was shown that the formation of iron silicate complexes would enhance the solubility of amorphous silica. It was proposed that at higher pH (above 3) iron oxyhydroxides would precipitate and dissociation of the ferric silicate complex would occur, resulting in a possible supersaturation of amorphous silica (Reardon 1979).

Vail (1952) stated that ferric salts would form a colloidal suspension with siliceous silicates. Hazel (1945) found that iron oxide would react with low silica concentrations to give flocculation, whilst at higher silica concentrations the iron oxide was recharged to a negative form. Hazel et al. (1949) suggested that polymerisation of the iron-silicate complexes would occur on aging, with the release of H^+ into the solution.

The sodium silicate solutions used in the flask experiments of Chapter 2 (2.4.2), and in the pot experiments of this chapter, would react with any acid present:

$$Na_2SiO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2SiO_3$$

This would then react with ferric iron, the complex formed would depend on the pH of the solution and the concentration of iron and silicic acid. Polymerisation occurred on aging when the concentration of added sodium silicate was great enough to give an alkaline reaction.

Chicken manure, woodwaste, phosphate, citrate, E.D.P.H.A., florisil, P.F.A. and sodium silicate were all used in the pot experiments (they were divided into three sets of pot experiments depending on the availability of each material). All the amendments, except sodium silicate, were used in conjunction with lime - the lime would raise the pH to a reasonable level and the amendment should stop acid regeneration by inhibiting pyrite oxidation. The sodium silicate by itself could cause an increase in the pH and therefore was not used with lime.

3.1.1 Pot Experiments

A series of pots was set up, each pot containing 520 g spoil (Baads spoil of size less than 2 mm mixed with finely ground up Baads pyrite to give approximately 3%FeS_2). The lime requirement was calculated as 21 tonnes ha^{-1} using $Ca(OH)_2$ and this translated into 21 g $Ca(OH)_2$ per pot. Each treatment was replicated four times, and each treatment was used with and without lime. The additions made were as follows:

Zero-control

Chicken maure - 5 g per pot (equivalent to 4.5 g oven dry weight)

Woodwaste - 20 g per pot (equivalent to 6.2 g oven dry weight)

Sodium dihydrogen phosphate - 1 g per pot

Trisodium citrate - 2 g per pot

E.D.P.H.A. - 0.5 g per pot

Florisil - 1.5 g per pot

The spoil and additions were mixed well in a bag before placing in the pot, each pot being made up individually.

The nitrogen, phosphorous and potassium content of the chicken manure was determined and used as the basis of the nutrient solution for all the other pots, so as to ensure that all the pots had initially the same nutrient status.

Nutrient Solution

In 500 cm^3 deionised water the following were dissolved:

75 g $NaNO_3$, 8.2 g $Ca(H_2PO_4)_2H_2O$, 1.25 g $MgSO_47H_2O$, 8.98 g KCl,

10 cm^3 of this solution was added to each of the pots, except for the chicken manure pots. This was equivalent to 20 kg Pha^{-1}, 94 kg Kha^{-1} and 250 kg Nha^{-1}.

The pots were sown with 0.1 g per pot of perrenial ryegrass and put in a growth room (average temp. 25 °C). The pots were regularly watered (150-250 cm^3 of water per week). After six weeks no growth had occurred in any of the pots. The pots were leached with 150 cm^3 of water and then allowed to dry completely. All the pots were then emptied into separate bags and well mixed. To all the unlimed pots 10.5g$Ca(OH)_2$ was added as the pH in these pots was too low to allow growth (approx. pH 2). All the pots were repacked and resown with 0.1 g perrenial ryegrass per pot. 10 cm^3 of nutrient solution was again added to each pot.

The pots were kept for one year in total (from the initial setting up). Grass did grow in the full-limed pots, but never really established itself in the half-limed pots. Approximately every two months the pots were leached with 100 or 150 cm^3 of water, the leachate collected and the grass harvested. The pH of the spoil was taken by placing a pH electrode in the top few centimetres of the spoil, but this tended to disturb the grass, so this was not done at every leaching. The leachates were analysed for acid, iron, sulphate and aluminium. Manganese was also determined in the last leachate. Aluminium and manganese were determined as these two elements are often found in toxic amounts in coal bings, as they are released into solution upon acidification of the spoil (Berg and Vogel 1973), and thus the concentration in solution can indicate the amount of acidification of the spoil which has occurred. The harvested grass was dried overnight in a 105 °C oven, cooled in a dessicator and then weighed. The grass was acid digested (by the method in Chapter 2 - 2.1.2) and the digests analysed for iron, manganese and aluminium. After the third harvest the growth in all the pots was very poor and the pots were resown with 0.15 g perennial ryegrass per pot. These pots had six leaches and five harvests in total (the results from before the initial resowing were ignored).

A second set of pots was set up using P.F.A. (this only became available later in the study). The lime rates used were again 21 g $Ca(OH)_2$ per pot and 10.5 g $Ca(OH)_2$ per pot whilst P.F.A. was used at 15 g per pot. The same nutrient solution as before was added to these pots and they were also sown with 0.1 g perennial ryegrass per pot. This set of pots had their own control pots, with the two rates of lime. They were kept in total for ten months and were resown with

0.1 g perennial ryegrass per pot after the first harvest as the growth was very poor. The leachate of these pots was analysed for silicon as well as the other constituents (manganese was measured throughout the period). These pots had five leaches and four harvests in total.

3.1.2 Effect of Various Amendments in Pot Experiments - First Set

The results of the leachate analyses, dry weight of harvested grass (for full-lime pots only) and the pH of the spoil are presented in Tables A13 (results for half-lime pots) and A14 (results for full-lime pots) in the Appendix. The analyses of the acid digests of the grass are not presented as all the values obtained for the metal concentrations were very low, with no difference between the amendments. Analysis of variance was done on all the results to test for significant differences between the effects of the different amendments (see Tables in Appendix). However due to the great variation in results for replicate pots which tended to occur (shown by large standard deviations), the analysis of variance must be treated with caution, but general trends can be noted.

There was a great difference in the results for the half-lime and full-lime pots, so they will be considered separately.

Half-Lime Pots

In the half-lime pots, the greatest difference between any of the amendments occurred in the third and fourth leachates(there was a significant difference between at least the lowest and the highest result for pH leachate, $mgH^{+}\ l^{-1}$, $mgSO_4^{2-}$ in leachate and $mgFe\ l^{-1}$ in these leachates- Table A13). Chicken manure and woodwaste pots showed the lowest acid, iron and sulphate concentrations in these leachates. Fig 3.1 shows that only chicken manure and woodwaste pots had decreasing concentrations of iron and acid by the third leach, whilst the control, E.D.P.H.A. and citrate pots showed their highest values for these products at the third leach. The phosphate and silicate pots had decreasing concentrations of iron by this leach, but the value was still very high, and the acid concentration of these pots reached a peak at the third leach. The much higher concentrations of iron for the phosphate and silicate pots, especially compared to the chicken manure and woodwaste pots, may have indicated that it was being kept in a soluble form by the phosphate and silicate. Ferric phosphate will dissociate in very acidic environments, thus releasing ferric iron into solution. The acid and iron in the chicken manure and woodwaste pots, may have been complexed onto solid constituents of the chicken manure or woodwaste and thus been retained in the spoil, which would account for the relatively low value of these constituents in these leachates. However, the initial differences in concentrations of acid and iron in the different leachates were lost by the end of the period.

Although these pots did have lime added to them (after the initial failure of growth), the lime had very little effect. The pH of the spoil and leachate was always less than 3.6 and these had all decreased by the second leach to less than 3 (apart from one spoil at pH 3.1). The grass never properly established itself, there being no growth by the second harvest (the results for the first harvest are not presented).

The results for the last leach showed significant differences for the concentrations of aluminium and manganese between the different treatments (Table A13). Both chicken manure and woodwaste pots had higher concentrations of these metals in the leachate. This was also shown for the iron concentrations, although it was not statistically significant in this case. Although this only occurred in the last

Figs 3.1-3.2 Concentration of Acid and Iron in Leachates of Pots

Fig 3.1 Half-Lime Pots

a. acid concentration

b. iron concentration

Fig 3.2 Full-Lime Pots

a. acid concentration

b. iron concentration

KEY

1 control

2 chicken manure

3 woodwaste

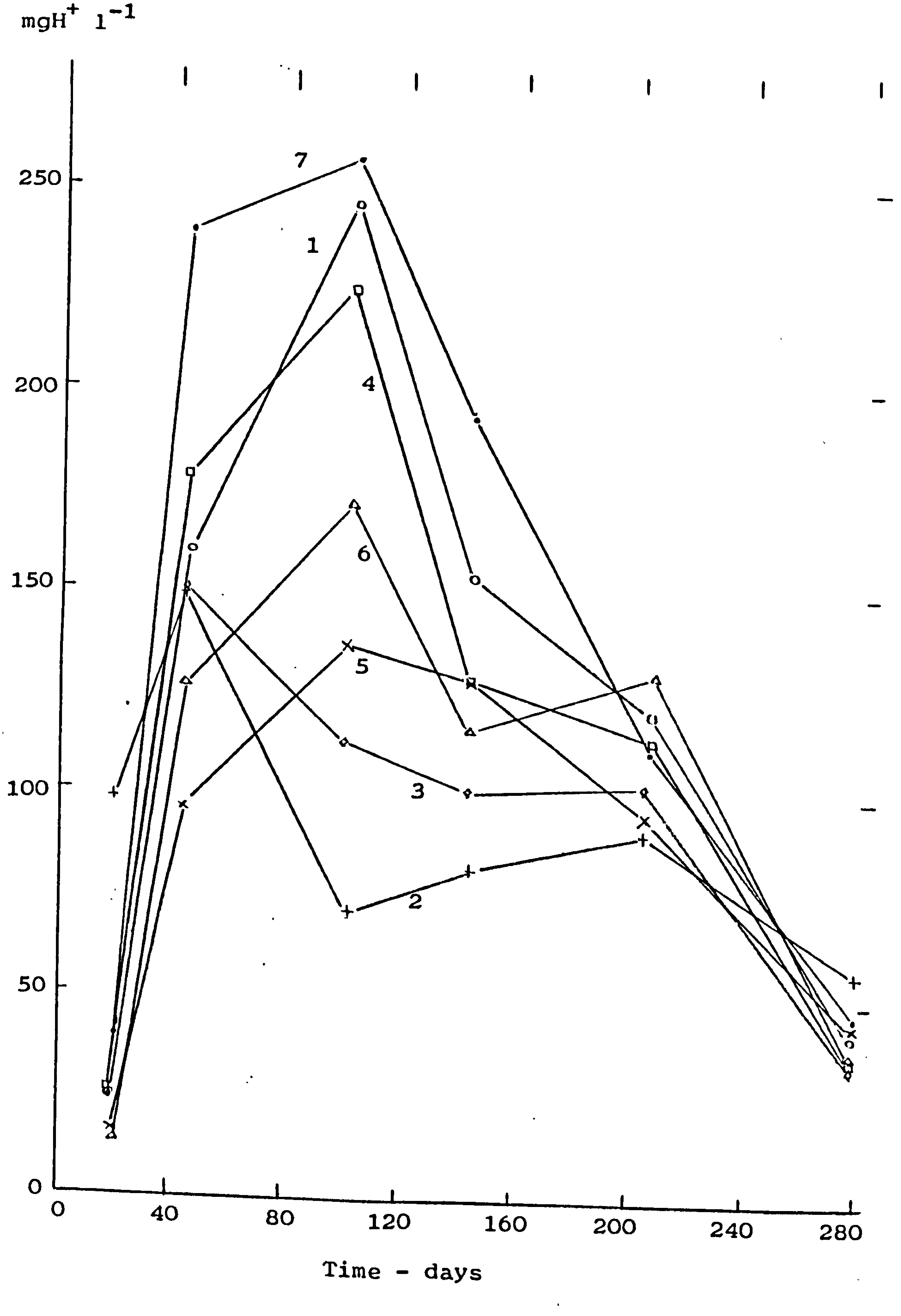
4 sodium dihydrogen phosphate

5 trisodium citrate

6 E.D.P.H.A.

7 florisil (silicate)

Fig 3.1.a.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Time - days
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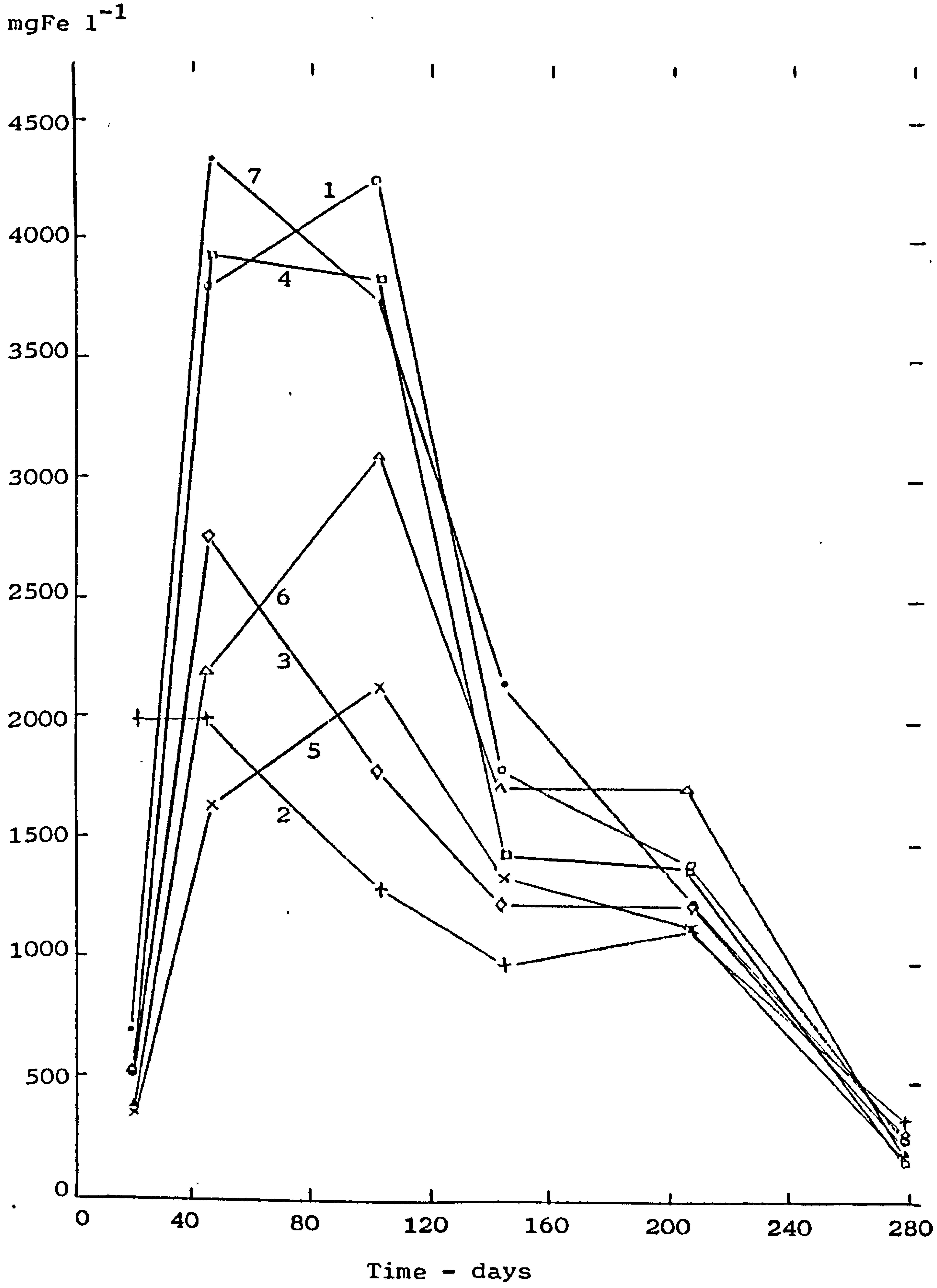
Fig 3.1.b.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1500
1000
500
0
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80
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160
200
240
280
Time - days
7
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4
6
3
5
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PAGE

NUMBERING

AS ORIGINAL

Fig 3.2.a.

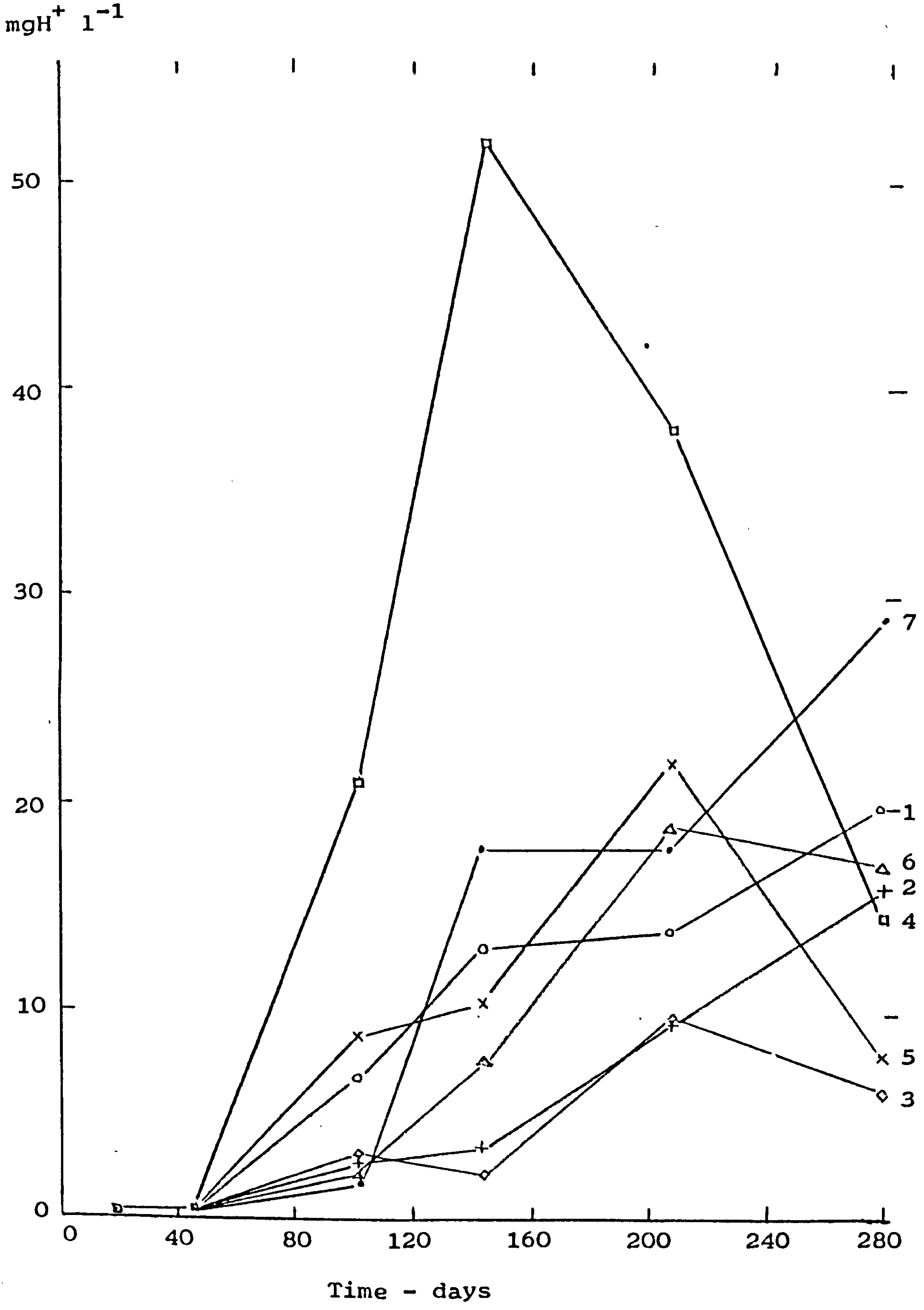
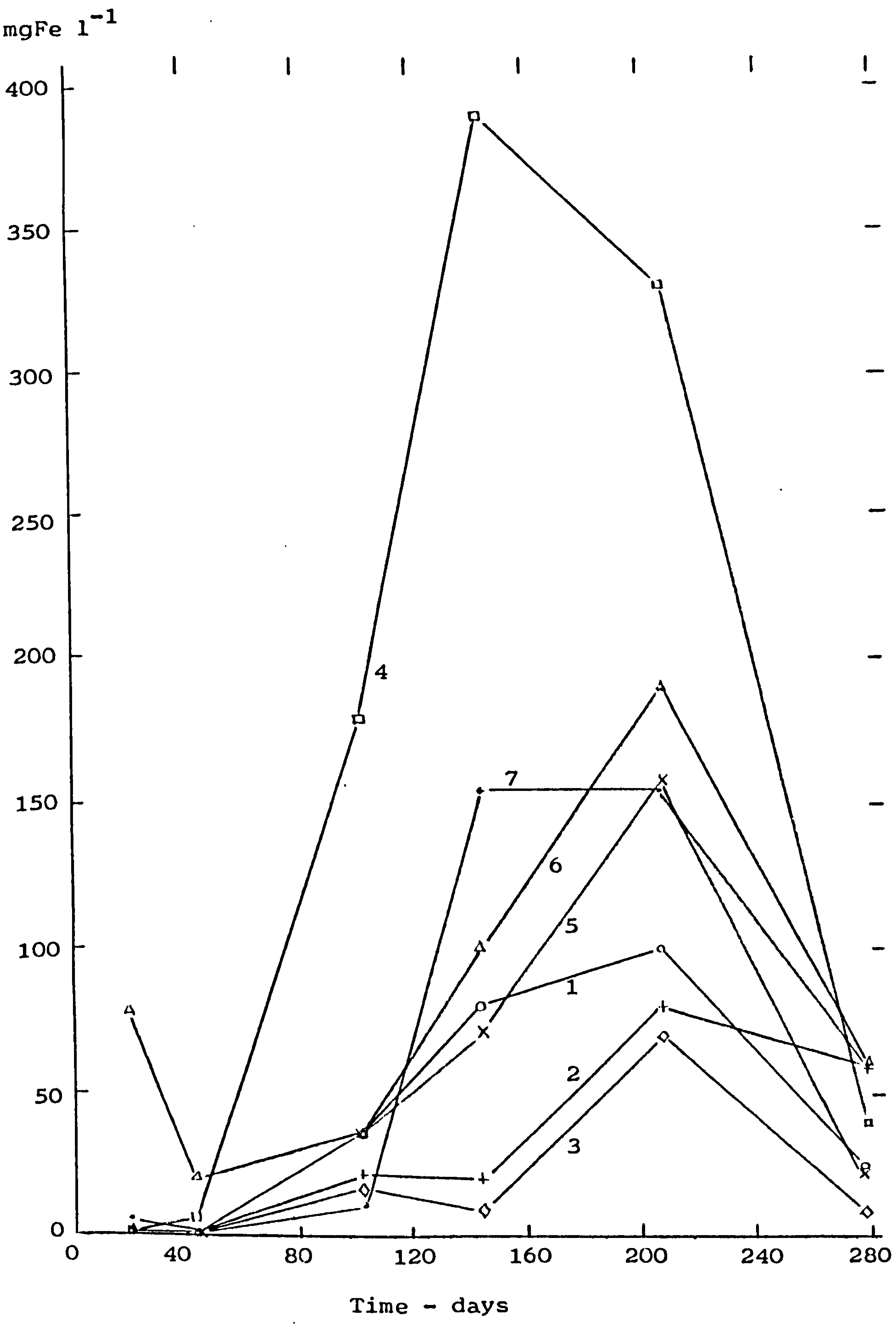

mgH$^+$ l^{-1}
0
10
20
30
40
50
0
40
80
120
160
200
240
280
Time - days
7
1
6
2
4
5
3

Fig 3.2.b.


mgFe l^{-1}
400
350
300
250
200
150
100
50
0
0
40
80
120
160
200
240
280
Time - days
4
7
6
5
1
2
3

leachate, and consequently it should not be given too great an emphasis, various possibilities for the increased concentrations can be proposed. As postulated above for iron, the solid constituents of the chicken manure and woodwaste may have complexed these metals, but by the end of the period the complexes may have been broken down due to the acid present in the pots, and thus the metals would have been released into the leachates. Alternatively the metals may have been complexed by soluble constituents of the chicken manure or woodwaste, and a proportion of these complexes may have been chelated onto solid constituents of the waste amendments, but were eventually leached out of the pots. Obviously with such a great variation in the pots, it is impossible to draw direct conclusions from the results, but the general trends of the metals in the different leachates are worth noting.

None of the amendments had a great effect on the pyrite oxidation. At such low pHs, as was the case in all these pots, the ferric iron oxidation of pyrite would be predominant. Although the acid production (shown in the leachate) was reduced in the chicken manure, woodwaste, citrate and E.D.P.H.A. pots compared to the other pots for the first part of the period, the pH of the spoil was very low in all the pots throughout the period. By the end of the period the concentration of acid, iron and sulphate in all the leachates was decreased, indicating a decrease in the pyrite oxidation rate, probably due to restricted diffusion of air into the pots.

Full-Lime Pots

Grass grew in all the full-lime pots. The pH of the spoil was maintained above 6 for the majority of the pots, but the pH of the leachates started to decrease by the third leach, and by the fith leach it was very low in all cases (Table A14). This difference between the pH of the spoil and the pH of the leachate has been found before (Trafford et al, 1973, Rimmer and Colbourn 1978). Trafford et al proposed that the soil surrounding the drainage channels was much more acidic than the bulk of the soil, causing the difference in the pH. The phosphate flasks showed very high iron, sulphate, aluminium and acid concentrations, at leach 4 (Table A14). The concentration of iron in the phosphate flasks started to decrease after leach 4, whilst in the other flasks it did not decrease until after the fifth leach (Fig 3.2.b). The chicken manure, silicate and control pots all had increasing acid concentrations throughout the period, whilst the other amendments had a decreased acid concentration by the end of the period (Fig 3.2.a). Overall both the chicken manure and woodwaste pots showed decreased acid, iron and aluminium concentrations compared to the other pots.

The dry grass weights reflect the difference already noted between the phosphate and the rest of the pots. The phosphate and control pots showed less growth than the other pots until the last harvest. Both the third and fourth harvests show significant differences between the grass weights. In the fourth harvest Scheffe's Least Significant Difference Test showed that the grass weight for the control and the phosphate pots was significantly different to that of the chicken manure pots. Although there was not a great difference between the harvest weights by the end of the period, the additive weights do show some differences between the treatments. Fig 3.3 shows mean ± standard deviation for all harvests added, first three harvests added and last two harvests added (it is divided in this way as the second resowing occurred after the third harvest). It can be seen that the phosphate and control pots consistently showed the poorest growth. Initially the citrate and E.D.P.H.A. pots had the best growth but then the chicken manure pots had better growth. Overall

Fig 3.3 Dry Weight of Harvested Grass from Full-Lime Pots

Fig 3.3.a All Harvests Added Together

Fig 3.3.b First 3 Harvests Added Together and Last 2 Harvests Added Together

Results are presented as mean ± standard deviation for each group of four pots.

KEY
1 control
2 chicken manure
3 woodwaste
4 sodium dihydrogen phosphate
5 trisodium citrate
6 E.D.P.H.A.
7 florisil (silicate)

Fig 3.3.a.

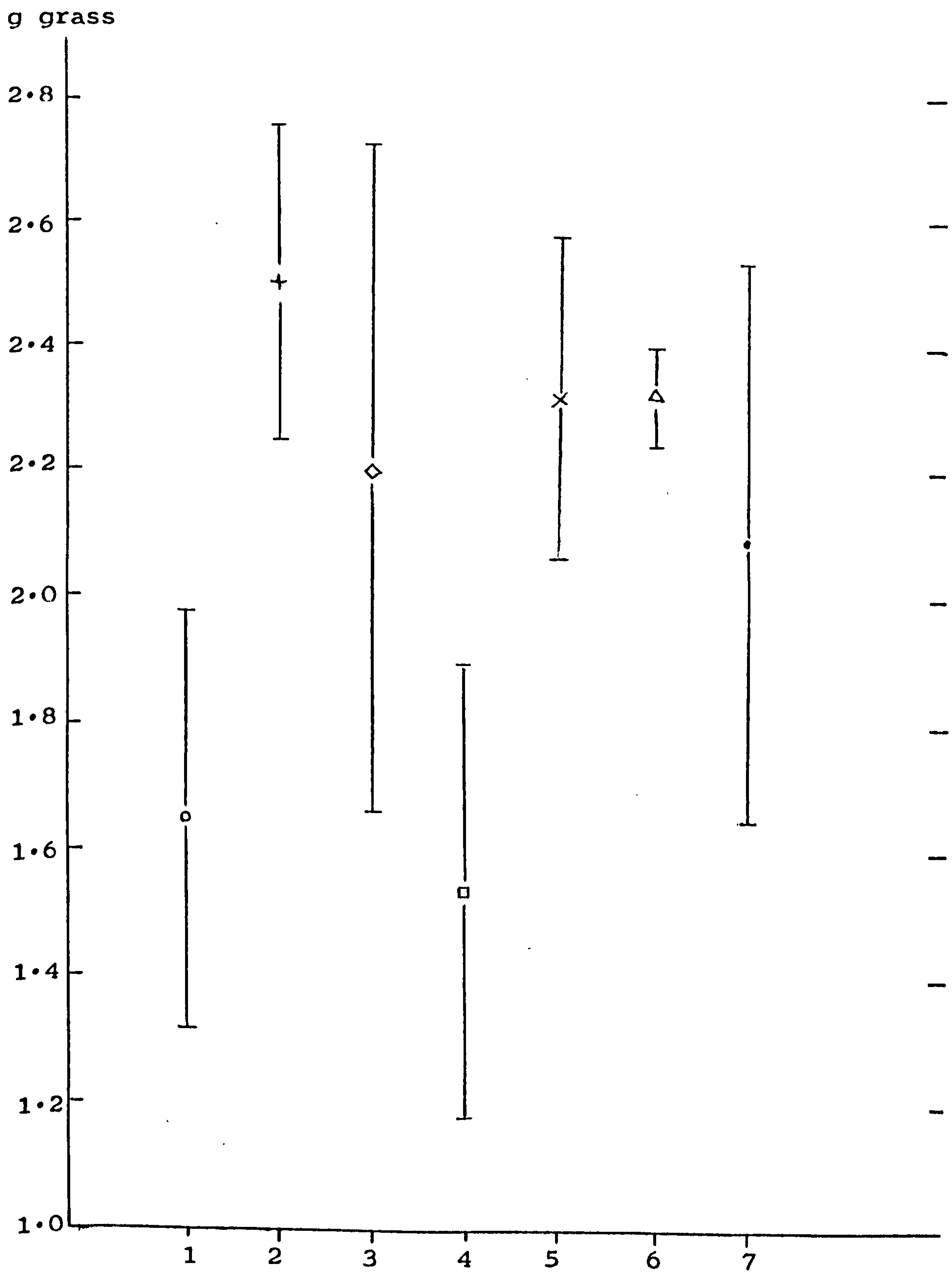
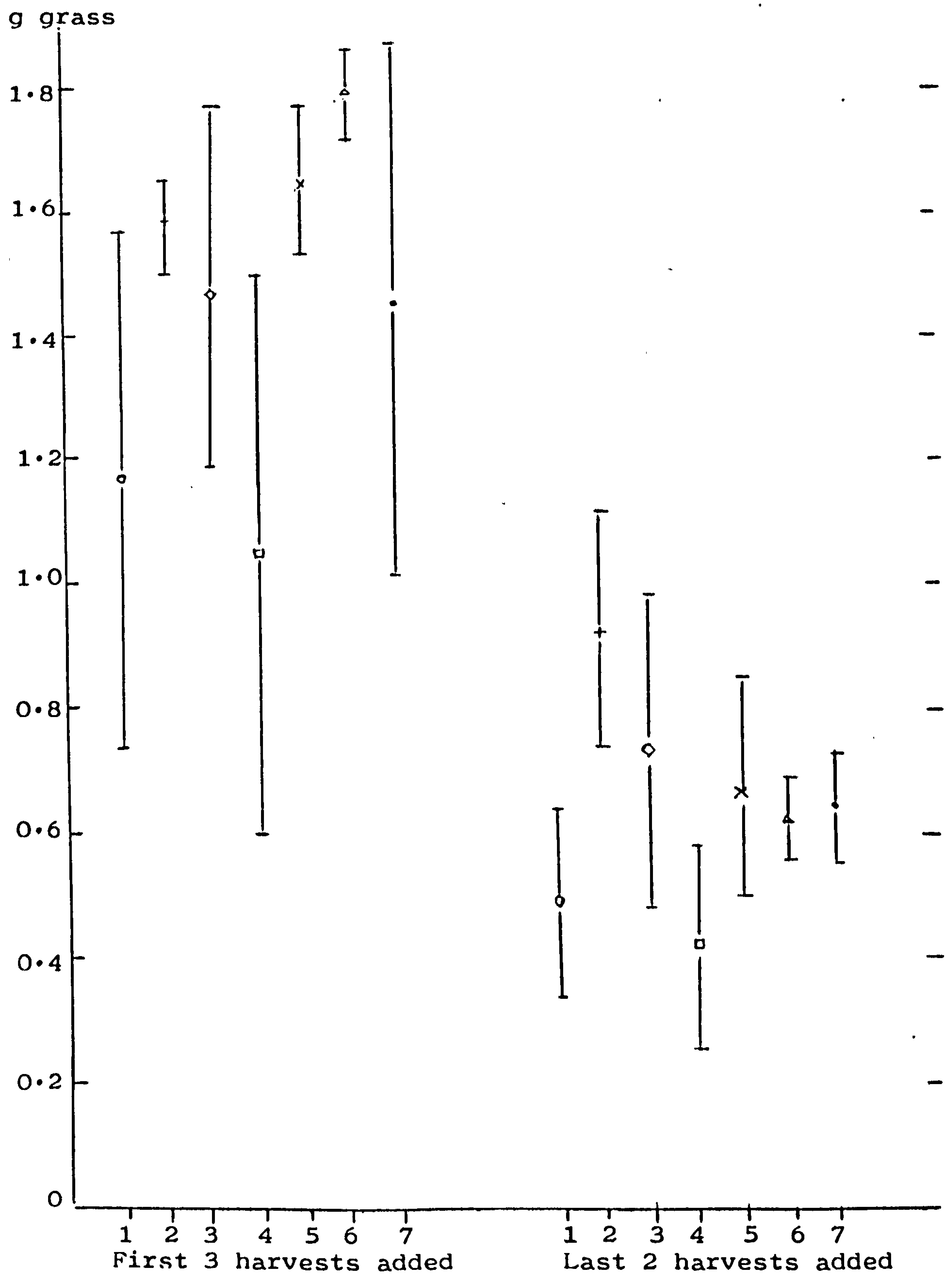


Fig 3.3.b.


g grass
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
1 2 3 4 5 6 7
First 3 harvests added
1 2 3 4 5 6 7
Last 2 harvests added

the chicken manure showed the best growth, phosphate and control pots showed the worst, with all the other amendments being approximately equal. The results for the last two harvests added show chicken manure and woodwaste to have slightly improved growth over all the other pots. As the woodwaste does not contain any nutrients, this improved growth cannot be attributed to the difference in nutrient status of the different pots (chicken manure contains nutrients that would only slowly be released, compared to the nutrient solution that was added to the pots). The slightly better growth in the chicken manure and woodwaste flasks corresponds to the generally lower acid and iron levels in the leachates of these pots compared to the leachates of the other pots. Therefore it would seem that the chicken manure and woodwaste were having a beneficial effect on the growth of the grass, but it is not possible to attribute this affect directly to a reduction in pyrite oxidation, due to the variation in the results of the analyses of the leachates. However, the reduced acid and iron levels, together with the better growth, may indicate some inhibibition of pyrite oxidation occurring in these pots. Chicken manure and woodwaste would also be expected to complex some of the aluminium and manganese released into the leachate due to acidification of the spoil.

The citrate, E.D.P.H.A. and silicate pots all had better growth than the phosphate and control pots, corresponding to the decreased iron, aluminium and acid levels in these pots compared to the phosphate pots (although not the control pots).

The phosphate plus lime enhanced the acid, iron and aluminium production, with consequently very poor growth of grass. The phosphate was added in the form of sodium dihydrogen phosphate which is slightly acidic, but it would not be expected to have such a great effect as this (its effect in the flasks was negligible). Although ferric phosphate can dissociate at low pH, the increased acid, iron and aluminium concentrations compared to the control pots would not be expected and the reason for it was unclear.

pH of Spoil

After the final leach and harvest the pots were destroyed and the spoil air-dried. The pH and titratable acidity were measured on the top and bottom half of the pots separately (the titratable acidity was measured by shaking 10 g spoil in 50 cm^3 deionised water for one hour, filtering the contents of the flask and titrating 5 cm^3 of this with standardised sodium hydroxide). All the limed pots had a pH of greater than 7, both top and bottom, there being no real difference between the amendments. All the half-lime pots had a pH between 2.8 and 3.1 and all had similar titratable acidity results. These results correspond to the pH of the spoil taken before destroying the pots and confirm that in the case of the full-lime pots the bulk spoil must have been considerably less acidic than the spoil surrounding the drainage channels (Trafford et al 1973), shown by the difference between the spoil pH and leachate pH.

It is obvious that none of the amendments were very successful at inhibiting pyrite oxidation. This is suprising considering the results of the flask experiments where these amendments were all successful at inhibiting the pyrite oxidation. There are obviously great differences between the situation in the flasks and that in the pots and this may explain the differences in the results. Obviously in the flasks the pyrite and amendment can make good contact, which will not be necessarily the case in the pots due to the ratio of amendment to spoil. It is quite possible that pyrite oxidation could occur in one area where there is no amendment, allowing an accumulation of acid in one area which could then affect other areas. If it was a soluble part of the amendment which complexed the iron, it may have been quickly leached out of the system and therefore was not effective, whereas in the flasks it would obviously not be leached away. The difference in different areas in the spoil is shown by the difference in the pH of the leachate and the spoil - obviously there was an accumulation of acid around the drainage channels which did not occur in the bulk of the spoil.

3.1.3 Effect of P.F.A.

The results for the P.F.A. pots are presented in Tables A15 and A16 in the Appendix. The results for the analyses of the acid digests of the grass are not presented due to the very low metal concentrations recorded. There was again great variance between the results for the replicate pots.

The analysis of variance for the half-lime pots (Table A15) showed very few significant differences. The concentrations of aluminium and manganese tended to be greater in the P.F.A pots than in the control pots, probably due to these elements being released from the P.F.A.. The concentration of silicon in the P.F.A. and control pots was very similar, suggesting that silica was not being released from the P.F.A. (if it was being released from the P.F.A. and then combining with the iron, as hoped, then a difference in the iron levels in the P.F.A. and control pots would have been expected, which did not occur).

In the full-lime pots, the P.F.A. pots tended to show higher acid, iron, aluminium and manganese concentrations than in the control pots (Table A16). The alkaline nature of the P.F.A. would be expected to decrease these concentrations, compared to lime alone. However, the higher metal concentrations could be due to there being released from the P.F.A., but this does not account for the increased acid production. The pH of the spoil was much higher than that of the leachate by the end of the period, as observed for the last set of full-lime pots.

The growth in the P.F.A. pots was better than that in the control pots. For the second harvest (at the third leach) there was a significant difference in the harvests of the P.F.A. and the control pots (this was reflected when all the harvests were added together). Therefore, even though the P.F.A. pots showed higher acid and metal concentrations than the control pots, the growth in the P.F.A. pots was greater than in the control pots.

Obviously the P.F.A. did not effectively inhibit the pyrite oxidation. This may have been due to the fact that silica was not being released from the P.F.A., and thus did not complex or precipitate the iron, or it may have been due to inadequate contact between the pyrite and P.F.A.. The increased growth of grass in the P.F.A. pots may have been due to the ash supplying essential micronutrients to the grass. Fail and Wochok (1977) found improved soy bean growth on acidic colliery spoils amended with fly ash and attributed it to increased porosity and soil moisture, as opposed to an increase in the pH, as the amount they had applied would only have increased the pH by 0.1. However, they used much greater quantities of fly ash in their study than used in these pots (7-8 cm of fly ash mixed into the top 15-20 cm of spoil), and the amount used in these pots would not have had such a great effect on the spoil physical properties.

3.1.4 Effect of Sodium Silicate

The sodium silicate solution was not obtained until towards the end of the project, so a long term pot experiment using this was not possible. However as the use of the sodium silicate in the flask experiments had been successful in maintaining the pH, a short term pot experiment was set up. Pots were prepared containing Baads spoil of less than 2 mm size with added Baads pyrite (less than 150 µm) to give 1%FeS_2. Sodium silicate solution of the following silicon concentrations were added, 200 cm^3 of each solution being used: 2%Si, 1%Si, 0.1%Si.

Control pots were also prepared, 200 cm^3 deionised water being added to these. There were three replicate pots for each silicate concentration. These were placed in the open so that they would be watered by the rain. Each pot was placed in a beaker so that the pH of the leachate could be measured at regular intervals. The leachate was discarded after the pH had been measured. Occasionally the spoil pH was also measured by placing the pH electrode in the top of the spoil.

The leachate of the pots containing the highest silicate concentration maintained a reasonably high pH up till day 78 (Fig 3.4), but the other silicate concentration pots maintained a high pH for a shorter length of time. Although the pH of the leachate in the highest silicate concentration pots decreased to about pH 3 by the end of the period, the pH of the spoil was still about 5 (Table A17 in the Appendix). However, if the pots had been left for a longer period, the pH of the spoil in these pots would probably have decreased to the same level as the pH of the spoil in all the other pots. Obviously the silicate solution was being leached out of the pots. Initially all the leachates from the treated pots were red, but only the highest silicate concentration pots had red leachates by day 85, and this was clear by the last day. Therefore the highest concentration silicate solution had the longest lasting effect, but it was not permanent.

Fig 3.4 pH of Leachate of Pots, with Added Sodium Silicate Solutions of Different Concentrations.

Results are presented as mean of leachate pH for each group of pots on each sampling day.

KEY

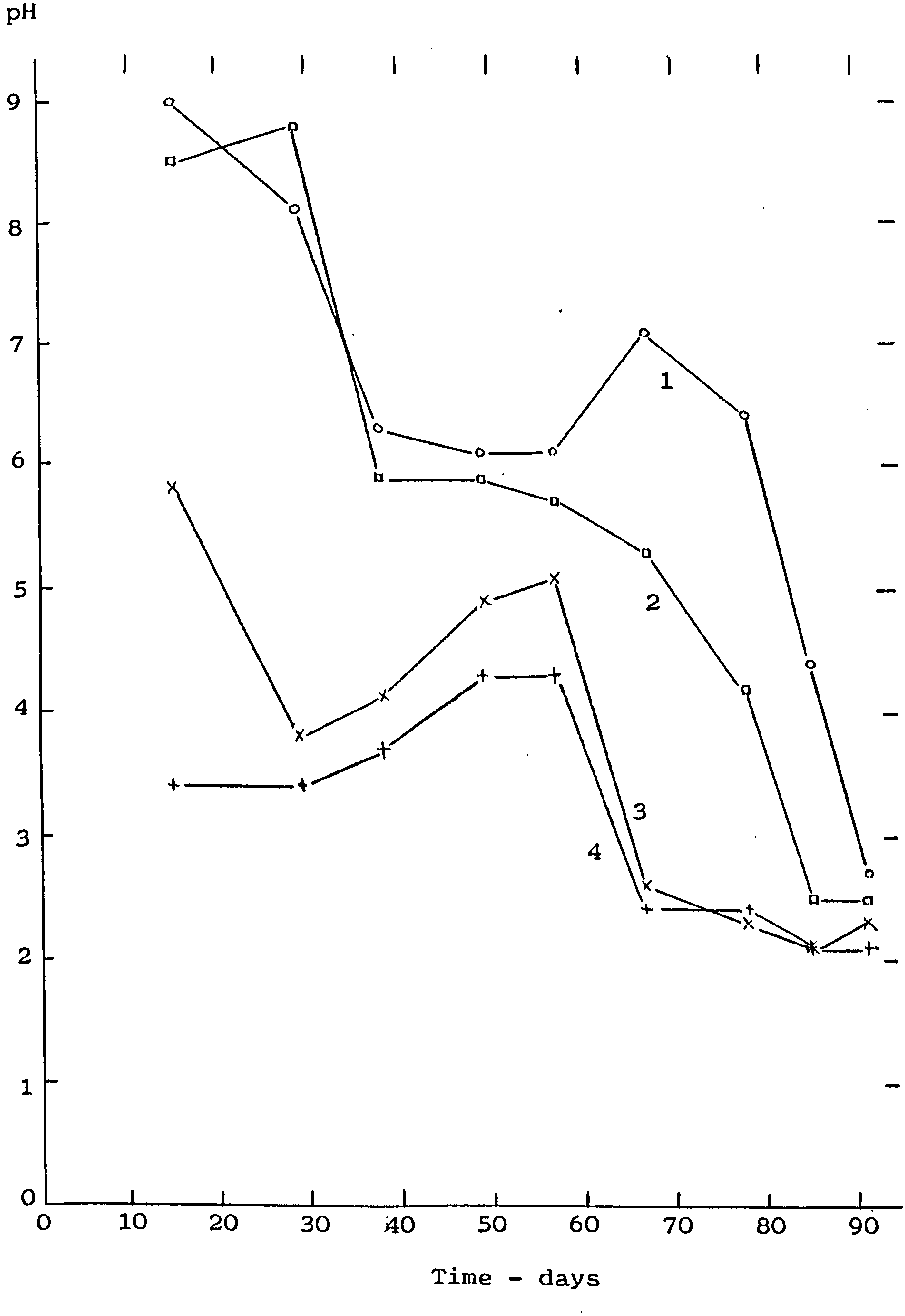
1 2% Si

2 1% Si

3 0.1% Si

4 control

Fig 3.4.



The situation in these pots was again different to the flask experiments. In the flasks the silicate solution was not leached, whereas in the pots it was. Tyco (1971) investigated the use of sodium silicate to neutralise the acid content of a spoil, and to form a gel to prevent water contacting the spoil. They found a silica/alumina gel formed within the spoil pile was most effective at reducing the acid and iron content of the spoil leachate. The combination of sodium silicate and sodium aluminate formed a more stable gel than sodium silicate alone, which used by itself was gradually washed out of the spoil pile(as was found in these pots). The good results obtained by Tyco using a silica/alumina gel would suggest that this was an adequate way to reduce the acid mine drainage of a spoil. However, they did not try to establish vegetation on the spoil. The roots of any vegetation would obviously disturb the gel in the interior and the surface of the spoil. Their treatment was based upon the prevention of contact between rainwater and the spoil particles by the formation of a gel, and thus any root system would presumably stop the gel being effective.

3.1.5 Conclusions

The laboratory flasks studies (Chapter 2) showed that pyrite oxidation could be inhibited by reducing the participation of the ferric iron in the oxidation. This was achieved by complexing either ferrous or ferric iron, or by precipitating ferric iron, using specific chemicals as well as waste materials. The attempts to inhibit pyrite oxidation in a more realistic setting - pot experiments - were not so successful. However, there was better growth of grass in the amended and full-limed pots (except phosphate pots) than in the control full-limed pots.

The different conditions in the pot experiments compared to the flask experiments were probably responsible for the apparent failure to inhibit pyrite oxidation. In the pot experiments, only low rates of amendments were used which would have led to inadequate contact between the amendment and pyrite, whilst in the flask experiments good contact between the pyrite and amendment would have occurred. Soluble constituents of the amendment would have been leached away in the pot experiments and thus their ability to have complexed or precipitated iron would have been lost, which obviously would not have happened in the flask experiments. The use of high rates of amendments was not investigated, but this might have overcome these problems.

The alternative to inhibiting pyrite oxidation is to treat the acidic spoil with lime to raise the pH to about 6. Obviously if the pH is maintained at a reasonably high level, then the oxidation of pyrite by ferric iron will be stopped and only the slow oxidation of pyrite by air will occur. However, normally acid regeneration occurs in limed pyritic spoils, and thus the ferric iron oxidation of pyrite can recommence. The use of lime in treating pyritic spoils will be discussed in the next chapter.

CHAPTER 4

Liming of Pyritic Colliery Spoil

4.1 Introduction

Lime is normally applied to acidic colliery spoil in order to increase the pH to a level which will allow the growth of vegetation. The increase in pH will obviously also inhibit the pyrite oxidation - by inhibiting the activity of *T. ferrooxidans* and by causing the precipitation of ferric iron, thus reducing the oxidation of pyrite to that by air alone. However, acid regeneration does occur on limed spoils, which causes *T. ferrooxidans* to become active and the ferric iron oxidation pathway of pyrite to dominate as the pH falls to below about 3.5. There are various other problems, as well as that of acid regeneration, related to the use of lime in reclamation schemes and some of these will be discussed in this chapter. Although no long term studies were established to study the various effects of lime, a few short term laboratory experiments were done which are relevant to the discussion on liming.

4.1.1 Lime Requirement of Pyritic Spoils

The amount of lime used in reclaiming pyritic spoil is normally based on the lime required to neutralise the existing acidity alone, or this plus an allowance for the amount of potential acidity due to the pyrite in the spoil. The lime requirement test measures the amount of lime required to raise the pH of the spoil to a certain pH, normally about 6. This is often done by shaking a known amount of spoil with different concentrations of lime water and measuring the resultant pH (this was the method used in this study). The amount of lime required is then calculated normally assuming a 15 cm plough layer. The potential acidity is determined by calculating the pyrite content (normally by the method in Chapter 2), and for every 1% of pyrite present 40 tonnes ha^{-1} of agricultural limestone need to be added to neutralise the acidity that can be produced by the oxidation of the pyrite. This is again based on neutralising the acid in the top 15 cm of the spoil. However, in some spoils there is neutralising capacity due to the presence of native carbonates (Caruccio 1978, Caruccio and Pelletier 1980, Caruccio et al. 1981). Bicarbonates ions are actually produced at the time of pyrite formation, and these may be retained within the spoil as carbonates providing neutralising potential, or they may have been leached away (van Breemen 1973). The acid neutralising capacity (ANC) can be determined (Costigan et al. 1981) and for every 1% of calcium carbonate equivalent or ANC the lime requirement can be reduced by 23t ha^{-1} (again based on a 15 cm layer of spoil). However the latter authors also recommended that the spoil should be limed down to a depth of 45 cm, as opposed to 15 cm to prevent subsoil acidification. If there is no ANC present in the spoil and a reasonably high pyrite content (over 1%) then rather high rates of limestone will be required, for example, Costigan et al. (1981) calculated that one spoil in Lancashire would require 280t ha^{-1} of lime for liming down to a depth of 45 cm (92t ha^{-1} for liming down to 15 cm). Obviously the cost of applying lime down to 45 cm would increase the overall cost of the reclamation.

4.1.2 Problems Associated with Liming

The use of high rates of lime does not guarantee that the spoil will not reacidify. Costigan et al. (1981) reported that spoils limed at 50t ha^{-1} reacidified after one year and another spoil reacidified within two years having been limed at 100t h^{-1}. Doubleday (1974) found that four applications of limestone totalling 100t ha^{-1} over two years was inadequate to neutralise the acidity in one spoil. Maclean and Dekker (1976) found that spoils containing greater than 4% pyritic sulphur would reacidify even when very high rates of limestone were applied. The reacidification of the spoil is due to the oxidation of the pyrtie in the spoil.

If reacidification of the spoil does occur, whether or not high rates of limestone have been applied, then the spoil must be relimed, as any vegetation which has been established will die.

If vegetation has been established on the spoil then lime cannot be ploughed in without destroying the vegetation. However, it has been found that surface dressings of lime do not penetrate the spoil and thus do not increase the spoil pH (Bloomfield et al.1982). Calcium carbonate is not very soluble and the leachate from the limed surface into the spoil will not contain any more alkalinity than a saturated solution of calcium carbonate (approximately 5 me l^{-1} at atmospheric carbon dioxide level, Costigan 1979), and therefore the effect on acidic spoil would be negligible.

Both coarse and fine ground limestones are used to overcome actual and potential acidity in pyritic spoils. Finely ground limestone used at high rates tends to inhibit growth more than coarsely ground limestone used at high rates (Gemmell 1981). However low rates of coarsely ground limestone do not tend to promote growth. These differences are due to the different dissolution rates of the limestones - coarsely ground limestone has a slower dissolution rate than finely ground limestone due to its smaller surface area. However the long term neutralising capacity of both materials is equivalent (Jefferies 1981). Coarse ground limestone can also become coated with a thin later of iron oxide thus making it unavailable for neutralising acidity (Barnhisel et al.1982).

Liming can cause various nutrient imbalances which will inhibit any growth on the spoil. The application of large amounts of calcium (as lime) can cause a magnesium deficiency in plants - due to a competitive effect between the two ions (Jeffereies 1981, Costigan et al. 1982). The latter authors suggested that this could be overcome by substituting magnesian limestone instead of calcite limestone (they also suggested that this would increase phosphate availability by reducing the addition of calcium ions and the beneficial effect on plant growth of magnesian limestone could be due to this as opposed to the greater availability of magnesium ions). Phosphate deficiencies are found in both limed and unlimed spoil (Costigan et al. 1982). At low pH phosphate can be precipitated by both iron and aluminium whilst at higher pH chemisorption can occur at the surfaces of iron and aluminium oxides and of calcium carbonate. Liming acidic colliery spoil will cause iron and aluminium species to be precipitated as amorphous oxides of high surface area onto which phosphate can be adsorbed. High liming rates will result in a large amount of free calcium in the spoil, which can also contribute to phosphate adsorption. Liming may also cause trace metal deficiencies - some metals are insoluble at higher pH's and therefore are not available for uptake by plants - for example, possible iron deficiencies have been reported when high rates of lime are applied to spoils (Gemmell 1973).

4.2 Factors Affecting the Rate of Lime Application

There are various assumptions underlying the use of lime in reclamation schemes. Two of these are that the spoil is homogeneous with respect to acid neutralising capacity as well as pyrite content, and that high rates of limestone will have a longer lasting effect than lower rates in maintaining the spoil pH. These two assumptions will now be discussed.

4.2.1 Variation in Spoil Composition

Part of the bing at Baads (where much of the pyrite used in this study was obtained) had reacidified after the initial reclamation. This showed that some areas of the bing had a higher pyrite content than other areas, which would be expected as different parts of the bing may have been dumped at different times and different types of material may have been dumped. The regrading of the spoils would not necessarily have redistributed all the spoil material evenly throughout the bing. A small area of the bing was studied in detail to ascertain the variation in acid and pyrite content. A 50 cm by 50 cm area was divided into a grid of 100 squares (each square was 25 cm^2). A sample was removed from the surface of each square (approximately 20 g), air dried and then ground up in a ball mill. Pyrite determinations were done on duplicate samples for each square. Titratable acidity was also measured - duplicate 5 g samples were shaken with 50 cm^3 of deionised water for one hour and the filtrate was titrated with standardised sodium hydroxide.

Table 4.1 shows the great variation of pyrite and acid distribution in the square. High pyrite areas can easily be identified, for example, column J, rows 4-9 and continuing into columns I and H. Areas with higher acid concentrations than the rest of the area can also be identified, for example, square A5. The pyrite exists as nodules or veins in the spoil material and thus the spoil cannot be adequately sampled to obtain a representative sample. This is shown by the very varying pyrite contents in this sampling. Also some areas of a bing may have a much higher overall pyrite content (shown by only some areas of a bing reacidifying) which may be missed in the sampling, which could

$\%\mathrm{FeS}_2$

	A	B	C	D	E	F	G	H	I	J
1	1.0	0.5	0.4	0.5	1.1	1.7	1.0	0.8	0.5	1.5
2	0.7	0.8	0.7	0.9	1.1	0.4	1.4	1.0	0.6	0.4
3	1.1	0.8	0.7	0.2	4.2	2.8	0.6	1.1	2.5	0.7
4	0.8	0.6	0.4	0.8	0.7	2.3	0.9	0.8	0.4	1.6
5	6.6	0.6	1.6	1.2	0.9	0.6	0.7	0.1	0.8	1.6
6	1.4	1.4	1.0	0.4	0.3	1.1	0.6	0.4	0.8	1.9
7	1.7	0.3	1.0	3.0	0.9	1.2	3.5	2.3	2.9	1.4
8	1.3	1.0	0.4	0.3	1.0	0.5	0.9	0.3	3.0	3.8
9	1.1	0.6	1.1	2.6	0.7	0.4	1.5	1.5	0.5	4.6
10	0.7	1.0	0.9	1.3	1.2	0.4	1.7	1.7	1.8	0.5

Samples taken at 5 cm intervals. No large lumps of pyritic spoil picked up.

Table 4.1 Variation in Pyrite and Acid Content in a 50 cm by 50 cm Area of Baads Bing.

$\mu g\ H^+\ g^{-1}$

	A	B	C	D	E	F	G	H	I	J
1	65	36	12	12	12	12	10	8	10	10
2	23	16	8	10	8	8	10	8	18	18
3	23	8	8	8	8	12	8	10	27	39
4	18	12	14	12	8	3	10	14	48	52
5	35	20	12	12	10	8	14	16	10	15
6	17	17	8	8	8	8	8	8	12	28
7	18	41	15	16	8	12	12	14	12	12
8	16	12	23	16	16	10	8	14	14	14
9	12	18	14	8	8	8	10	14	14	18
10	12	13	12	10	10	8	20	33	33	19

Samples taken at 5 cm intervals. No large lumps of pyritic spoil picked up.

Table 4.1 cont. Variation in Pyrite and Acid Content in a 50 cm by 50 cm Area of Baads Bing.

lead to an underestimate of the amount of lime required to neutralise the potential acidity. However if areas of lower pyrite content receive the amount of lime calculated for an area of high pyrite content, then they will obviously be overlimed. Even if areas of high pyrite content could be identified, the addition of large amounts of lime to these areas would be totally impractical in normal large scale reclamation schemes.

4.2.2 Use of Different Rates of Lime

A series of pots containing spoil from two different bings, Foulshiels and Auchencruive, which had pyrite contents of approximately 0.2%, had been set up as a long term study on liming rates. The experiment was monitored over its later stages as part of the present project.

The two spoils had been limed at different rates, each rate being used on three pots for each spoil. The rates of lime used were equivalent to 0, 10, 20, 30 and 40t $CaCO_3$ ha^{-1}. The pots were regularly watered and the spoil pH measured by placing a pH electrode in the top few cm of the wet spoil. After day 155 for Foulshiels spoil and day 75 for Auchencruive spoil the pots were no longer watered regularly, but measurements were still taken at irregular intervals, after thoroughly watering the pots.

The results are presented as the average pH reading for each lime rate in Table 4.2. Both the spoils were quite acidic (shown by the zero lime rate). Initially the different lime rates raised the pH to different levels. However this was only a temporary effect, the pH for all the lime rates dropped to approximately the same value. For Foulshiels waste there was less than one pH unit difference between the lowest (excluding zero) and highest lime rates by day 100. For the Auchencruive waste there were no measurements made between day 75 and day 229, Foulshiels Spoil - pH

Lime Rate ($t\,CaCO_3 ha^{-1}$)	Day	7	15	33	47	56	75	100	112	120	126	133	147	155	309	338	463
0		3.9	2.4	2.8	3.9	3.4	3.4	3.3	3.6	3.7	3.8	3.6	3.6	3.6	3.8	3.7	3.4
10		8.8	8.2	8.2	8.0	7.4	7.6	7.6	7.7	7.8	7.9	7.7	7.8	7.9	7.5	7.6	7.3
20		10.1	9.9	8.4	8.9	8.0	8.1	7.9	7.9	7.8	8.2	7.9	7.9	8.0	7.5	7.6	7.5
30		11.6	11.3	9.3	9.0	9.3	8.9	8.0	8.1	8.4	8.4	8.3	8.1	8.3	7.6	7.7	7.4
40		11.7	12.0	9.9	9.3	9.7	9.5	8.1	8.4	8.8	9.3	8.7	8.7	8.4	7.7	7.8	7.5

Auchencruive Spoil - pH

Lime Rate ($t\,CaCO_3 ha^{-1}$)	Day	20	32	40	46	53	67	75	229	258	283
0		3.4	3.2	3.6	3.1	3.2	3.1	3.4	2.8	3.5	3.6
10		8.0	7.7	7.5	7.5	8.0	7.9	7.8	7.2	7.6	7.4
20		8.6	9.3	9.1	8.6	9.1	8.9	8.6	7.5	7.7	7.5
30		10.3	10.7	10.6	10.2	10.1	10.3	10.1	7.6	7.8	7.5
40		10.0	10.3	10.7	10.5	10.4	10.3	10.2	7.8	7.7	7.6

Table 4.2 Effect of Different Rates of Lime on Spoil pH

and the pH of the higher lime rates obviously dropped between these days, there being very little difference between the pH measurements by day 229. These results suggest that although a high liming rate may initially increase the pH to a greater extent than a lower liming rate, this effect is only temporary. After about three months the pH of all the limed pots was similar and thus the effect of the high rate of lime was lost. Baads spoil limed at two different rates - 25 and 50 t ha^{-1} showed no difference in spoil pH or yield of grass after two growing seasons (J. Devlin, personal communication), again showing that higher rates of lime do not necessarily benefit the spoil. These two spoils (Foulshiel and Auchencruive) are quite representative of the pyritic spoils found in Central Scotland, i.e., a pH of about 3 and average pyrite contents of about 0.2%. In spoils of higher pyrite content, the pH would drop much quicker than in these spoils and the resultant final pH be much lower, too low to allow the establishment of vegetation.

Therefore high rates of lime may not be particularly effective at maintaining the spoil pH at a reasonable level longer than lower rates of lime. It may therefore be more practical to apply enough lime to raise the pH to about 6, and then, in the aftercare of the site, small amounts of lime should be applied to maintain the pH at a reasonable level. Once vegetation had been established and a reasonable soil built up, the continued application of lime should be unnecessary. However, it is difficult to apply lime effectively to a reclaimed site without damaging any established vegetation.

4.3 Use of Lime Water as Opposed to Dry Lime

The application of lime after vegetation has been established tends to be ineffective without the ripping up of the vegetation to allow proper incorporation of the lime. The next experiments investigated different methods of applying lime, either as dry lime or in solution, and their success at maintaining a reasonable spoil pH.

4.3.1 Effect of Lime Water on Spoil pH

Glass columns containing 40 g spoil were prepared - Baads spoil, less than 2 mm in size, with added Baads pyrite, less than 150 μm, to give a pyrite content of 4% was used. The lime requirement of the spoil was determined to ascertain the weight of calcium hydroxide or calcium carbonate required to raise the pH to 6, and the concentration of lime water (using calcium hydroxide) required to raise the pH to 4, 6 or 8. For the addition of dry lime to the spoil, the dry spoil and either calcium hydroxide or calcium carbonate were mixed thoroughly before the columns were packed. After packing they were then leached slowly with 250 cm^3 deionised water. The other columns containing dry spoil were leached slowly with 250 cm^3 of the appropriate concentration of lime water (24 hour leach). The amounts of dry lime and the concentrations of lime water used were:

dry $CaCO_3$ - 0.31 g
dry $Ca(OH)_2$ - 0.41 g
Lime water-
pH raised to 4 - normality 0.019
pH raised to 6 - normality 0.034
pH raised to 8 - normality 0.047

Control columns were also prepared in which the columns containing the spoil were leached with 250 cm^3 deionised water only. Nine columns were prepared for each treatment. At intervals all the columns were leached slowly (over about 24 hours) with 250 cm^3 deionised water. The leachates were analysed for acid (pH and titratable acidity), and iron and calcium by atomic absorption spectrophotometry. (Manganese and aluminium were also determined in the leachate but there were only negligible amounts present). After each leaching one column of each treatment was destroyed and the spoil air-dried. 5 g portions (duplicated) from the top and the bottom of the column (and also in the later tests from the middle of the column) were shaken for 1 hour with 50 cm^3 deionised water, then filtered and the filtrate tested for pH and titratable acidity. After the last leachate one column of each treatment was used for pH and titratable acidity as before, whilst the other two columns were destroyed and used for calcium analysis. The spoil from these columns was air dried, and two duplicate samples from the top, middle and bottom of the column were shaken with normal ammonium acetate (pH 7.0) for 1 hour (in centrifuge tubes). The tubes were then centrifuged for 15 minutes, the supernatant decanted, and the spoil again shaken with normal ammonium acetate for 30 minutes. The tubes were again centrifuged and the supernatant decanted. Calcium was determined in both extracts.

The pH of the leachates was low for all the columns, and there was very little difference between the different treatments for iron and acid - the results were in the order that would be expected for the treatments. However the concentration of calcium in the leachates was much higher in the dry limed cases than in the lime-watered cases (Table 4.3). This was also supported by the results of the calcium analysis of the spoil at the end of the period, (Table 4.4) the lime-watered cases having retained much more calcium than the dry-limed cases. Most of the added calcium was retained in the spoil in the lime-watered columns (Table 4.5) with a significant amount compared to the control case only being leached out on day 93. The pH of the shaken spoil also showed a great difference between the treatments (Table 4.6). Whilst the pH of the dry-limed spoil decreased down the columns, the

pH

	Day 10	30	42	49	58	93
Control	3.9	3.0	3.3	3.5	3.4	2.8
Limewater to pH 4	3.6	4.1	3.4	3.8	3.5	3.0
Limewater to pH 6	3.6	4.1	3.6	3.7	3.4	3.0
Limewater to pH 8	3.6	4.2	3.7	4.0	3.6	3.2
Dry $Ca(OH)_2$	5.9	4.2	3.8	3.9	3.4	3.0
Dry $CaCO_3$	7.0	3.9	3.7	3.7	3.6	3.2

mg H^+ l^{-1}

	Day 10	30	42	49	58	93
Control	4.1	11.6	5.3	3.7	3.3	20.6
Limewater to pH 4	3.9	2.9	3.1	2.0	1.9	12.7
Limewater to pH 6	4.4	2.9	2.6	2.0	1.9	10.8
Limewater to pH 8	4.6	2.5	2.0	1.4	1.4	7.4
Dry $Ca(OH)_2$	0.6	3.1	3.1	1.8	2.1	13.9
Dry $CaCO_3$	0.5	2.6	2.3	1.5	1.8	9.7

Results are presented as mean of the three columns of each treatment that were not destroyed until day 93.

Table 4.3 Analysis of Leachates of First Set of Columns mg Fe l^{-1}

	Day 10	30	42	49	58	93
Control	60	171	102	55	60	282
Limewater to pH 4	59	54	39	24	24	183
Limewater to pH 6	70	42	30	21	20	148
Limewater to pH 8	76	29	20	12	12	97
Dry $Ca(OH)_2$	2	25	30	11	21	187
Dry $CaCO_3$	3	17	21	10	16	135

mg Ca l^{-1}

	Day 10	30	42	49	58	93
Control	18	25	10	5	3	9
Limewater to pH 4	16	12	14	9	8	60
Limewater to pH 6	19	19	21	12	13	90
Limewater to pH 8	47	30	25	12	14	90
Dry $Ca(OH)_2$	87	134	80	36	35	77
Dry $CaCO_3$	103	157	88	37	38	117

Table 4.3 Continued.

μgCa g Spoil^{-1}

		Extract 1	Extract 2
Control			
Column 1	Top	22	14
	Middle	21	14
	Bottom	23	16
Column 2	Top	29	10
	Middle	23	9
	Bottom	22	8
Limewater to pH 4			
Column 1	Top	3750	833
	Middle	1325	297
	Bottom	705	112
Column 2	Top	3750	1230
	Middle	1262	176
	Bottom	506	57
Limewater to pH 6			
Column 1	Top	6022	1371
	Middle	2360	290
	Bottom	1197	140
Column 2	Top	6256	2057
	Middle	2596	358
	Bottom	941	103

Results are presented as mean of duplicate samples for three sections of each column.

Table 4.4 Analysis of Calcium Content of Destroyed Columns at End of Experiment - 2 Columns for Each Treatment.

μgCa g Spoil^{-1}

		Extract 1	Extract 2
Limewater to pH 8			
Column 1	Top	7137	2546
	Middle	3923	1264
	Bottom	1923	359
Column 2	Top	6454	1985
	Middle	2998	837
	Bottom	1525	261
Dry $Ca(OH)_2$			
Column 1	Top	556	66
	Middle	590	147
	Bottom	1328	125
Column 2	Top	145	25
	Middle	271	70
	Bottom	531	116
Dry $CaCO_3$			
Column 1	Top	242	75
	Middle	421	130
	Bottom	663	203
Column 2	Top	106	22
	Middle	106	19
	Bottom	123	19

Table 4.4 Continued.

	Column	mg Ca Added	mg Ca Retained
Limewater to pH 4	1	95	84
	2	95	83
Limewater to pH 6	1	170	136
	2	170	147
Limewater to pH 8	1	235	205
	2	235	170
Dry $Ca(OH)_2$	1	169	33
	2	169	14
Dry $CaCO_3$	1	165	21
	2	165	5

Results are for each column used for calcium analysis (2 columns for each treatment).

Table 4.5 Amount of Calcium Added to Each Column Compared to that Retained at End of Period by Each Column

		pH					
	Day	10	30	42	49	58	93
Control	Top	3.7	3.4	3.3	3.4	3.3	3.3
	Middle	-	-	-	3.2	3.1	3.2
	Bottom	3.4	3.3	3.3	3.3	3.1	3.1
Limewater to pH 4	Top	7.0	7.9	6.7	6.7	5.8	6.8
	Middle	-	-	-	4.2	4.2	4.7
	Bottom	3.4	3.7	3.7	3.7	3.5	3.3
Limewater to pH 6	Top	7.2	7.2	7.4	6.5	6.5	7.7
	Middle	-	-	-	7.3	5.8	7.4
	Bottom	3.8	3.8	4.0	3.8	3.8	3.6
Limewater to pH 8	Top	7.2	7.5	7.3	7.0	-*	7.0
	Middle	-	-	-	7.5	-	7.5
	Bottom	4.4	3.8	4.2	3.9	-	3.7
Dry $Ca(OH)_2$	Top	7.0	4.4	4.3	5.2	3.4	3.0
	Middle	-	-	-	5.2	4.5	2.8
	Bottom	7.2	4.6	3.4	5.2	5.2	2.8
Dry $CaCO_3$	Top	7.4	6.0	4.1	3.2	4.1	3.1
	Middle	-	-	-	4.0	3.2	3.8
	Bottom	7.1	7.8	4.5	3.7	3.9	3.5

Results are presented as mean of duplicate samples.

* Spoil from this column lost on day 58.

Titratable acidity results not presented as they just reflect the pH.

Table 4.6 <u>pH of Shaken Spoil - One Column Destroyed After Each Leach</u>

Fig 4.1 pH of Spoil of Top Part of Columns Treated with Limewater or Dry Lime.

KEY

1 control

2 limewater to pH 4

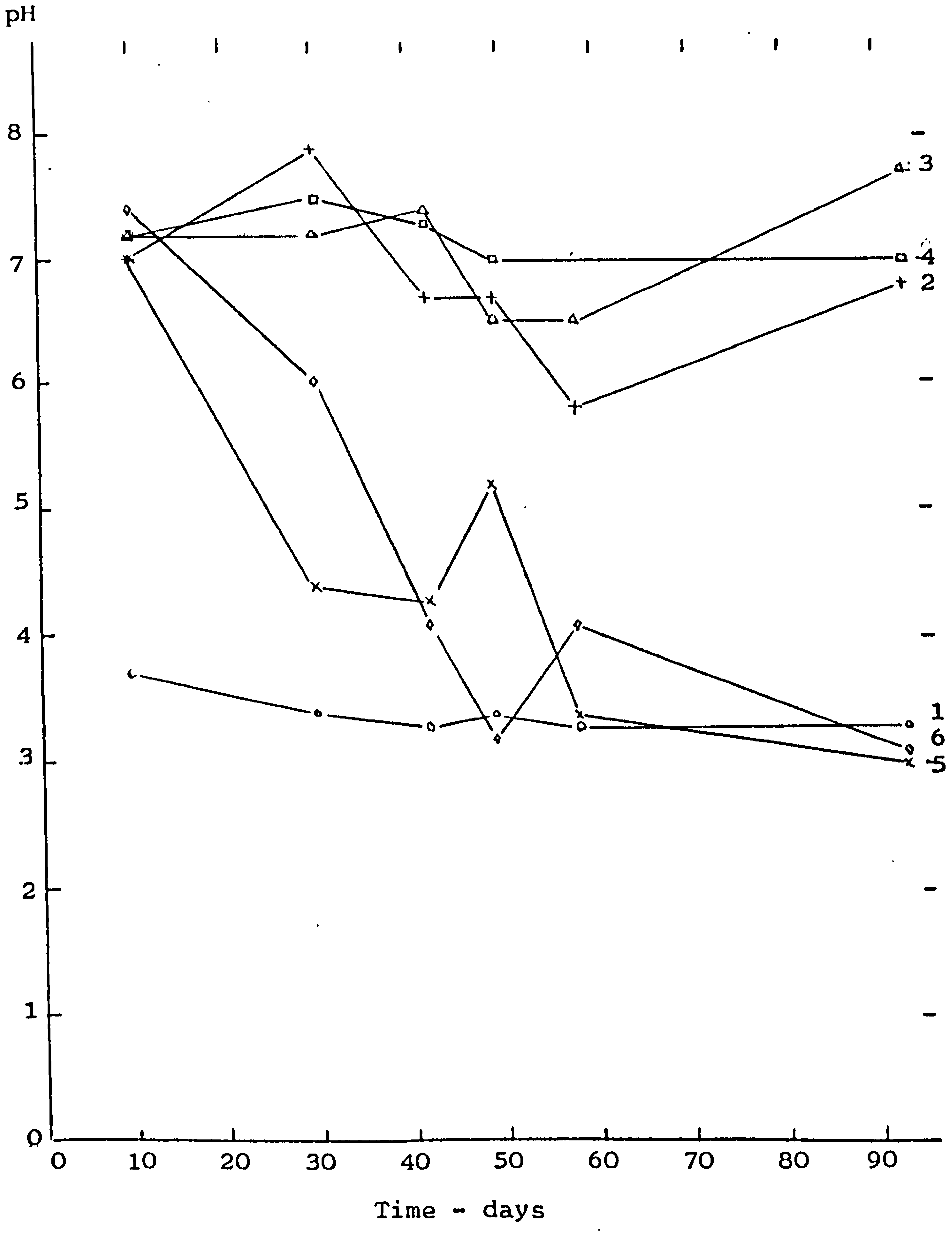
3 limewater to pH 6

4 limewater to pH 8

5 dry $Ca(OH)_2$

6 dry $CaCO_3$

Fig 4.1.



pH of the spoil in the lime-watered columns remained at a reasonably high level, especially in the top part of the columns (Fig 4.1). The higher pH in the top part of these columns corresponded to the higher calcium content of the top part of the columns (Table 4.4).

The addition of lime in solution was more effective at maintaining the pH than the addition of dry lime. Neither calcium hydroxide or calcium carbonate are very soluble - the solubility product for $CaCO_3$ is 4.8×10^{-9} and for $Ca(OH)_2$ is 5.5×10^{-6} at room temperature. Dissolving the lime in water before adding it to the spoil meant that there was a greater concentration of calcium in solution than in the dry lime cases, and this was able to saturate the exchange sites in the spoil.

Thus the effect of the lime water on the spoil seemed to be due to cation exchange as well as a neutralising effect. It should be possible to achieve the same effect using a neutral compound by saturating the cation exchange sites of the spoil with a cation and thus excluding the hydrogen ions from the sites.

4.3.2 Saturation of Cation Exchange Sites of Spoil

The cation exchange capacity of the spoil was measured. Triplicate columns (containing 10 g of spoil and 10 g of acid washed sand thoroughly mixed) were leached slowly with 200 cm^3 of normal potassium acetate (pH 7.0), then with 100 cm^3 of 90% ethanol and then with 200 cm^3 of normal ammonium acetate. The potassium in the last leachate (made up to 250 cm^3) was determined using flame emission. The cation exchange capacity calculated form this was 48 me 100 g^{-1} spoil.

Another series of columns were prepared in which the spoil was either saturated or half saturated with magnesium or calcium. The columns again contained 40 g spoil of the same concentration of pyrite as before and were leached slowly with solutions of $MgCl_26H_2O$, $CaCl_22H_2O$ and $Ca(OH)_2$, containing enough of the cation to saturate or half saturate the column (calculated form the above cation exchange capacity). The amount of chemicals used were equivalent to 230 mg Mg, 115 mg Mg, 385 mg Ca and 193 mg Ca, the calcium being supplied both as a neutral solution and an alkaline solution. The initial amount of solution used was 500 cm^3 for each column, so that all the added calcium hydroxide would dissolve. After the initial leach the columns were leached with 250 cm^3 of deionised water at intervals. The leachate was analysed for iron, calcium, magnesium and acid. After each leach one column for each treatment was destroyed and analysed for acid, calcium and magnesium in the same way as in the first set of columns. Calcium and magnesium (determined in the same extracts as calcium) were determined in the extracted spoil after each leachate, not only after the last leachate as happened for the first set of columns.

The analysis of the leachates of the initial leach and the first leach with deionised water showed that the majority of the magnesium and calcium added as the chloride was not retained in the spoil but came out in the leachate (Table 4.7).

Solution	mg of cation added	mg of cation in initial leach	mg cation in first leach with deionised water
Magnesium	230	200	25
Chloride	115	100	10
Calcium	385	285	38
Chloride	193	115	30
Calcium	385	48	26
Hydroxide	193	40	37

Table 4.7 Amount of Cation Removed by First Two Leaches

pH Spoil

Column		Day	1	19	42	66	92	125
Full	Top		7.5	7.4	7.0	6.8	7.0	7.2
	Middle		7.4	7.4	6.9	6.9	7.0	7.4
	Bottom		7.3	7.1	5.6	5.4	4.8	3.4
Half	Top		6.8	7.2	6.9	6.8	6.9	7.1
	Middle		7.3	7.3	6.0	3.0	3.0	3.1
	Bottom		4.3	4.3	4.1	3.0	3.0	3.0

µg Ca g Spoil^{-1}

		Day	1	19	42	66	92	125
Full	Top		19000	11900	14600	12580	10010	12000
	Middle		4000	6080	3880	4630	3540	3230
	Bottom		3040	2170	2320	1630	2080	820
Half	Top		7660	8420	6250	6250	3250	5100
	Middle		3360	2830	1890	630	970	630
	Bottom		1030	1250	1230	370	600	400

Table 4.8 Analysis of Columns Either Saturated or Half Saturated with Calcium Hydroxide - Shaken Spoil

pH

Column	Day 1	19	42	66	92	125
Full	3.6	3.7	3.2	2.7	2.3	2.1
Half	3.5	3.4	3.6	2.6	2.3	2.0

mg H^+ l^{-1}

	Day 1	19	42	66	92	125
Full	6.1	3.6	6.2	11	20	11
Half	6.7	8.6	10.2	14	18	15

mg Fe l^{-1}

	Day 1	19	42	66	92	125
Full	83	34	87	136	200	105
Half	82	112	172	174	220	90

mg Ca l^{-1}

	Day 1	19	42	66	92	125
Full	96	106	110	180	160	115
Half	80	153	84	120	120	82

Results are presented as mean of the columns that were not destroyed until day 125.

Table 4.9 Analysis of Columns Either Saturated or Half Saturated with Calcium Hydroxide - Leachate Results

(The amount of magnesium and calcium, added as chloride, which was retained was correspondingly low). The pH of the spoil and leachate in these columns was about 3. These columns were therefore destroyed as the amount of cation left in these columns was insignificant. The calcium hydroxide columns were continued to confirm the first set of results.

The calcium hydroxide again maintained a high pH of the spoil throughout the period, (Table 4.8), the effect being greater in the fully saturated columns than in the half saturated columns as would be expected. By the end of the period those columns that had 385 mg Ca added initially had retained 193 mg Ca, and those which had 193 mg Ca added had retained 74 mg Ca, i.e. a third to a half of the original calcium added was retained in the columns. The leachates (Table 4.9) contained slightly higher amounts of acid, calcium and iron than did the limewatered columns of the previous experiment.

4.3.3 Cation Exchange Capacity of Spoil

The fact that the calcium and magnesium when added as chloride solutions were not retained in the acid spoil suggested that the cation exchange capacity (CEC) of the spoil was pH dependent. This supposition was tested by repeating the cation exchange capacity test already described, but substituting normal potassium acetate buffered at pH 5 and unbuffered potassium chloride (which gave a pH of about 3) for the normal potassium acetate at pH 7 in the first determination. This gave cation exchange capacities of 21.8 me 100 g^{-1} at pH 3 and 24.6 me 100 g^{-1} at pH 5. Obviously there was a large difference between these values and that recorded at pH 7 (48 me 100 g^{-1}) showing that the cation exchange capacity of the spoil was pH dependent. However, the amount of calcium and magnesium retained in the columns was still less than was expected, calculated from the CEC at pH 3 (which was the pH of the leachate and the spoil in these columns). (In the magnesium case 100 mg should have been retained but only 30 mg was retained after the first leach, in the calcium case 168 mg should have been retained and only 100 mg was retained initially).

Pratt (1961) investigated the liming of soils with a pH-dependent CEC and found that the amount of calcium carbonate required to neutralise a soil and the pH-dependent CEC of the soil (CEC at pH 8 minus CEC at pH of the soil) were approximately equal. In the columns of this experiment the amount of calcium carbonate required to raise the pH to 7 was equivalent to 203 mg whilst the pH-dependent CEC (using CEC at pH 7 minus CEC at pH 3) was equivalent to 224 mg. These values are quite close which corresponds to the findings of Pratt. He also suggested that the reaction of calcium carbonate with soils having a pH-dependent CEC consisted of an initial increase in the soil pH due to the hydrolysis of the calcium carbonate. Hydrogen ions would then dissociate from the pH-dependent ion exchange sites and calcium ions would be simultaneously adsorbed onto these sites. H_2CO_3 would form and then dissociate to H_2O and CO_2. As neutral salts were not adsorbed onto the sites, he assumed that the hydrogen ions would only dissociate due to an increase in the pH. Obviously the calcium hydroxide used in the lime-watered columns would also cause an increase in the pH, and the overall effect would be the same as for calcium carbonate. The dry lime did not have the same effect as there was not such a great concentration of calcium in solution and thus it was not able to effectively saturate the ion exchange sites.

Limewater maintained the spoil at a higher pH for a longer period of time and gave a more uniform spoil pH than did the dry lime. However, in a field situation it may be more quickly leached away and therefore not be so effective. Also the spaying of limewater may not be very practical for a reclamation scheme. The application of limewater would probably also cause the same problems as caused by the application of high rates of lime, and might also damage any vegetation if sprayed directly on to it.

4.3.4 Conclusion

The variation in pyrite content on bings causes problems in adequate sampling and the subsequent application of lime to overcome the potential acidity of the pyrite. Large lumps of pyritic spoil can be still picked up on Baads bing, showing that not only is the pyrite unevenly distributed throughout the bing, but even some years after regrading large lumps of spoil have still not broken down and the pyrite contained in them has still not oxidised. The use of high rates of lime to overcome the potential acidity of the pyrite may not be more effective in the long term than lower rates of lime and can also cause nutrient deficiencies. The use of limewater was investigated and was found to be more effective at maintaining a reasonable spoil pH than the use of dry lime. However the practicality of using limewater in the field or its effectiveness in a long term experiment were not investigated.

CHAPTER 5

Studies on Pyrite

5.1 Introduction

This chapter concentrates on pyrite itself. The differential iron method for the determination of pyrite is first examined, and its accuracy for spoils of differing pyrite contents is discussed. Pyrite from different locations can vary in their reactivity, and therefore pyritic samples from three different areas were examined - two were known to oxidise at a reasonable rate whilst the other oxidised only very slowly. Initially all the samples were identified as pyrite by infra-red spectroscopy and then the difference in the reactivity of the different samples was examined using flask experiments. Possible reasons for the difference in reactivity were then investigated.

5.2 Determination of Pyrite, by the Differential Iron Method

Various methods have been used in the past to determine the presence and quantity of pyrite in a spoil (or soil). Many of these methods were reviewed by Costigan (1979), and included those based on the reduction of pyrite to hydrogen sulphide and on the oxidation of pyrite to iron and sulphate, with subsequent determination of the products. The method used throughout this project (described in Chapter 2) was based upon the method recommended by a working party, which was established to find a reproducible, relatively fast method to determine pyrite content in coal mine spoils (Dacey and Colbourn 1979).

The sequential method involves the removal of non-pyritic iron from the spoil by refluxing with hydrochloric acid, followed by the extraction of the pyritic iron with nitric acid. The iron in the nitric acid extract was determined by atomic absorption spectrophotometry and the percentage of pyrite in the spoil calculated. Obviously if all the non-pyritic iron was not removed by the hydrochloric acid reflux, then an over-estimate of the pyrite content would occur. It may also be possible that one nitric acid reflux would not be sufficient to oxidise all the pyrite present in the spoil, which would then result in an under-estimate of the percentage of pyrite. These two factors were investigated in the following experiments. The amount of pyrite in the spoil was also calculated from the amount of sulphate present in the nitric acid reflux, and this result was compared to the results obtained from the iron determination.

5.2.1 Non-Pyritic Samples

Initially a pyrite determination was performed on three materials which are normally thought of as non-pyritic : two subsoils taken from soils of the Dunlop and Dreghorn Series (Mitchell and Jarvis, 1956) and acid washed sand. A blank determination was also included. The pyrite determination method was described in Chapter 2.

Sample	%FeS_2
Dunlop	0.10
Dreghorn	0.02
Sand	0.00
Blank	0.00

The results are presented as the mean of duplicate flasks.

Table 5.1 Determination of Pyrite in Non-Pyritic Materials

The results (Table 5.1) showed that the sand and blank did not contain pyrite, but there was a positive result for the two soils, Dunlop and Dreghorn, which indicated that there is probably a fault in this method, as it was improbable that the soils contained pyrite. Therefore the method was investigated to try to identify the fault.

The pyrite determination on these two soils was repeated, but four hydrochloric acid refluxes each lasting half an hour were used instead of two, to try to ensure that all the non-pyritic iron was removed before the nitric acid reflux. After each reflux with hydrochloric acid the filtrate and washings were collected and made up to a known volume, and the iron determined in each of these solutions.

The extra hydrochloric acid refluxes did remove more iron although the final pyrite percentage was not significantly altered (Table 5.2), as the amount of extra iron removed before the final stage was very small (for example, in the case of Dunlop 1, the 4th HCl extract only removed 0.7 mgFe g^{-1} soil). Obviously the final result cannot be

		mgFe l^{-1} (250 cm^3 volume)					
Sample	Reflux	1st HCl	2nd HCl	3rd HCl	4th HCl	HNO_3	$\%FeS_2$
Dunlop 1		310	20.0	4.7	2.8	1.4	0.08
Dunlop 2		310	20.0	5.2	3.3	2.2	0.13
Dreghorn 1		85	4.5	2.2	0.6	0.3	0.02
Dreghorn 2		85	2.9	1.8	0.3	0.3	0.02

Table 5.2 Determination of Pyrite, Using Extra Hydrochloric Acid Refluxes - Non-Pyritic Soils.

considered completely accurate, as such low concentrations of iron were involved. However the fact that the method showed that pyrite was present in non-pyritic samples shows that there is an error in the method. Presumably there is iron present in some soil fractions that is not released by the hydrochloric acid but is attacked by the nitric acid, or is only released after extreme attack by acid, the nitric acid acting as a fifth acid extract (after the four hydrochloric acid extracts).

5.2.2 Pyritic Spoils

Although the effect of extra hydrochloric acid refluxes was not very significant in the case of non-pyritic soils, in that it did not affect the final pyrite percentage result, the experiment was repeated using pyritic spoils, to see the effect in these cases.

Baads pyrite of a high concentration and Baads pyrite diluted with spoil to two different concentrations were used for the pyrite determinations. Four samples of each concentration were used, two of which had four hydrochloric acid refluxes instead of the normal two. The iron was again measured in all the extracts.

More iron was released in the extra hydrochloric refluxes, as was the case for the non-pyritic soils (Table 5.3). The highest pyrite samples unexpectedly showed a higher pyrite percentage after the extra hydrochloric acid refluxes. The extra refluxes had no effect on the final calculated pyrite concentration in the case of the lowest pyrite concentrations. For all the other samples the extra refluxes resulted in a greater variation between the results for the duplicate samples, which was not expected as the removal of more non-pyritic iron would be expected to lead to a more accurate result. However, it would seem that some of the spoil constituents were quite resistant to the hydrochloric acid, but the repeated refluxes did attack these

		mgFe l^{-1} (250 cm^3 volume)					
		Reflux					%FeS_2
Concentration	Sample	1st HCl	2nd HCl	3rd HCl	4th HCl	HNO_3	
	1	190	11.0	---	---	1100	58.8
Undiluted	2	200	9.0	---	---	1100	57.4
	3	195	12.5	2.20	2.00	1200	64.5
	4	205	9.5	2.30	1.90	1200	59.1
	5	70	4.00	---	---	130	7.0
Diluted to	6	65	4.60	---	---	120	6.1
level 1	7	55	3.30	1.40	1.00	80	4.4
	8	55	4.60	2.40	1.00	110	6.3
	9	40.0	2.50	---	---	7.0	0.4
Diluted to	10	36.0	2.60	---	---	6.0	0.3
level 2	11	42.0	2.70	1.00	1.00	6.5	0.4
	12	45.0	2.70	2.80	1.00	6.0	0.3

The results for each pair were not averaged, due to the variability between the duplicates.

Table 5.3 Determination of Pyrite, Using Extra Hydrochloric Acid Refluxes - Pyritic Spoils.

constituents and released more iron. Due to the variability in the pyrite percentage results, it was difficult to ascertain whether this had a significant effect on the results, although it obviously did lead to the greater variability in the results.

It was also possible that the nitric acid reflux was not releasing all the pyritic iron, so this supposition was tested. Three concentrations of Baads pyrite were again used, two being diluted with spoil, but not necessarily to the same concentration as before. Each set was refluxed with hydrochloric acid twice, and then with nitric acid twice, both nitric acid refluxes lasted for one hour.

The second nitric acid reflux did remove more iron showing that the first nitric acid extract was incomplete (Table 5.4). For samples 1 and 2 the extra iron released would have caused an increase in the calculated pyrite percentage of 3%, for samples 3 and 4 about 0.5%, and for samples 5 and 6 about 0.1%. This ordering corresponds to the higher the pyrite content the less easily is all the pyritic iron removed. At the highest pyrite concentration the effect was obviously quite marked.

5.2.3 Sulphate Determination

The nitric acid reflux should oxidise all the pyrite in the sample, so the pyrite content could be determined from the amount of sulphate in the nitric acid extract.

		mgFe l^{-1} (250 cm^3 volume)		%FeS_2
Sample	Reflux	1st HNO_3	2nd HNO_3	
1		1300	60	67.9
2		1300	60	68.9
3		110	6.5	6.3
4		105	13.0	5.7
5		7	1.05	0.4
6		6	1.05	0.3

%FeS_2 was calculated from the first nitric acid extract.

Table 5.4 Determination of Pyrite - The Effect of an Extra Nitric Acid Reflux on Pyritic Spoil.

The sulphate determination method was described in Chapter 2. However, barium nitrate can be coprecipitated with the barium sulphate, so the method was modified to allow for this.

Modified Method for Sulphate Determination

5 cm^3 of the nitric acid extracts (first only) from the previous experiment were placed in centrifuge tubes (10 cm^3) of known dry weight. They were placed in a boiling water bath for ten minutes and then 2 cm^3 of 5% $BaCl_2$ solution was added to each tube dropwise. The tubes were left in the boiling water bath for a further ten minutes. After the tubes were cooled they were centrifuged for ten minutes at 2500 rpm, and the supernatant decanted. 5 cm^3 of 2M HCl was then added to each of the tubes and they were replaced in the boiling water bath for ten minutes (care was taken to ensure that the precipitates were well mixed with the acid). The cooled tubes were then centrifuged again and the supernatant decanted. The precipitates were washed with ethanol, the tubes again centrifuged and the supernatant decanted. After drying in an oven overnight, the tubes were cooled and weighed and the sulphate concentration determined. Duplicate samples for each of the nitric acid refluxes were used and the percentage pyrite determined from the sulphate concentrations.

The pyrite percentages from the sulphate determinations and the iron determinations from the last experiment are presented in Table 5.5. There were obviously discrepancies between the two sets of results. Samples 5 and 6 had very low concentrations of pyrite and in order to calculate these from the sulphate concentrations, a correspondingly low concentration of sulphate would have to be determined. If the pyrite content was 0.3%, then 0.2 mg of barium sulphate would have to be measured (on the basis of the weights and

	% FeS_2	
Sample	From Sulphate Determination	From Iron Determination
1	69.5	67.9
2	71.1	68.9
3	5.6	6.3
4	6.2	5.7
5	0.8	0.4
6	0.9	0.3

Table 5.5 Comparison of Pyrite Percentages, Calculated from Sulphate Concentration and Iron concentration in Nitric Acid Extract.

volumes used here). It was not possible to weigh to such a degree of accuracy on the balances used in this project. This shows the inadequacy of the gravimetric method for sulphate determination at low sulphate concentrations - the turbidimetric method for sulphate determination may have given more accurate results at these low concentrations, which could then have been used to calculate the pyrite content.

For the other four samples the discrepancy between the two results is up to 2%. The accuracy of the sulphate determination method can be impaired due to the presence of various cations or anions which can be coprecipitated (Vogel 1979). The nitrate ion can be coprecipated and the modified method employed here may not have succeeded in removing all the nitrate precipitated. This would have caused an increase in the final measured weight, but it is impossible to put a numerical value on the amount involved.

These studies have shown that the differential iron method for determination of pyrite cannot be considered completely accurate, probably due to the incomplete removal of iron at any stage. The effect of extra hydrochloric acid refluxes was rather unclear, but the extra nitric acid reflux had a more definite effect. The greatest effect of the extra nitric acid reflux was at the highest pyrite content, but the greatest relative effect in relation to actual pyrite content was at the lowest pyrite content.

Dacey and Colbourn (1979) in their report stressed the importance of repeatability of results for a particular operator as opposed to the reproducibility of results between different operators. They found that the sequential hydrochloric acid/nitric acid method as well as another method (high temperature oxidation method) showed the best repeatability for a particular operator, although the reproducibility was not particularly good. The results in this project also show that the method has certain failings - the effect of the extra nitric acid refluxes and the fact that pyrite was determined in non-pyritic soils. At high pyrite concentrations the relative effect of these would not be too great. However, at lower pyrite concentrations, which are those normally encountered in the field, the relative effect would be greater. Very low pyrite concentrations of 0.1% may be meaningless (the non-pyritic Dunlop soil showed this concentration). This could affect the application of lime when the potential acidity due to the presence of pyrite is being taken into account.

However, the use of the method as an indication of the amount of pyrite present or as a tool to compare large differences in spoil pyrite contents is acceptable, and the inadequacies of the method would not really affect the value of the method in these cases as a relatively fast, cheap technique.

5.3 Comparison of Three Different Pyrite Samples.

Pyrite from three different sources was available during the project. Two of these types of pyrite, Baads and Durham, were used in the incubation studies. The other sample, Ballachulish, was known to be rather inactive, as on standing it in a warm room white salts of sulphates due to pyrite oxidation were not formed, which always happened on leaving the other two samples in a warm place. The reactivity of pyrite is very important, if it does not oxidise at a reasonably fast rate, there will not be the consequent problems of the acid. Various reasons have been suggested for the differing reactivity of different types of pyrite (these were discussed in Chapter 1). They include:

(a) grain size - framboidal pyrite is generally considered to be more reactive than euhedral pyrite (Caruccio 1970, Pugh et al.1981),

(b) association of trace metals with the pyrite, for example, titanium was found to be associated with stable pyrite and silver with reactive pyrite (Caruccio 1972),

(c) presence of other metal sulphides - this would cause a decrease in the rate of pyrite oxidation, whilst the rate of release of the metals from the other sulphides would be increased (Nordstrom 1982),

(d) association of carbonates with the pyrite causing the pyrite to be inactive, which can be removed by acid washing (Temple and Delchamps 1953),

(e) presence of T. ferrooxidans.

Various studies were made on the Baads, Durham and Ballachulish pyrite samples to try to determine the differences between the three samples. These studies consisted of i.r. spectroscopy (to confirm that all the samples were pyrite), incubation studies (to determine the

Fig 5.1 Photographs of Pyrite Samples from (a) Baads, (b) Durham and (c) Ballachulish

difference in reactivity of the samples), and electron microscopy (to try to determine structural differences).

5.3.1 Visible Differences Between the Samples

The pyrite from Baads and Durham came from coal waste tips, and occurred as thin veins or nodules throughout the material. The pyrite from Ballachulish occurred as discrete lumps in the slate (Fig. 5.1) although examination of these lumps under a microscope showed that they were not composed purely of pyrite. Lumps of material containing pyrite could easily be found in the field in all three locations. The percentage of pyrite in these lumps was much higher for Baads and Durham (normally greater than 60%) than for Ballachulish (less than 4%). All samples also contained pyrite disseminated throughout the material which was visible under a microscope but not by the naked eye. White salts of sulphates due to pyrite oxidation quickly formed on the Baads and Durham samples on leaving them in a warm atmosphere, but this did not happen for the Ballachulish samples, showing that the first two samples were more reactive.

5.3.2 I.R. Identification of Samples

The infra red spectrum of pyrite has been previously determined (Liese 1974, Soong and Farmer 1978). The spectrum shows peaks at 415-410 cm^{-1} (strong), 348-345 cm^{-1} (medium) and 292-285 cm^{-1} (weak). These three peaks in the stated range of frequencies are specific for pyrite, other sulphides showing different peaks. Therefore the i.r. spectra of all three samples were obtained to confirm that they all contained pyrite.

The samples were finely ground and potassium bromide discs containing the samples prepared. The spectra was obtained from 4000 cm^{-1}

Sample	Peaks		
Baads	415(s)	345(m)	290(w)
Durham	415(s)	345(m)	290(w)
Ballachulish	415(s)	345(m)	290(w)

Table 5.6 I.R. Spectra of Three Samples

to 200 cm^{-1} on a Perkin-Elmer 580 spectrophotometer. All three samples showed the three characteristic peaks for pyrite (Table 5.6), thus confirming that they all contained pyrite.

5.3.3 Reactivity of Pyrite Samples

It has been reported that all types of pyrite can be reactive-unreactive ones being activated by either acid washing (to neutralise any native carbonate material present) or by pulverising (to increase the surface area) or by incubating with T. ferrooxidans (which catalyse the pyrite oxidation)(Temple and Delchamps 1953, Costigan 1979). However, Caruccio (1970) found that finely ground pyrite (non-framboidal) did not oxidise even after exposure to conditions which caused other pyrite to decompose.

An incubation experiment was set up to compare the reactivities of the three different samples. Each of the samples was ground in a ball-mill, until it was of a size less than 150 µm. 5 g of the material was suspended in 100 cm^3 of deionised water (three flasks for each sample were set up). At each sampling date 15 cm^3 of the solution was removed from each of the flasks and replaced by 15 cm^3 of deionised water. The solutions removed from the flasks were tested for pH, titratable acidity, total iron and sulphate concentrations.

Fig 5.2 Comparison of Release of Oxidation Products From Three Different Pyrite Samples.

Fig 5.2.a pH of Solution.

Fig 5.2.b Total Iron in Solution.

Fig 5.2.c Concentration of Sulphate in Solution.

KEY

1 Baads

2 Durham

3 Ballachulish

Fig 5.2.a.

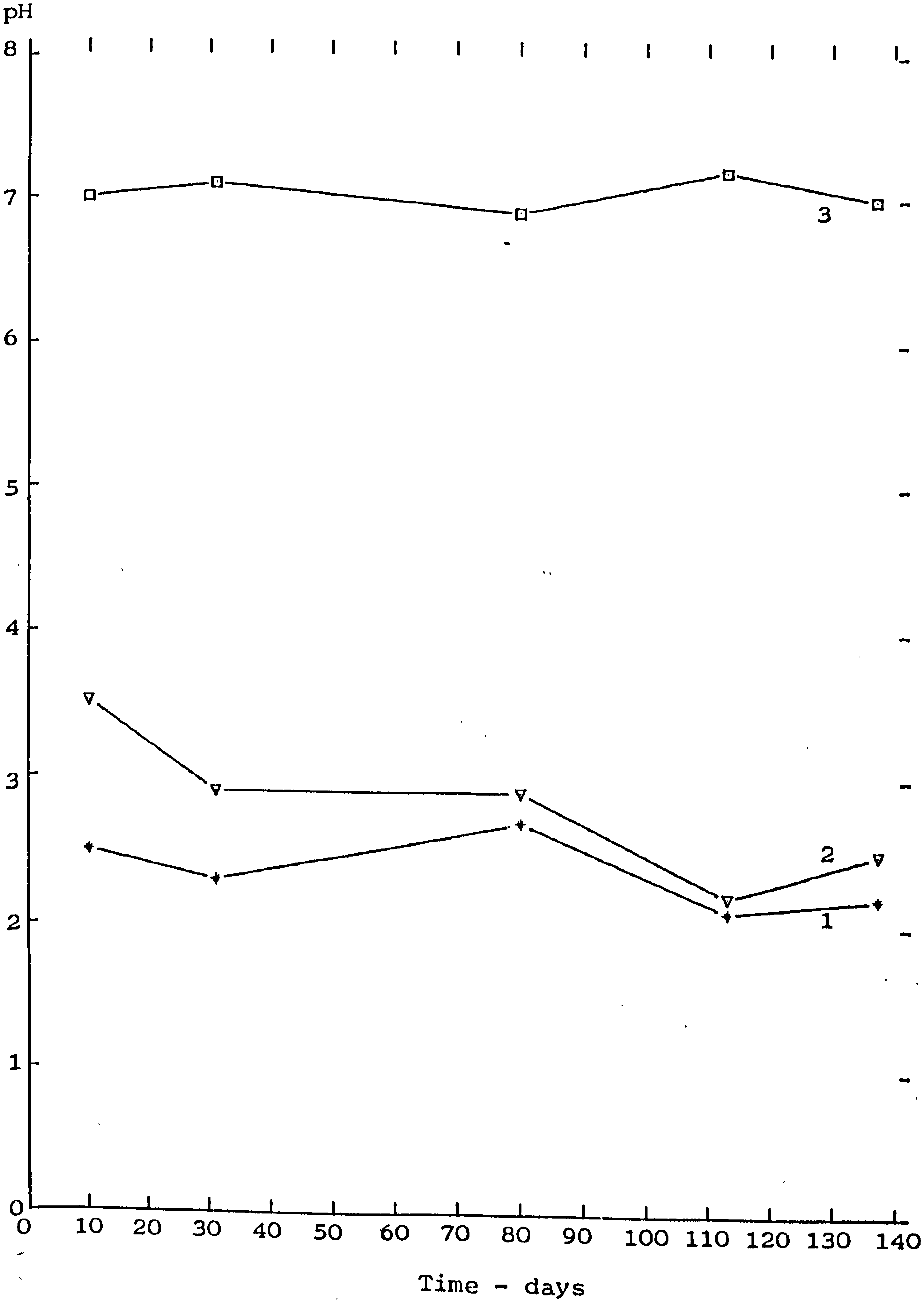

pH
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
Time - days
3
2
1

Fig 5.2.b.

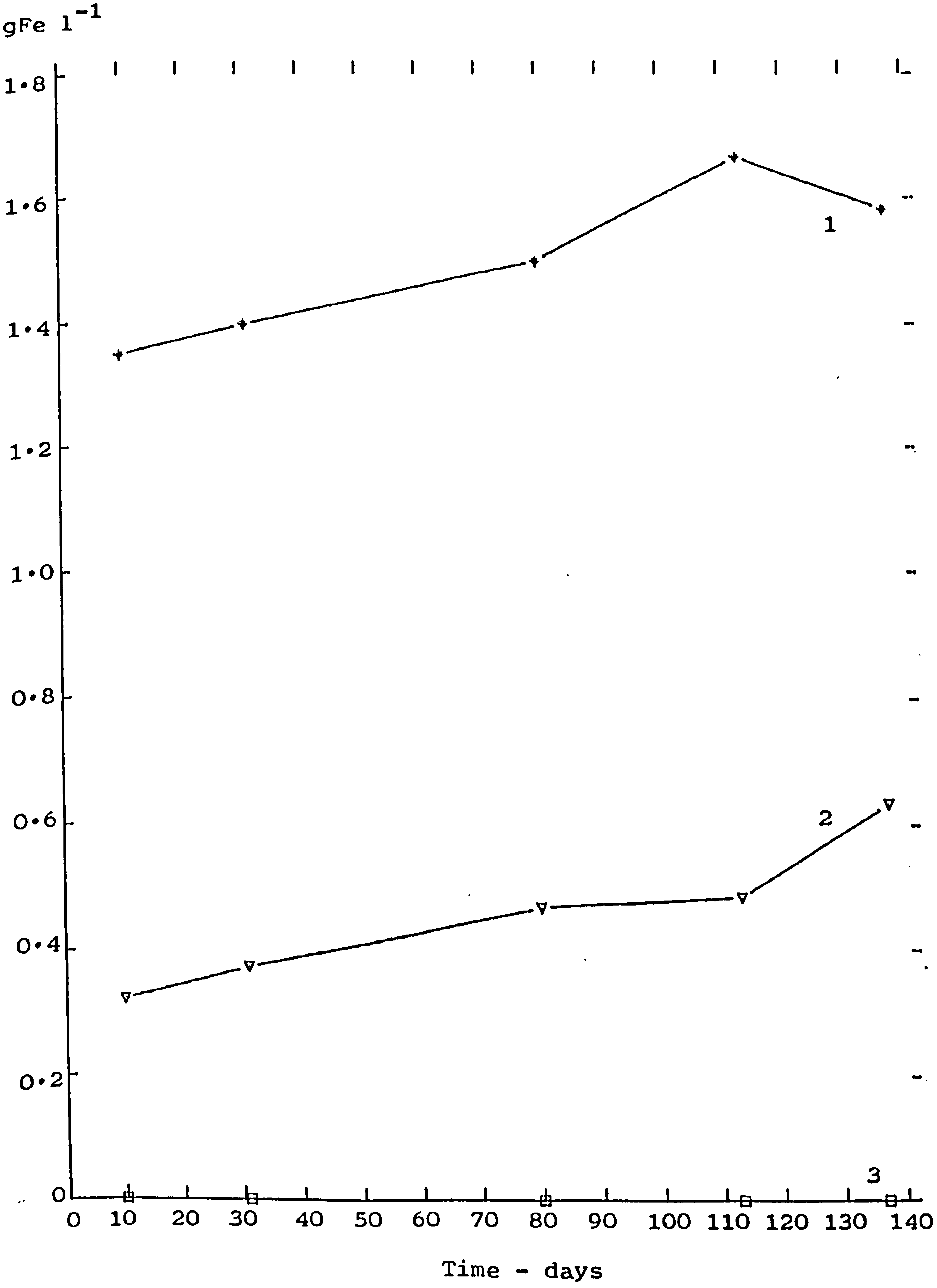
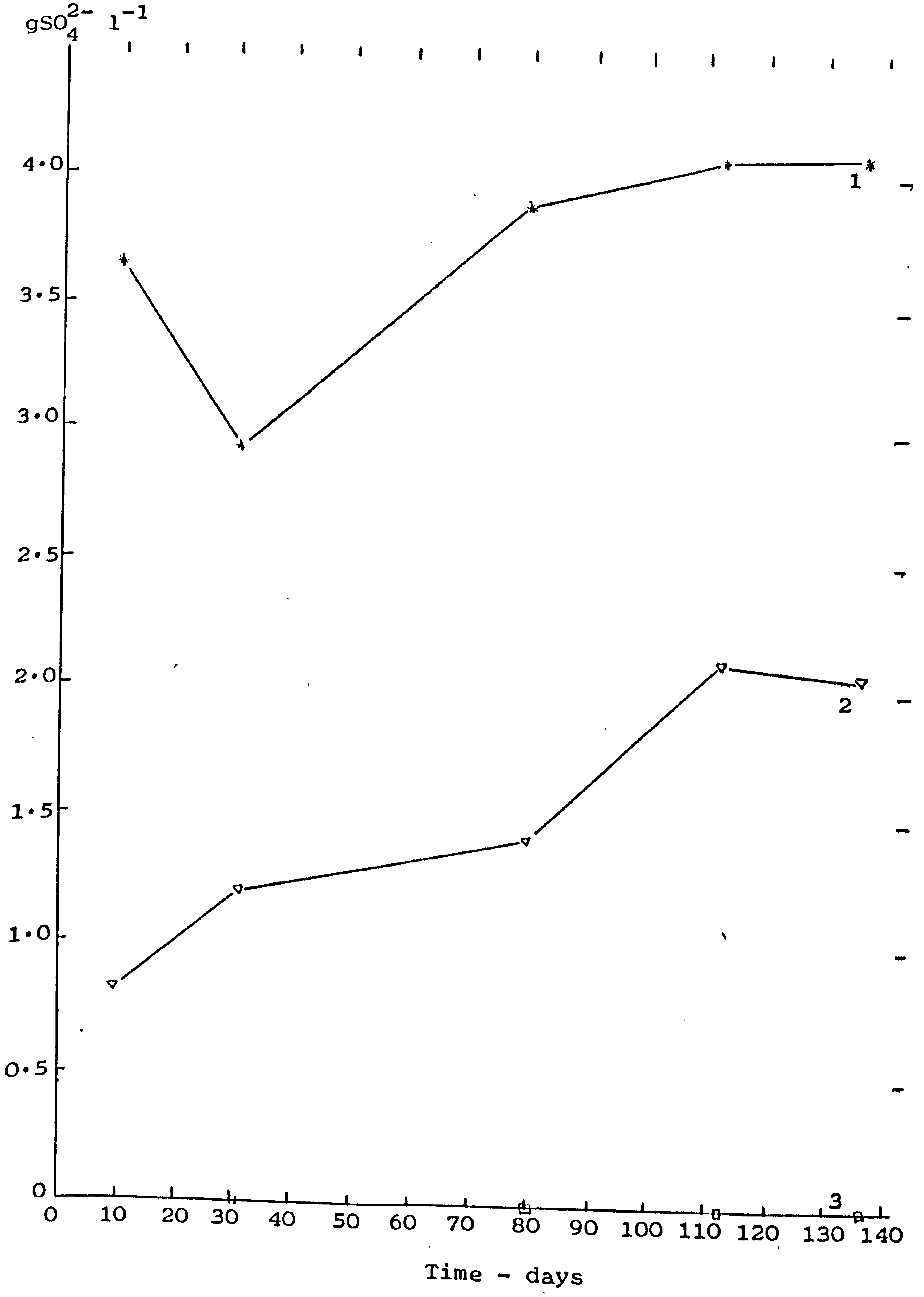

gFe l^{-1}
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
1
2
3
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
Time - days

Fig 5.2.c.


$gSO_4^{2-}\ l^{-1}$
4·0
3·5
3·0
2·5
2·0
1·5
1·0
0·5
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
Time - days
1
2
3

pH

	Day 10	31	80	113	137
Baads	2.5	2.3	2.7	2.1	2.2
Durham	3.5	2.9	2.9	2.2	2.5
Ballachulish	7.0	7.1	6.9	7.2	7.0

$mgH^+ \ l^{-1}$

	Day 10	31	80	113	137
Baads	66	67	75	83	77
Durham	18	23	29	37	39
Ballachulish	0.2	0.5	0.5	0.4	0.3

$gFe \ l^{-1}$

	Day 10	31	80	113	137
Baads	1.35	1.40	1.50	1.67	1.58
Durham	0.32	0.37	0.47	0.48	0.63
Ballachulish	0	0	0	0	0

$gSO_4^{2-} \ l^{-1}$

	Day 10	31	80	113	137
Baads	3.66	2.94	3.87	4.07	4.07
Durham	0.82	1.20	1.43	2.12	2.06
Ballachulish	0	0	0	0	0

Results are presented as mean of triplicate flasks.

Table 5.7 Comparison of Release of Oxidation Products from Different Pyrite Samples.

The initial concentration of the pyrite in the three samples was Baads 66%, Durham 68% and Ballachulish 1.2%. The accompanying figures (5.2 a,b,c) show the pH and the iron and sulphate concentrations for the three samples, the full results are in Table 5.7.

Baads pyrite consistently produced more acid, sulphate and iron than the Durham sample, even though the initial pyrite contents of both samples was very similar. The Ballachulish pyrite did not produce acid, iron or sulphate. Although the Ballachulish sample contained a much lower percentage of pyrite than the other two samples, it has already been shown in Chapter 2 that Baads pyrite diluted with spoil will still produce large quantities of acid, iron and sulphate, so the varying pyrite percentage compositions are not the explanation for the difference in reactivity between the samples. This is also supported by the fact that Baads pyrite produced more oxidation products than did Durham, even though it had a similar initial pyrite content.

To test whether acid washing and/or incubation with <u>T. ferrooxidans</u> would activate the Ballachulish sample, extra flasks of Baads and Ballachulish pyrite had been set up (three of each). After 31 days 50 cm^3 of the solution was removed from the Ballachulish flasks and replaced by 50 cm^3 of solution from the Baads flasks. This would thus acidify the Ballachulish sample and incubate it with <u>T. ferrooxidans</u>.

	Day 80	113	137
pH	2.8	2.6	2.6
mgH^+/l	29	26	23
gSO_4^{2-}	1.24	1.21	1.20
mgFe/l	152	100	91

Results are presented as mean of triplicate flasks.

Table 5.8 <u>Release of Oxidation Products from Ballachulish Sample with Added Baads Solution</u>.

Obviously the Baads solution caused the increase in the sulphate iron and acid levels in the flasks compared to the previous set of Ballachulish flasks, but over the period the concentration of these products decreased, presumably due to the dilution at each sampling date (Table 5.8). Therefore the Ballachulish sample, even when acidified and innoculated with T. ferrooxidans did not oxidise at an appreciable rate. (This pyrite does oxidise as iron staining in small depressions presumably previously holding pyrite, can be seen in the field, but the oxidation must be extremely slow, so that in the time period involved here, there were no measurable amounts of products).

These studies showed that out of the three samples, the Baads sample was most reactive and the Ballachulish sample was least reactive. Obviously a Ballachulish type of pyrite would not cause the same environmental problems as those caused by Baads and Durham types of pyrite. The following study was performed in order to try to find structural differences between the pyrite samples, to try account for the difference in reactivity of the samples.

5.3.4 Separation of Pyrite

Relatively pure samples of pyrite were needed to distinguish structural differences between the three different samples under study. Various different methods can be used to separate minerals from their host material, two of which are electromagnetic separation and heavy liquid separation. These methods were considered but not used - the first due to the inadequacy of the available equipment and the second due to the toxicity and consequent disposal problems of the heavy liquids which would need to be employed for the separation. It was also found that hand-picking of the pyrite under a microscope as suggested by some authors was not possible.

The use of heavy liquids for the separation of pyrite (Arora et al. 1978, Pugh et al. 1981, Ainsworth et al, 1982) employs the fact that the specific gravity of pyrite is 5.0 g cm^{-3}. Normally tetrabromoethane (specific gravity 2.9 g cm^{-3}) is used to separate the pyrite from the rest of the material, as most of the host material would have a specific gravity of less than 2.95 cm^{-3}, for example, illite clays have a specific gravity of about 2.7 g cm^{-3}. An alternative method also employs the fact that pyrite has a higher specific gravity than its host material, and uses a rising column of water to separate the pyrite, the dense pyrite falling to the bottom of the column at the fastest rate. Frost (1959) reported a very good separation of pyrite using a glass elutriating column. This method was employed in this project as it is relatively simple, inexpensive and has none of the hazards associated with the use of heavy liquids.

The apparatus is illustrated in Fig. 5.3. The water enters at the bottom of the column and as it rises up the column its velocity is reduced by about 50 percent as it enters the next largest portion of the column. The sample to be separated is placed in the column and the densest constituents of the sample fall quickest through the column. The sample had to be closely sized otherwise efficient separation would not be possible. This can be seen from Stokes Law:

$$v = \frac{g(\sigma-\rho)d^2}{18\eta}$$

v = settling velocity

g = acceleration due to gravity

σ = density of settling particle

ρ = density of water

η = viscosity of water

d = diameter of particle

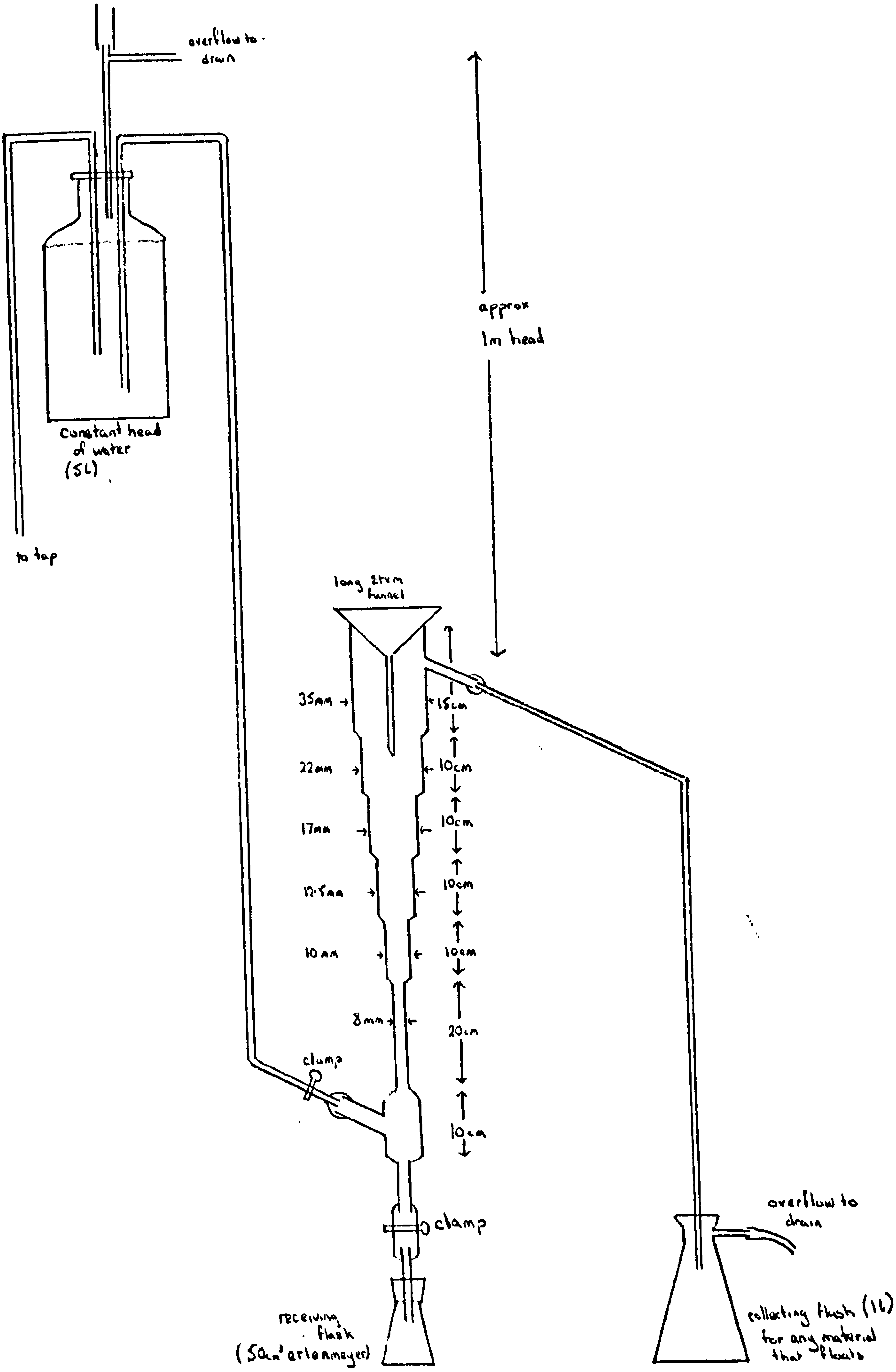


Fig 5.3. Diagram of Elutriating Apparatus (Frost 1959).

Either an increase in the diameter or an increase in the density of a particle would cause an increase in the velocity of the particle settling through the water. Unless the sample is closely sized less dense material will settle through the water at the same rate as pyrite of a smaller diameter.

Finely ground samples of pyrite were sieved but the smallest sieve size available had a pore size of 53 μm and the majority of the samples passed through this size sieve. Consequently the samples passed through the column were not necessarily of a small size range.

The samples had to be dispersed or wetted before passing through the column - Baads and Durham samples were dispersed using an ultrasonic probe and Tween 85 was used to wet the Ballachulish samples. Approximately 10 g samples were then quickly washed into the top of the elutriating column down the long stemmed funnel (this ensured that the sample was introduced below the overflow point and at a point where the velocity of the water was quite low). The flow of the rising water was controlled by the clamp on the tube of the inflowing water. It was adjusted so that one portion of the sample was held suspended in the smallest diameter part of the column at its base (this portion of the sample should have contained the pyrite). The flow of water was then decreased so that this portion of the sample would fall into the collecting flask. After the desired portion of the sample had fallen into the flask the flow of water was increased to stop any more of the sample falling into the flask. The flask could then be removed by tightening the appropriate clamp and a new flask (filled with water) could then be put into place. The procedure was repeated to collect other fractions of the sample.

Each of the different sieved size ranges were used in the column (150-105 μm, 105-53 μm, less than 53 μm). Some samples were passed through the column more than once to try to obtain a better separation. Examination of the fractions collected from the larger diameter range under a microscope showed that the pyrite was still associated with other material, so these samples were reground using a mortar and pestle. They were then again passed through the column. (A better method may have been to initially treat the sample with acetic acid, to dissolve the carbonate matrix, as suggested by Raiswell and Plant (1980). This, combined with grinding the sample might have helped separate the pyrite from its associated material, before it was passed through the column).

The concentration of the final separated samples was determined using the standard pyrite determination method, but scaled down so that it could be done in a centrifuge tube, to take account of the small amount of material.

The results were quite variable, but the concentration of pyrite in the Baads and Durham samples was quite high (Table 5.9). However, the actual recovery was very low - when a 10 g sample was used only about 1 g of separated material was obtained. This was probably due to the problem of obtaining a closely sized diameter range. Pyrite of the greatest diameter would settle fastest, but pyrite of a smaller diameter would settle at the same rate as non-pyritic material of a larger diameter. The separation of the Ballachulish pyrite was much less successful. These initial samples contained much less pyrite than the other samples, but it was more easily isolated by hand than the other samples as it occurred in discrete lumps in the material. However when these lumps were removed from the bulk of the material, examination of them under a microscope showed that there was still other non-pyritic material with the pyrite, and the recovery of the pyrite was very poor.

Sample	%FeS_2
Baads 1	90
Baads 2	78
Durham 1	77
Durham 2	83
Ballachulish 1	15
Ballachulish 2	12

Table 5.9 Concentration of Pyrite in Separated Samples

5.3.5 Comparison of Pyrite Samples by Electron Microscopy

Electron microscope pictures have been used extensively to show structural differences between various types of pyrite, and these structural differences are used to explain differences in reactivity. The various types of structures found by different authors were described in Chapter 1. Lowson (1982) suggested the broad classification of pyrite into framboidal pyrite - grains of pyrite with few or no cyrstal faces grouped into spherical aggregates, which tends to be considered the most reactive type of pyrite - and euhedral pyrite - well-crystalline - which is more stable than framboidal pyrite.

Electron micrographs were obtained for the Baads, Durham and Ballachulish pyrite, using samples that had been separated in the elutriating column. The Baads and Durham pyrite were very similar and the whole slide seemed to consist of the same material - only the Durham slide is reproduced here (Fig. 5.4). The diffraction pattern (Table 5.10) confirmed that these samples were pyrite. These two samples could not easily be classified into any of the categories described in Chapter 1. However, they were clearly not the well crystalline euhedral pyrite. The Ballachulish sample looked completely different from the other

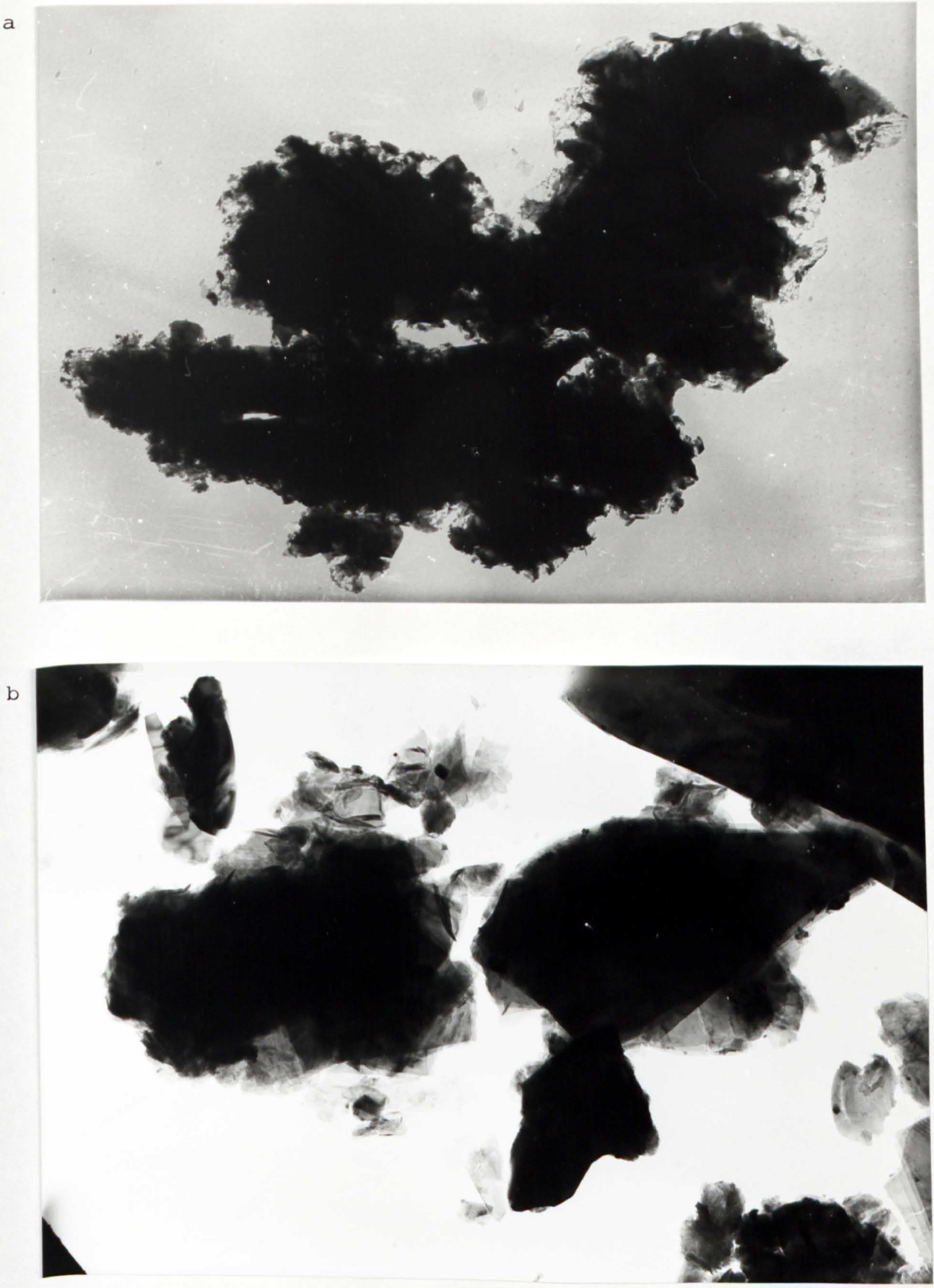


Fig 5.4 Electron Micrographs of Pyrite Samples from (a) Durham and (b) Ballachulish

Durham Sample	FeS_2 (pyrite)
3.14	3.13
2.73	2.71
----	2.42
2.19	2.21
1.64	1.63
1.50	1.50

Table 5.10 Electron Microscope Diffraction Patterns - The d Spacing of Durham Sample Compared to the Standard Pyrite d Spacing.

samples (Fig 5.4) and various pictures of this were taken. The diffraction pattern from this sample was very complicated and consequently no species could be defined from the pattern. There was much less pyrite in the Ballachulish sample than in the other samples and it may have been that it was more difficult to distinguish the Ballachulish pyrite from its host material, especially if the pyrite was quite crystalline and if the host material was crystalline. None of the structure observed throughout the Baads and Durham pyrite could be seen in the Ballachulish samples. As it is known that the Ballachulish sample did actually contain pyrite, it can be assumed that there was a definite structural difference between the Ballachulish sample and the other two samples. As other studies have shown that it is framboidal pyrite that is reactive and euhedral pyrite which is stable, it could be tentatively said that the Baads and Durham pyrite was framboidal pyrite whilst Ballachulish pyrite was euhedral pyrite.

The studies have shown that different types of pyrite have different reactivities. Even after grinding, acid washing and innoculating with T. ferrooxidans the Ballachulish pyrite did not oxidise at an appreciable rate. The electron micrographs showed that there was distinct structural differences between the reactive Baads and Durham pyrite and the stable Ballachulish pyrite. These were tentatively assigned to framboidal and euhedral pyrite respectively, on the basis of their reactivity and due to there being a definite difference in the structures. Even if these assignments are incorrect it has still been shown that there was a structural difference between the two types of reactive pyrite compared to the stable pyrite under study. The difference in structure probably explains the difference in reactivity.

CHAPTER 6

Practical Implications of the Study

There is increasing concern about various environmental problems, many of which were created by man's activities, for example, problems caused by waste disposal - both domestic and industrial, the latter including the reclamation of colliery spoil, - and also the detrimental effects of acid rain. Chemical studies to try to elucidate the mechanisms causing the environmental problems should be able to point to possible solutions.

In colliery spoil one of the main factors causing environmental problems is that of pyrite oxidation. The production of acid by the oxidation causes an increase in many metal ion concentrations, a decrease in the nutrient status of the spoil and a degradation of the physical properties of the spoil. These conditions mean that it is very difficult to establish vegetation on the spoil. The acid and metal ions can also infiltrate streams and rivers, polluting the water and often the surrounding land as well.

The chemical studies in this project, of pyrite oxidation in incubation flasks, showed that the relatively rapid rate of pyrite oxidation occurred via ferric iron. The oxidation was successfully inhibited by interfering with the role of ferric iron - a bactericide was used to inhibit the oxidation of ferrous iron to ferric iron; iron was complexed either by specific chemicals such as ethylenediamine-di(o-hydroxyphenyl acetic acid)(E.D.P.H.A), trisodium citrate or sodium silicate, or by waste materials such as chicken manure or woodwaste; and ferric iron was precipitated by phosphate or pulverised fuel ash (PFA).

In these flask studies the conditions were ideal for precipitation, complexation or chelation onto solid materials such as the woodwaste, as the pyrite was finely ground, and the pyrite and amendment were in suspension insuring contact between the iron and amendment. However, in the pot experiments the contact was reduced, and the inhibition of the oxidation was not so successful. The situation would presumably be even worse in the field.

In the laboratory experiments it was also found that limewater was more effective than dry lime in maintaining a reasonable spoil pH - due to the fact that the limewater not only neutralised existing acidity but also saturated the cation exchange sites with calcium. However, the spraying of limewater in the field may not be a very practical situation, and could also harm any vegetation which has been established if used to alleviate acid regeneration after the initial reclamation.

Even though the pot experiments were not very successful, various points have come out of the chemical studies, leading to suggestions of possible solutions in the attempts to overcome the problems caused by pyrite oxidation in colliery spoil.

The pot studies showed that lime or another alkaline amendment needs to be added to increase the spoil pH to a reasonable level to allow the establishment of vegetation. However, even though none of the amendments managed to significantly increase the spoil pH without the addition of lime, the growth of grass in the pots with amendments plus lime was better than in the limed only pots (with the exception of the phosphate plus lime pots). Therefore the amendments were having a beneficial effect on the spoil status - the chicken manure may have improved the nutrient status compared to the other pots (the nutrients from the chicken manure would only be slowly released whereas the nutrient solution added to the other pots would not have been retained in the spoil for very long); PFA may have supplied essential micro nutrients to the grass (although it may have also supplied toxic elements) or the alkaline nature of the PFA may have helped to neutralise the acid generated from the pyrite oxidation; woodwaste, citrate and EDPHA may have all acted as sources of organic substrates for bacteria essential to the development of a good soil; but the possible beneficial effects of florisil in these kind of terms is unclear. However, all of these amendments may actually have been inhibiting the pyrite oxidation, even though this was not really shown by the results of the study. Thus it would be sensible to use any of the waste materials - chicken manure, woodwastes or PFA - in reclamation schemes as they all improved the growth of grass and they should also be relatively cheap as they are waste products.

Obviously to reclaim pyritic colliery spoil, the pH must be raised to a reasonable level and then a vegetation cover must be built up. Lime can be used to raise the pH and the addition of organic waste materials such as woodwaste and chicken manure would help to increase the organic matter of the spoil, increasing the chance of vegetation being established. If a reasonable organic matter content is built up - by the addition of chicken manure and woodwastes as well as by the breakdown of plant debris - then this will act as a sink for ferrous and ferric ions in the same way as the chicken manure and woodwaste were shown to act. It should also act as a sink for other metal ions that are released into the spoil due to an increase in the acidity of the spoil. Woodwastes would also improve the spoil physical properties (as discussed in Chapter 3) whilst chicken manure would improve the spoil nutrient status. In order to maintain vegetation on the spoil, the spoil will normally require aftercare. Bloomfield et al (1982) showed that vegetation benefits from extra nutrients added after the initial reclamation, and the spoil will often need to be relimed due to acid regeneration. Although the effective application of lime entails ploughing it into the spoil, which will destroy any vegetation that has been established, it is better that this should happen than the spoil be allowed to reach a very low pH, which would cause the death of the plants anyhow.

It may be possible to substitute PFA instead of lime, at least in the initial reclamation scheme, as it is also an alkaline material (although different sources of PFA vary in their neutralising capacity). Chicken manure and PFA applied to acidic colliery spoil should produce a reasonable growing medium. Organic wastes have been shown to improve the fertility of lagooned PFA (Rippon and Wood 1975) - it was suggested this was due to the chicken manure acting as a microbial fertilizer as the PFA itself was sterile. PFA should neutralise the acidity of the colliery spoil and perhaps supply essential micronutrients for plant growth, and chicken manure should act as a source of nutrients as well as an organic substrate for bacteria. This kind of solution would be a suitable way of disposing of the three waste materials - colliery spoil, PFA and chicken manure - with better soil conditions as the result.

The quantity of materials applied to the spoil is important. High rates of amendments would increase contact between the pyrite and amendment and thus improve the chance of the amendment inhibiting pyrite oxidation. PFA has been used at very high rates in other studies to treat acidic mine spoils - Plass and Capp (1974) used PFA at about 60 tonnes ha^{-1}, whilst Plank et al. (1975) reported that it could be used at rates of up to 288 tonnes ha^{-1} to treat acidic soils. (In the pot experiments of this study it was used at only 15 tonnes ha^{-1}). Wittwer et al. (1980) found that hardwood bark applied as a mulch at a rate of 80 m^3 ha^{-1} (a 5 cm depth of bark) increased the spoil moisture content and decreased spoil temperature, whilst Koon and Graves (1980) found that hardwood bark applied at about 132 m^3 ha^{-1} improved the growth of legumes in the initial reclamation. In the pot experiments of this study woodwastes were applied at much lower rates (20 tonnes ha^{-1}). However chicken manure, if applied at very high rates, can cause problems due to the production of ammonia. In this study it was used at 5 tonnes ha^{-1}, but Bradshaw et al. (1973) suggested applying it at 12 tonnes ha^{-1} as a fertilizer for colliery spoil. Therefore all three waste materials could be applied at higher rates than used in this study, but care must be taken not to apply too much chicken manure. The amendments could all be applied at the same time as the lime and fertilizer for the site, and thus its incorporation should not increase the cost of reclamation.

It may also be possible to use these waste materials in other ways to cope with the problems caused by pyrite oxidation. Woodwastes or PFA could be used as interception ditches between rivers or streams and the pyritic area - the PFA could neutralise some of the drainage whilst the woodwaste would act as a sink for metal ions. This would help to prevent the pollution of the watercourse and may help to inhibit the formation of ochre in drains, which has been shown to be a major problem near pyritic soils (Bloomfield 1972). Woodwastes in particular could also be used in localised areas, for example, around tree roots, to help the establishment of the trees. The use of chicken manure in concentrated localised areas would probably not be very useful, due to its high nitrogen content.

The availability of the waste materials must be taken into account - transport is very expensive and therefore it would only be economical to use relatively local supplies of the waste materials. Also the type of pyrite involved must be considered - there is no point in applying relatively expensive treatments to a Ballachulish type of pyrite (i.e. relatively unreactive), if the only point is to try to inhibit the pyrite oxidation, as opposed to improve the spoil or soil conditions.

It must be recognised that the reclamation of pyritic colliery spoil involves aftercare of the site as well as the initial reclamation - it is highly improbable that a site could be successfully reclaimed with only one treatment. The sites must be carefully managed until a reasonable vegetation cover is properly established. This approach may not be immediately acceptable to local authorities generally in charge of these schemes, due to their various financial constraints. However, it is obviously totally uneconomical to reclaim a site and then allow it to revert to its original condition - once it is decided to reclaim a site, it must be a reasonably long term committment. As suggested by this study a cost effective method would be to use local waste materials to help alleviate the problems of acidic colliery spoil.

APPENDIX

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(Numbers in brackets refer to relevant chapter and section for each table).

Day	pH	$mgSg^{-1}$	$mgSO_4^{2-}g^{-1}$	$mgFe^{2+}g^{-1}$	$mgFe^{3+}g^{-1}$	$mgH^{+}g^{-1}$
0	2.8	18.9	71.3	11.0	3.39	0.94
2	2.5	20.5	59.5	17.4	0.45	1.03
4	2.5	9.5	60.5	19.7	0.60	1.11
6	2.4	15.2	62.5	22.1	0.64	1.17
8	2.4	14.7	55.9	20.9	0.00	1.21
10	2.5	13.4	75.9	15.6	1.22	1.18
12	2.5	14.2	78.7	20.3	2.17	1.39
14	2.6	10.7	62.3	19.4	1.37	1.48
16	2.6	21.8	80.6	22.3	1.75	1.40
19	2.4	16.2	92.4	22.6	1.34	1.45
21	2.6	13.6	89.9	26.0	2.82	1.58
23	2.6	6.3	81.0	24.6	2.25	1.53
27	2.4	9.9	86.5	30.9	0.00	1.60
30	2.3	15.5	82.4	30.0	1.66	1.56
34	2.4	21.0	93.4	37.0	2.42	1.70
37	2.4	17.6	96.6	29.8	2.63	1.83
43	2.4	22.8	88.6	35.7	0.00	1.92
48	2.1	30.4	105.0	39.4	3.55	2.06
51	2.0	28.7	116.6	36.3	2.99	2.20
56	2.1	26.6	123.1	38.1	4.58	2.23
62	2.0	32.0	123.4	41.4	4.33	2.37

Results are presented as mean of triplicate flasks.

Table A1 Release of Oxidation Products from Baads Pyrite in Solution.

pH

Day	0	1	6	13	19	27	34	47	63	74	100	121
Control	2.4	2.1	2.0	2.0	1.9	1.9	2.0	2.4	2.3	2.2	2.1	2.2
O-phenanthroline	2.4	2.2	2.3	2.0	2.0	2.9	2.8	2.8	2.5	2.3	2.1	2.3
Panacide	2.7	2.2	2.1	2.3	2.4	2.1	2.1	2.3	2.5	2.3	2.3	2.4
0.5 g $FeCl_3$	1.2	1.1	0.6	0.5	0.8	0.7	0.5	0.9	1.2	1.2	1.1	1.2
2.5 g $FeCl_3$	1.2	0.7	0.3	0.5	0.5	0.4	0.4	0.7	1.1	1.1	1.1	1.2

$mgH^{+}\ g^{-1}$

Day	1	6	13	19	27	34	47	63	74	100	121
Control	0.85	0.85	0.92	0.93	1.05	1.01	1.04	1.16	1.28	1.45	1.58
O-phenanthroline	0.67	0.70	0.73	0.75	0.39	0.38	0.35	0.38	0.39	0.52	0.62
Panacide	0.79	0.75	0.77	0.73	0.71	0.68	0.66	0.67	0.72	0.76	0.77
0.5 g $FeCl_3$	10.0	10.2	9.3	8.7	8.1	7.5	7.2	6.7	6.1	6.0	5.5
2.5 g $FeCl_3$	18.1	16.7	16.2	14.1	13.4	13.0	10.9	10.8	9.9	9.4	9.1

Results are presented as mean of triplicate flasks. Only pH was measured on day 0.
Extra o-phenanthroline added after day 19.

Table A2 Effect of Altering Ferrous or Ferric Iron Concentration on the Oxidation of Pyrite - Baads Pyrite

$mgSO_4^{2-}\ g^{-1}$

	Day 1	6	13	19	27	34	47	63	74	100	121
Control	50.6	42.3	43.3	45.7	53.1	47.5	50.6	55.4	67.8	68.8	77.1
O-phenanthroline	39.1	41.0	39.1	35.7	37.0	33.9	37.8	42.6	48.3	46.4	52.5
Panacide	41.6	40.8	39.6	38.0	45.8	36.5	32.7	36.1	35.2	37.5	40.2
0.5 g $FeCl_3$	43.4	49.8	48.4	52.0	55.2	49.3	46.8	49.1	58.7	56.2	56.3
2.5 g $FeCl_3$	31.5	54.2	65.6	70.4	71.4	63.5	56.4	60.4	64.6	65.5	67.2

$mgFe\ g^{-1}$

	Day 1	6	13	19	27	34	47	63	74	100	121
Control				13.7	13.8	18.6	18.9	19.6	19.3	20.8	19.8
O-phenanthroline	NOT			11.6	11.1	14.4	14.0	14.6	13.5	16.1	15.4
Panacide	MEASURED			10.7	10.3	12.5	13.7	12.0	12.4	11.8	11.2
0.5 g $FeCl_3$				37.0	38.2	38.3	31.4	39.2	36.3	30.4	30.4
2.5 g $FeCl_3$				138.8	121.3	131.7	103.8	112.8	124.5	97.8	88.0

Table A2 Continued.

pH

Day	0	1	6	13	19	27	34	47	63	74	100	121
Control	4.4	4.3	3.8	2.9	2.5	2.3	2.4	2.4	2.5	2.4	2.3	2.4
O-phenanthroline	4.8	4.9	3.7	2.8	2.7	5.3	5.3	5.2	5.1	4.2	2.9	2.5
Panacide	8.4	6.1	4.2	3.4	3.1	3.1	3.1	2.8	3.0	2.7	2.6	2.6
0.5 g $FeCl_3$	1.4	0.8	0.8	0.9	1.0	0.7	0.7	1.1	1.4	1.3	1.4	1.4
2.5 g $FeCl_3$	1.2	0.6	0.4	0.4	0.9	0.4	0.6	0.8	1.2	1.1	1.3	1.1

$mgH^+ g^{-1}$

Day	1	6	13	19	27	34	47	63	74	100	121
Control	0.07	0.17	0.26	0.40	0.50	0.51	0.59	0.69	0.79	0.92	0.99
O-phenanthroline	0.03	0.05	0.15	0.23	0.14	0.14	0.15	0.16	0.17	0.22	0.25
Panacide	0.03	0.10	0.15	0.19	0.23	0.26	0.30	0.27	0.34	0.41	0.45
0.5 g $FeCl_3$	9.9	9.3	8.8	7.9	7.5	6.8	6.6	6.2	5.4	5.6	5.2
2.5 g $FeCl_3$	18.0	16.9	15.8	14.3	13.3	12.1	11.7	10.7	9.6	9.3	8.8

Results are presented as mean of triplicate flasks. Only pH measured on day 0.
Extra o-phenanthroline added after day 19.

Table A3 Effect of Altering Ferrous or Ferric Iron Concentration on the Oxidation of Pyrite - Durham Pyrite

$mgSO_4^{2-}\ g^{-1}$

Day	1	6	13	19	27	34	47	63	74	100	121
Control	4.8	10.2	12.0	17.7	27.6	24.8	27.7	33.1	40.2	43.1	46.8
O-phenanthroline	12.8	6.3	12.1	18.8	23.8	16.5	17.6	20.8	26.0	24.8	30.3
Panacide	6.9	7.8	12.3	11.9	14.8	8.5	12.5	14.6	16.3	19.2	20.9
0.5 g $FeCl_3$	4.4	11.5	14.6	19.2	25.1	20.8	21.6	22.4	32.2	32.7	36.9
2.5 g $FeCl_3$	10.9	24.9	41.1	39.7	44.3	37.5	35.0	35.4	41.6	40.0	44.1

$mgFe\ g^{-1}$

Day	1	6	13	19	27	34	47	63	74	100	121
Control				5.8	8.4	10.0	12.2	12.2	13.1	13.9	13.5
O-phenanthroline		NOT		4.8	5.5	6.4	6.7	8.5	9.4	10.6	10.9
Panacide		MEASURED		2.2	3.7	4.8	5.0	5.8	6.8	6.5	7.2
0.5 g $FeCl_3$				32.4	31.4	24.6	24.2	32.0	30.7	26.1	23.5
2.5 g $FeCl_3$				133.4	128.4	112.8	105.6	112.4	107.8	93.3	85.4

Table A3 continued.

<u>pH</u>

Amount of O-phenanthroline Added (g)	Day 1	10	18	30	50	64	85
0.0	2.6	2.5	2.7	2.6	2.5	2.5	2.4
0.05	2.6	2.5	2.7	2.6	2.5	2.5	2.3
0.10	2.7	2.5	2.8	2.5	2.5	2.5	2.4
0.2	2.9	3.3	3.2	2.6	2.6	2.5	2.4

$\underline{\mathrm{mgH^{+}\ g^{-1}}}$

Amount of O-phenanthroline Added (g)	Day 1	10	18	30	50	64	85
0.0	1.50	1.78	2.03	2.43	3.00	3.40	4.06
0.05	1.38	1.31	1.58	1.41	2.24	2.51	3.16
0.1	0.92	0.93	1.30	1.36	1.86	2.14	2.73
0.2	0.78	0.72	0.90	0.88	1.06	1.33	1.98

Results are presented as mean of duplicate flasks.

Table A4 <u>Effect of Different Concentrations of O-phenanthroline on Oxidation of Pyrite - Baads Pyrite</u>

$mgSO_4^{2-}\ g^{-1}$

Amount of O-phenanthroline Added (g)	Day 1	10	18	30	50	64	85
0.0	72.5	83.4	101.0	120.1	143.3	154.0	182.2
0.05	67.1	70.3	114.1	97.5	115.1	117.4	166.0
0.1	63.9	80.2	89.6	109.2	117.1	117.8	181.3
0.2	60.7	67.0	89.1	96.2	55.1	64.1	189.0

$mgFe^{2+}\ g^{-1}$

Amount of O-phenanthroline Added (g)	Day 1	10	18	30	50	64	85
0.0	18.3	28.0	30.6	36.6	41.0	48.6	57.6
0.05	16.6	25.5	28.3	34.0	37.8	43.9	52.0
0.1	15.4	26.5	29.3	32.9	38.7	41.9	52.9
0.2	17.6	26.4	30.0	34.3	38.6	41.9	56.4

Table A4 Continued.

pH

Amount of O-phenanthroline Added (g)	Day 1	10	18	30	50	64	85
0.0	4.3	3.3	3.6	2.9	2.8	2.8	2.5
0.05	5.1	3.5	3.5	2.9	2.7	2.7	2.5
0.1	5.8	5.3	4.7	4.0	2.9	2.7	2.5
0.2	6.0	5.8	5.6	5.7	5.2	4.5	2.8

$\text{mgH}^{+}\ \text{g}^{-1}$

Amount of O-phenanthroline Added (g)	Day 1	10	18	30	50	64	85
0.0	0.31	0.65	0.90	1.17	1.49	1.82	2.25
0.05	0.14	0.25	0.55	0.73	1.47	1.50	1.96
0.1	0.10	0.17	0.31	0.26	0.50	0.77	1.04
0.2	0.12	0.12	0.23	0.16	0.19	0.31	0.40

Results are presented as mean of duplicate flasks.

Table A5 Effect of Different Concentrations of O-phenanthroline on Oxidation of Pyrite - Durham Pyrite

$mgSO_4^{2-}\ g^{-1}$

Amount of O-phenanthroline Added (g)	Day 1	10	18	30	50	64	85
0.0	10.5	22.3	36.1	51.7	81.5	96.4	105.0
0.05	7.3	19.2	35.6	57.5	77.7	64.7	90.7
0.1	12.3	28.1	36.1	52.4	45.0	57.2	85.5
0.2	6.4	23.8	19.0	31.2	22.9	32.8	76.1

$mgFe^{2+}\ g^{-1}$

Amount of O-phenanthroline Added (g)	Day 1	10	18	30	50	64	85
0.0	6.0	13.0	16.3	21.3	26.1	33.9	36.8
0.05	5.4	8.6	15.1	19.3	30.0	29.1	34.5
0.1	5.0	5.1	14.3	14.3	22.3	26.0	30.8
0.2	4.8	7.1	12.3	16.5	23.8	26.3	35.9

Table A5 Continued.

Baads Pyrite

Amount of O-phenanthroline Added (g)	Amount of O-phenanthroline Needed (g)						
	Day 1	10	18	30	50	64	85
0.0	0.09	0.14	0.15	0.18	0.20	0.24	0.28
0.05	0.08	0.12	0.14	0.27	0.19	0.22	0.26
0.1	0.07	0.13	0.14	0.16	0.19	0.21	0.26
0.2	0.08	0.13	0.15	0.17	0.19	0.21	0.28

Durham Pyrite

Amount of O-phenanthroline Added (g)	Amount of O-phenanthroline Needed (g)						
	Day 1	10	18	30	50	64	85
0.0	0.03	0.06	0.08	0.10	0.13	0.17	0.18
0.05	0.02	0.04	0.07	0.09	0.15	0.15	0.17
0.1	0.02	0.02	0.07	0.07	0.11	0.13	0.15
0.2	0.02	0.03	0.06	0.08	0.12	0.13	0.18

Table A6 Amount of O-phenanthroline Needed to Complex all the Iron in Solution - Amount of Iron in Solution Shown in Table A4 (Baads) and Table A5 (Durham).

			$mgFe^{2+}\ l^{-1}$											
Buffer Solution	to pH	Day	1	4	5	7	8	11	13	15	18	21	29	35
	2.3		200	200	200	200	200	200	200	200	200	200	200	200
phthalic acid/ phthalate	2.6		200	200	200	200	200	200	200	200	200	200	200	200
	3.0		200	200	200	200	200	200	200	195	190	195	185	190
	3.4		200	200	200	200	200	200	200	195	185	175	170	170
	3.6		200	200	200	200	200	185	175	175	170	170	170	160
	3.4		200	200	200	200	200	200	200	195	185	175	170	170
acetic acid/ acetate	4.0		200	190	190	190	185	170	170	160	145	145	135	135
	5.0		175	115	110	85	80	60	50	45	30	20	15	0
	5.8		110	40	10	0	0							
Baads Solution	2.9		80	75	70	45	40	10	0	0				
Durham Solution	3.4		55	45	40	35	10	1	0	0				

Results are presented as mean of duplicate flasks.

Table A7 Comparison of Rate of Oxidation of Ferrous Iron in Solutions Buffered to Different pH's and of Ferrous Iron Isolated from Baads and Durham Flasks.

$mgFe^{2+}\ l^{-1}$

Baads	Day 1	3	6	9	17	23	35	45
Control	90	90	63	40	10	1	0	0
0.1 g O-phenanthroline	90	90	85	85	85	85	85	85
0.025 cm^3 Panacide	90	90	85	85	85	85	85	85

Durham	Day 1	3	6	9	17	23	35	45
Control	50	45	40	20	5	1	0	0
0.1 g O-phenanthroline	45	40	40	40	40	40	40	40
0.025 cm^3 Panacide	45	40	40	40	40	40	40	40

Results are presented as mean of duplicate flasks.

Table A8 Inhibition of Ferrous Iron Oxidation by O-phenanthroline and Panacide

		pH						
	Lime Rate (g)	Day 1	13	27	34	49	60	91
Control	0.0	2.8	3.1	2.8	2.8	2.7	2.6	2.6
	0.4	4.0	3.5	3.0	2.9	2.7	2.6	2.5
	0.8	6.6	4.6	3.5	3.2	3.0	2.8	2.6
O-phenanthroline	0.0	3.4	4.2	3.4	3.1	2.8	2.7	2.4
	0.4	5.2	4.7	5.4	4.0	3.6	2.9	2.5
	0.8	7.2	5.9	7.6	7.3	7.7	7.3	3.6
Panacide	0.0	3.2	3.2	3.1	3.0	2.9	2.8	2.7
	0.4	4.6	4.0	4.0	3.6	3.4	3.3	3.0
	0.8	7.5	5.7	7.4	7.0	7.3	7.2	6.9
Sodium Dihydrogen Phosphate	0.0	3.1	3.2	3.0	3.0	2.9	2.7	2.7
	0.4	3.8	3.7	3.4	3.3	3.0	2.8	2.7
	0.8	5.6	4.8	5.2	4.3	4.6	5.3	3.4
Disodium Hydrogen Phosphate	0.0	6.8	6.6	6.6	6.5	6.5	6.4	6.4
	0.4	7.0	6.8	6.9	6.8	6.7	6.5	6.6
	0.8	7.2	6.9	7.1	7.0	6.9	6.8	6.8
Trisodium Citrate	0.0	6.2	6.8	7.0	7.0	8.0	8.0	8.0
	0.4	6.2	7.0	7.2	7.3	8.0	8.0	8.4
	0.8	6.7	7.3	7.8	7.7	8.3	8.3	8.6

Results are presented as mean of duplicate flasks.

Trisodium citrate flasks not sampled on day 1 (pH only measured on day 1).

Table A9 Effect of Various Amendments, With and Without Lime on Oxidation of Pyrite

		mgH^+ g^{-1} Spoil						
	Lime Rate (g)	Day 1	13	27	34	49	60	91
Control	0.0	0.09	0.11	0.16	0.16	0.17	0.21	0.33
	0.4	0.03	0.05	0.10	0.11	0.15	0.16	0.31
	0.8	0.01	0.02	0.03	0.03	0.06	0.08	0.14
O-phenanthroline	0.0	0.03	0.04	0.04	0.06	0.14	0.17	0.32
	0.4	0.01	0.01	0.01	0.02	0.06	0.10	0.24
	0.8	0.01	0.02	0.01	0.01	0.01	0.02	0.05
Panacide	0.0	0.06	0.07	0.12	0.11	0.13	0.15	0.19
	0.4	0.03	0.04	0.04	0.04	0.04	0.07	0.14
	0.8	0.01	0.02	0.01	0.01	0.01	0.02	0.02
Sodium Dihydrogen Phosphate	0.0	0.31	0.30	0.36	0.27	0.25	0.24	0.25
	0.4	0.31	0.29	0.48	0.26	0.25	0.22	0.26
	0.8	0.26	0.27	0.27	0.25	0.23	0.21	0.22
Disodium Hydrogen Phosphate	0.0	0.11	0.15	0.15	0.15	0.14	0.13	0.13
	0.4	0.06	0.10	0.10	0.10	0.11	0.10	0.11
	0.8	0.06	0.08	0.07	0.07	0.08	0.08	0.08
Trisodium Citrate	0.0	--	0.04	0.03	0.04	0.02	0.01	0.0
	0.4	--	0.04	0.04	0.04	0.01	0.01	0.0
	0.8	--	0.04	0.02	0.04	0.0	0.0	0.0

Table A9 Continued.

		mgFe g^{-1} Spoil						
	Lime Rate (g)	Day 1	13	27	34	49	60	91
Control	0.0	0.54	0.82	1.69	1.87	1.54	1.78	3.24
	0.4	0.24	0.12	0.74	0.27	1.21	1.31	1.56
	0.8	0.0	0.01	0.02	0.04	0.09	0.18	0.47
O-phenanthroline	0.0	0.03	0.25	0.81	1.00	1.67	1.88	3.32
	0.4	0.03	0.45	0.91	0.94	0.85	1.15	2.52
	0.8	0.0	0.08	0.32	0.37	0.49	0.41	0.51
Panacide	0.0	0.49	0.49	0.99	1.10	1.23	1.42	2.20
	0.4	0.10	0.10	0.20	0.19	0.35	0.53	1.15
	0.8	0.0	0.0	0.0	0.0	0.0	0.01	0.06
Sodium Dihydrogen Phosphate	0.0	0.02	0.01	0.01	0.02	0.02	0.02	0.03
	0.4	0.02	0.0	0.01	0.01	0.01	0.01	0.03
	0.8	0.0	0.01	0.01	0.04	0.02	0.03	0.03
Disodium Hydrogen Phosphate	0.0	0.03	0.02	0.01	0.05	0.01	0.01	0.01
	0.4	0.0	0.0	0.0	0.02	0.01	0.01	0.01
	0.8	0.0	0.01	0.02	0.02	0.01	0.01	0.05
Trisodium Citrate	0.0	--	3.10	1.55	0.26	0.01	0.01	0.01
	0.4	--	2.25	2.85	0.29	0.01	0.02	0.01
	0.8	--	0.75	0.02	0.02	0.01	0.01	0.05

Table A9 Continued.

	Lime Rate (g)	Day 1	13	27	34	49	60	91
		$mgSO_4^{2-}\ g^{-1}$ Spoil						
Control	0.0	8.7	12.3	14.5	14.2	13.7	14.7	20.4
	0.4	11.9	14.4	14.8	16.2	16.2	16.9	19.1
	0.8	7.3	9.2	8.9	8.5	10.9	10.9	14.3
O-phenanthroline	0.0	7.9	5.7	9.8	13.4	14.8	18.6	20.8
	0.4	11.5	8.9	16.4	15.5	14.0	15.7	24.8
	0.8	8.3	12.0	11.4	11.2	10.2	9.6	16.7
Panacide	0.0	9.2	10.5	11.2	11.5	12.0	12.2	15.7
	0.4	10.1	11.0	10.6	11.3	13.1	9.9	15.7
	0.8	9.1	13.8	13.2	13.0	10.7	10.1	13.6
Sodium Dihydrogen Phosphate	0.0	8.1	9.1	10.0	12.7	10.6	13.2	17.8
	0.4	11.9	13.0	11.7	13.7	11.9	13.8	23.3
	0.8	7.9	12.3	11.4	12.7	9.6	11.9	18.6
Disodium Hydrogen Phosphate	0.0	9.7	11.8	10.5	11.8	8.5	9.6	13.6
	0.4	11.7	12.8	13.9	11.2	10.2	11.9	16.1
	0.8	9.9	6.7	11.9	12.0	11.2	11.4	13.8
Trisodium Citrate	0.0	--	15.2	19.8	17.1	0.0	0.0	0.0
	0.4	--	23.5	19.0	14.1	0.0	0.0	0.0
	0.8	--	17.1	19.0	9.4	0.0	0.0	0.0

Table A9 Continued.

pH

Day	1	7	34	47	68
Control	2.5	2.6	2.4	2.5	2.4
O-phenanthroline	2.5	2.3	4.6	3.5	2.4
Panacide	2.5	2.4	2.5	2.4	2.4
Sodium Dihyrogen Phosphate	2.5	2.5	2.3	2.4	2.3
Disodium Hydrogen Phosphate	2.5	2.2	2.9	2.6	2.4
Trisodium Citrate	2.5	2.4	4.5	3.4	2.8

$mgH^{+}\ g^{-1}$

Day	1	7	34	47	68
Control	1.63	1.68	2.55	2.68	3.38
O-phenanthroline	1.71	1.70	0.68	0.73	0.86
Panacide	1.74	1.74	1.82	1.75	1.92
Sodium Dihydrogen Phosphate	1.67	1.69	1.99	1.75	2.14
Disodium Hydrogen Phosphate	1.71	1.73	0.95	1.05	1.40
Trisodium Citrate	1.73	1.76	0.75	0.89	1.18

$mgSO_4^{2-}\ g^{-1}$

Day	1	7	34	47	68
Control	74.6	77.8	139.0	132.5	160.1
O-phenanthroline	76.9	77.4	93.0	74.4	103.2
Panacide	75.6	85.0	90.5	77.7	86.6
Sodium Dihydrogen Phosphate	86.0	79.1	85.0	92.7	123.3
Disodium Hydrogen Phosphate	79.5	77.9	115.7	94.2	120.7
Trisodium Citrate	72.8	78.9	108.5	105.9	122.7

Results are presented as mean of duplicate flasks.

Table A10 Effect of Various Amendments on Pyrite Oxidation

$mgFe\ g^{-1}$

	Day 1	7	34	47	68
Control	25.4	27.5	41.2	39.6	61.3
O-phenanthroline	26.8	26.6	25.6	30.5	45.4
Panacide	27.2	27.7	31.9	29.3	43.2
Sodium Dihydrogen Phosphate	27.0	27.8	1.5	1.7	6.6
Disodium Hydrogen Phosphate	27.1	27.9	0.1	0.2	1.3
Trisodium Citrate	27.7	28.3	35.0	36.6	52.3

$mgFe^{2+}\ g^{-1}$

	Day 1	7	34	47	68
Control	17.6	27.5	39.5	37.4	44.1
O-phenanthroline	17.2	26.6	28.6	32.6	36.5
Panacide	17.2	27.7	31.9	29.3	43.2
Sodium Dihydrogen Phosphate	17.4	27.8	0.5	0.5	3.3
Disodium Hydrogen Phosphate	17.6	27.9	0.0	0.0	0.5
Trisodium Citrate	17.8	28.3	7.3	7.0	16.0

Table A10 Continued.

pH

	Day 12	25	39	67	88
Control	2.5	2.2	2.2	2.1	2.0
Woodwaste	2.5	2.7	2.5	2.4	2.2
Chicken Manure	2.5	6.9	6.1	7.5	7.4
E.D.P.H.A.	2.5	2.1	2.0	2.2	2.2
Florisil	2.5	3.2	2.9	2.6	2.4

$mgH^{+}\ l^{-1}$

	Day 12	25	39	67	88
Control	21.9	40.5	72.0	136.0	260.0
Woodwaste	22.1	16.7	29.0	45.0	55.0
Chicken Manure	22.1	4.0	8.5	2.0	0
E.D.P.H.A.	24.0	38.0	46.2	58.5	73.0
Florisil	26.1	4.0	9.0	33.5	63.0

$gSO_4^{2-}\ l^{-1}$

	Day 12	25	39	67	88
Control	0.57	2.47	4.37	6.96	9.00
Woodwaste	0.55	1.66	2.15	2.68	3.35
Chicken Manure	0.60	2.10	1.60	0.94	0.11
E.D.P.H.A.	0.62	2.05	2.29	2.70	3.33
Florisil	0.60	2.11	2.63	3.71	5.19

Results are presented as of duplicate flasks.

Additions made on day 13.

Table A11 Effect of Waste Materials and Specific Chemicals on Oxidation of Pyrite

$mgFe\ l^{-1}$

	Day 12	25	39	67	88
Control	313	900	725	1300	3800
Woodwaste	300	293	330	405	775
Chicken Manure	318	130	100	23	3
E.D.P.H.A.	330	775	875	575	1150
Florisil	343	17	59	350	975

$mgFe^{2+}\ l^{-1}$

	Day 12	25	39
Control	98	100	135
Woodwaste	98	55	120
Chicken Manure	95	0	118
E.D.P.H.A.	68	---	---
Florisil	64	12	0

(The ferrous iron determination was not continued after day 39 as the solution in the flasks were all slightly coloured and this interferred with the colormetric determination. The solution in the E.D.P.H.A. flasks turned red upon the addition of the E.D.P.H.A. after day 12 and thus ferrous iron could not be determined in these flasks).

Table A11 Continued.

pH

	Day 12	35	47	68	104	138	161
Control	3.3	2.8	2.8	2.6	2.7	2.2	2.2
PFA	7.0	5.2	5.0	4.4	3.8	3.5	3.0
Florisil	7.0	5.6	4.9	3.7	3.5	3.0	2.7
1.5% Si	11.2	10.6	10.6	10.1	9.5	10.0	10.0
0.75% Si	10.7	10.2	10.0	9.3	9.3	9.8	9.6
	Day 22	34	55	91	125	148	
0.15% Si	8.5	7.8	7.2	7.1	7.0	6.9	
0.015% Si	3.2	3.1	2.6	3.0	2.3	2.2	

$mgH^{+}\ l^{-1}$

	Day 12	35	47	68	104	138	161
Control	12.5	18.5	23.0	33.6	54.7	72.0	70.7
PFA	1.1	0.7	0.7	1.3	4.7	9.7	9.7
Florisil	0.4	0.4	0.9	2.2	8.7	16.7	17.2
1.5% Si	0	0	0	0	0	0	0
0.75% Si	0	0	0	0	0	0	0
	Day 22	34	55	91	125	148	
0.15% Si	0	0.2	0.4	0.4	0.7	0.7	
0.015% Si	10.7	14.0	22.5	38.4	53.3	56.0	

Results are presented as mean of triplicate flasks.

Table A12 Effect of Silicon-Containing Amendments on Pyrite Oxidation

$gSO_4^{2-}\ l^{-1}$

	Day 12	35	47	68	104	138	161
Control	0.92	1.16	1.28	1.45	2.58	3.26	3.45
PFA	0.61	1.11	1.15	1.15	1.38	1.63	1.27
Florisil	0.84	1.23	1.09	1.38	1.50	1.95	2.02

	Day 22	34	55	91	125	148
0.015% Si	1.04	0.96	1.11	1.90	2.61	2.82

(Sulphate test not possible for flasks containing 1.5%, 0.75% and 0.15% Si)

$mgFe\ l^{-1}$

	Day 12	35	47	68	104	138	161
Control	180	230	328	418	550	800	847
PFA	0.0	0.1	0.2	0.3	0.9	10	15
Florisil	1.7	0.1	4.3	11.8	100	157	186
1.5% Si	130	88	65	2.8	1.4	1.1	1.7
0.75% Si	153	128	196	170	88	47	6.0

	Day 22	34	55	91	125	148
0.15% Si	103	123	113	90	83	84
0.015% Si	210	260	332	330	500	753

Table A12 Continued.

mgSi l^{-1}

	Day 12	35	47	68	104	138	161
Control	5	8		11	15	15	19
PFA	11	26		53	60	67	83
Florisil	47	59		88	80	80	86
1.5% Si	15000	11200		2700	380	170	310
0.75% Si	7500	5400		5300	1200	980	980

	Day 22	34	55	91	125	148
0.15% Si	710		670	600	500	450
0.015% Si	120		110	60	60	65

Si not measured on day 47 and 34.

Table A12 Continued.

pH of Spoil

Day	20	46	102	144	207	278
Control	2.9 (0.3)	* 2.5 (0.5)	2.3 (0.3)	2.0 (0.3)	---	2.4 (0.2)
Chicken Manure	2.2 (0.3)	2.3 (0.2)	2.4 (0.3)	2.7 (0.5)	---	2.8 (0.7)
Woodwaste	3.4 (0.4)	2.6 (0.5)	2.3 (0.4)	2.1 (0.2)	---	2.5 (0.17)
Sodium Dihydrogen Phosphate	3.6 (1.5)	2.3 (0.4)	2.1 (0.4)	2.1 (0.2)	---	2.4 (0.2)
Trisodium Citrate	3.1 (0.8)	3.1 (0.3)	2.4 (0.2)	2.0 (0.1)	---	2.4 (0.3)
E.D.P.H.A.	3.4 (0.3)	2.2 (0.1)	2.2 (0.4)	2.0 (0.1)	---	2.3 (0.1)
Florisil	2.5 (0.4)	2.3 (0.3)	2.3 (0.4)	2.4 (0.7)	---	2.3 (0.1)

Results are presented as the mean for each group of four pots. The standard deviation for each group is in brackets.
* indicates a significant difference between groups for that sampling, using $\alpha = 0.05$.
pH spoil not measured on day 207.

Table A13. Analysis of Half-Lime Pots

pH of Leachate

Day	20	46	102	144	207	278
Control	3.3 (0.8)	* 2.2 (0.1)	* 2.0 (0.1)	* 2.1 (0.0)	* 1.8 (0.1)	2.4 (0.0)
Chicken Manure	2.4 (0.1)	2.4 (0.1)	2.4 (0.1)	2.4 (0.1)	1.9 (0.0)	2.5 (0.1)
Woodwaste	3.0 (0.2)	2.3 (0.1)	2.3 (0.1)	2.3 (0.0)	1.8 (0.0)	2.5 (0.1)
Sodium Dihydrogen Phosphate	2.9 (0.3)	2.3 (0.1)	2.0 (0.1)	2.3 (0.1)	1.7 (0.8)	2.4 (0.1)
Trisodium Citrate	3.1 (0.1)	2.3 (0.1)	2.1 (0.1)	2.2 (0.2)	1.8 (0.1)	2.3 (0.1)
E.D.P.H.A.	3.2 (0.4)	2.3 (0.1)	2.1 (0.0)	2.2 (0.1)	1.7 (0.1)	2.3 (0.0)
Florisil	2.8 (0.3)	2.2 (0.1)	2.0 (0.1)	2.0 (0.1)	1.8 (0.1)	2.2 (0.0)

Table A13 Continued.

$\text{mgH}^{+}\ 1^{-1}$ (Leachate)

	Day 20	46	102	144	207	278
Control	24 (15)	159 (114)	* 245 (115)	* 154 (27)	120 (22)	40 (5)
Chicken Manure	98 (45)	149 (108)	71 (28)	81 (16)	90 (19)	50 (11)
Woodwaste	23 (10)	151 (56)	112 (36)	101 (16)	103 (19)	34 (25)
Sodium Dihydrogen Phosphate	25 (14)	177 (97)	225 (100)	128 (26)	114 (20)	35 (5)
Trisodium Citrate	16 (2)	96 (10)	137 (26)	128 (37)	94 (26)	44 (17)
E.D.P.H.A.	13 (5)	126 (41)	171 (61)	116 (18)	130 (46)	37 (6)
Florisil	38 (36)	238 (86)	257 (67)	192 (37)	111 (5)	45 (3)

Table A13 Continued.

mgFe 1^{-1} (Leachate)

Day	20	46	102	144	207	278
Control	510 (235)	3800 (2350)	* 4250 (2000)	* 1800 (360)	1400 (250)	270 (75)
Chicken Manure	2000 (1050)	2000 (350)	1300 (430)	1000 (245)	1150 (400)	330 (55)
Woodwaste	510 (25)	2750 (1250)	1800 (600)	1250 (180)	1250 (265)	295 (110)
Sodium Dihydrogen Phosphate	510 (250)	3950 (2150)	3850 (900)	1450 (280)	1400 (185)	180 (50)
Trisodium Citrate	350 (41)	1650 (360)	2150 (470)	1350 (390)	1150 (310)	200 (125)
E.D.P.H.A.	375 (29)	2200 (900)	3100 (700)	1750 (310)	1750 (650)	200 (43)
Florisil	700 (600)	4350 (2350)	3750 (1500)	2150 (370)	1250 (110)	260 (42)

Table A13 Continued.

$mgSO_4^{2-}$ in Leachate

Day	20	46	102	144	207	278
Control	17.0 (8.5)	31.6 (4.8)	* 37.9 (4.4)	* 36.5 (7.3)	34.6 (4.9)	17.1 (7.8)
Chicken Manure	32.6 (10.5)	30.8 (3.9)	18.8 (7.2)	24.8 (4.3)	28.3 (6.4)	18.3 (2.3)
Woodwaste	13.2 (2.3)	37.4 (8.7)	28.8 (9.2)	28.2 (3.8)	32.5 (5.2)	19.9 (4.6)
Sodium Dihydrogen Phosphate	15.4 (2.8)	33.6 (10.8)	38.6 (1.1)	31.8 (5.0)	34.4 (5.0)	15.6 (2.3)
Trisodium Citrate	16.1 (0.5)	31.1 (2.2)	32.0 (3.1)	29.8 (9.3)	31.5 (7.2)	17.7 (5.2)
E.D.P.H.A.	11.8 (0.8)	31.2 (6.1)	38.0 (6.8)	35.2 (5.1)	34.2 (5.9)	17.1 (2.2)
Florisil	17.2 (7.9)	40.6 (5.4)	40.2 (3.8)	39.9 (4.5)	33.1 (1.4)	18.9 (1.2)

Table A13 Continued.

	mgAl l^{-1} (leachate)						mgMn l^{-1} (leachate)
Day	20	46	102	144	207	278	278
Control	42.5 (9.6)	221 (106)	335 (160)	178 (37.7)	164 (110)	* 96 (77)	* 2.0 (0.6)
Chicken Manure	173 (33.0)	150 (81)	106 (46.8)	115 (36.9)	264 (61)	179 (82)	3.5 (1.3)
Woodwaste	108 (22.2)	230 (93)	168 (46.5)	142 (29.9)	306 (61)	193 (38.4)	4.5 (0.4)
Sodium Dihydrogen Phosphate	33.2 (8.5	210 (139)	295 (105)	160 (11.5)	292 (54)	67 (25.5)	1.8 (0.5)
Trisodium Citrate	33.5 (5.7)	138 (49.7)	275 (86)	178 (104)	298 (84)	125 (94)	2.5 (1.5)
E.D.P.H.A.	21.0 (7.9)	144 (34.7)	235 (70)	143 (28.7)	284 (68)	74 (28.3)	1.6 (0.4)
Florisil	44.0 (23.5)	291 (39.4)	368 (97)	223 (59)	253 (28.9)	89 (36.1)	1.8 (0.3)

Mn only measured in last leach.

Table A13 Continued.

pH of Spoil

	Day 20	46	102	144	207	278
Control	6.9 (0.1)	6.5 (0.5)	5.9 (0.7)	6.7 (0.2)	--- ---	6.9 (0.1)
Chicken Manure	6.7 (0.4)	6.6 (0.3)	6.4 (0.4)	7.0 (0.2)	--- ---	7.1 (0.4)
Woodwaste	6.8 (0.1)	5.9 (0.9)	5.3 (0.8)	6.7 (0.6)	--- ---	6.9 (0.4)
Sodium Hydrogen Phosphate	7.0 (0.2)	6.1 (0.3)	6.3 (0.6)	7.1 (0.3)	--- ---	7.1 (0.5)
Trisodium Citrate	6.6 (0.1)	6.9 (0.6)	6.6 (0.6)	6.8 (0.5)	--- ---	7.5 (0.2)
E.D.P.H.A.	6.8 (0.4)	6.4 (0.6)	6.3 (0.4)	6.8 (0.4)	--- ---	7.3 (0.2)
Florisil	7.0 (0.4)	7.0 (0.3)	6.7 (0.3)	6.8 (0.3)	--- ---	7.2 (0.3)

Results are presented as the mean for each group of four pots. The standard deviation for each group is in brackets.
* indicates a significant difference between groups for that sampling, using $\alpha = 0.05$.
pH spoil not measured on day 207.

Table A14. Analysis of Full-Lime Pots.

pH of Leachate

Day	20	46	102	144	207	278
Control	7.5 (0.3)	6.1 (0.5)	3.9 (1.0)	4.5 (2.4)	2.7 (0.5)	3.1 (1.1)
Chicken Manure	7.4 (0.5)	6.5 (0.2)	4.7 (1.3)	5.2 (1.8)	3.2 (0.8)	3.0 (0.4)
Woodwaste	7.7 (0.1)	6.8 (0.4)	4.8 (1.3)	6.8 (1.8)	3.1 (0.4)	3.7 (0.6)
Sodium Dihydrogen Phosphate	7.9 (0.2)	6.0 (1.3)	4.4 (2.5)	2.6 (0.2)	2.3 (0.2)	3.0 (0.3)
Trisodium Citrate	8.0 (0.1)	7.1 (0.3)	3.9 (1.5)	4.6 (1.8)	2.7 (0.5)	3.6 (0.6)
E.D.P.H.A.	7.9 (0.1)	6.9 (0.5)	5.5 (1.4)	5.0 (2.2)	2.9 (0.7)	3.1 (0.4)
Florisil	8.0 (0.2)	6.7 (0.3)	5.3 (1.8)	3.5 (1.0)	2.7 (0.5)	3.1 (0.5)

Table A14 Continued.

$mgH^+ l^{-1}$

Day	20	46	102	144	207	278
Control	0.2 (0)	0.2 (0)	6.8 (7.3)	* 13 (12)	14 (6.0)	20 (20)
Chicken Manure	0.2 (0)	0.2 (0)	2.8 (3.4)	3.3 (1.5)	9.4 (6.4)	16 (7.4)
Woodwaste	0.2 (0)	0.2 (0)	3.0 (3.4)	2.1 (1.9)	9.9 (3.1)	6.2 (4.2)
Sodium Dihydrogen Phosphate	0.2 (0)	0.2 (0)	21 (32)	52 (30)	38 (18)	15 (11)
Trisodium Citrate	0.2 (0)	0.2 (0)	8.9 (8.2)	10 (9.4)	22 (17)	8.0 (4.7)
E.D.P.H.A.	0.2 (0)	0.2 (0)	2.1 (2.0)	7.7 (12)	19 (15)	17 (16)
Florisil	0.2 (0)	0.2 (0)	1.7 (1.1)	18 (25)	18 (11)	29 (21)

Table A14 Continued.

mgFe 1^{-1}

Day	20	46	102	144	207	278
Control	* 1.3 (0.7)	* 1.3 (1.2)	36 (55)	* 80 (80)	* 100 (55)	24 (28)
Chicken Manure	2.5 (1.6)	1.2 (1.5)	22 (32)	20 (11)	80 (60)	60 (45)
Woodwaste	3.8 (1.2)	1.2 (0.7)	16 (22)	9 (9)	70 (46)	9 (8)
Sodium Dihydrogen Phosphate	2.1 (2.3)	5.0 (8)	180 (280)	390 (220)	330 (140)	39 (42)
Trisodium Citrate	1.6 (1.6)	0.4 (0.3)	37 (38)	70 (65)	160 (120)	21 (22)
E.D.P.H.A.	80 (10)	20 (8)	37 (3.0)	100 (60)	190 (110)	60 (50)
Florisil	4.5 (3.0)	2.3 (3.5)	11 (16)	155 (230)	155 (100)	60 (80)

Table A14 Continued.

			mgSO_4^{2-} in Leachate			
	Day 20	46	102	144	207	278
Control	8.9 (0.5)	5.6 (1.3)	4.2 (3.4)	* 10.0 (2.0)	10.8 (1.7)	13.2 (8.1)
Chicken Manure	7.3 (1.6)	5.0 (1.2)	3.7 (0.5)	9.0 (0.2)	10.6 (2.5)	11.8 (2.2)
Woodwaste	8.4 (0.6)	5.8 (2.7)	3.9 (0.3)	7.5 (1.4)	10.2 (2.0)	8.9 (2.6)
Sodium Dihydrogen Phosphate	9.4 (1.3)	7.2 (1.3)	5.3 (5.0)	17.1 (4.4)	16.6 (5.6)	11.3 (4.8)
Trisodium Citrate	11.5 (2.9)	7.6 (0.5)	2.9 (2.7)	16.1 (2.7)	15.1 (4.2)	10.8 (2.4)
E.D.P.H.A.	8.2 (1.2)	6.2 (0.7)	2.4 (1.5)	10.7 (1.5)	11.2 (1.7)	13.2 (5.9)
Florisil	7.7 (1.2)	6.4 (1.6)	3.6 (0.7)	13.2 (5.2)	12.9 (2.0)	16.8 (5.7)

Table A14 Continued.

			mgAl l^{-1} (leachate)				mgMn l^{-1} (leachate)
Day	20	46	102	144	207	278	278
Control	0	0	30.3 (15.9)	* 25.7 (21.0)	56 (25.3)	71 (89)	2.3 (2.6)
Chicken Manure	0	0	5.9 (10.7)	4.5 (3.1)	31.2 (20.4)	39.0 (25.6)	1.3 (0.6)
Woodwaste	0	0	1.3 (2.5)	3.5 (3.4)	24.5 (17.0)	19.5 (15.2)	0.7 (0.5)
Sodium Dihydrogen Phosphate	0	0	58 (77)	108 (52)	133 (61)	52 (47.6)	1.7 (1.3)
Trisodium Citrate	0	0	25.0 (20.1)	26.7 (30.2)	91 (74)	29.2 (20.0)	0.9 (0.7)
E.D.P.H.A.	0	0	5.4 (9.8)	16.5 (29.2)	67 (54)	95 (130)	1.9 (2.5)
Florisil	0	0	5.3 (6.7)	40.0 (61)	78 (58)	93 (75)	1.4 (1.0)

Mn only measured in last leach.

Table A14 Continued.

Dry Weight (mg) of Harvested Grass

	Day 46	102	144	207	278
Control	235 (17)	488 (127)	* 443 (231)	* 182 (142)	303 (237)
Chicken Manure	335 (10)	576 (35)	670 (71)	633 (109)	289 (114)
Woodwaste	274 (27)	614 (72)	700 (101)	530 (86)	270 (295)
Sodium Dihydrogen Phosphate	188 (45)	514 (132)	443 (189)	176 (105)	245 (229)
Trisodium Citrate	300 (65)	638 (75)	710 (46)	476 (150)	198 (104)
E.D.P.H.A.	260 (52)	646 (54)	785 (36)	446 (91)	177 (30)
Florisil	248 (89)	569 (178)	630 (194)	347 (187)	294 (218)

Table A14 Continued.

pH of Spoil

	Day	55	120	202	251	298
Control		---	2.1 (0.2)	---	---	2.6 (0.1)
PFA		---	2.1 (0.3)	---	---	2.6 (0.3)

pH of Leachate

	Day	55	120	202	251	298
Control		2.0 (0.1) *	2.2 (0.3)	2.2 (0.0)	2.2 (0.1)	2.5 (0.1)
PFA		2.2 (0.1)	2.0 (0.1)	2.2 (0.1)	2.2 (0.1)	2.4 (0.0)

Results are presented as the mean for each group of four pots. The standard deviation for each group is in brackets .

pH spoil not measured on days 55, 202 and 251.

* indicates a significant difference between the two groups on that day, using $\alpha = 0.05$.

Table A15 Analysis of PFA, Half-Lime Pots

$mgH^{+}\ l^{-1}$ (leachate)

	Day	55	120	202	251	298
Control		79 (23)	88 (25)	182 (26)	137 (20)	91 (18)
PFA		61 (15)	125 (71)	155 (48)	* 99 (19)	70 (10)

$mgSO_4^{2-}$ in leachate

	Day	55	120	202	251	298
Control		23 (4)	26 (7)	40 (2)	38 (4)	27 (5)
PFA		21 (3)	30 (9)	36 (4)	30 (7)	22 (2)

$mgFe\ l^{-1}$ (leachate)

	Day	55	120	202	251	298
Control		1050 (245)	1000 (270)	2050 (520)	1650 (375)	750 (210)
PFA		690 (250)	1450 (800)	1750 (650)	1500 (425)	500 (85)

Table A15 Continued.

mgAl l^{-1} (leachate)

	Day	55	120	202	251	298
Control		120 (31)	109 (42)	220 (50)	156 (9)	79 (25)
			*			
PFA		143 (40)	206 (67)	223 (70)	139 (29)	91 (19)

mgMn l^{-1} (leachate)

	Day	55	120	202	251	298
Control		2.5 (0.4)	2.0 (0.3)	2.4 (0.3)	1.9 (0.2)	1.4 (0.3)
		*	*			*
PFA		7.4 (1.8)	5.5 (1.6)	3.9 (1.6)	1.8 (0.8)	2.2 (0.5)

mgSi l^{-1} (leachate)

	Day	55	120	202	251	298
Control		51 (17)	22 (7)	58 (10)	57 (4)	38 (10)
PFA		69 (17)	30 (13)	56 (8)	51 (12)	44 (7)

Table A15 Continued.

pH of Spoil

	Day 55	120	202	251	298
Control	---	6.8 (0.1)	---	---	6.7 (0.1)
PFA	---	6.8 (0.1)	---	---	6.8 (0.1)

pH of Leachate

	Day 55	120	202	251	298
Control	6.7 (0.4)	7.2 (0.2)	3.6 (1.0)	4.2 (2.1)	3.2 (0.3)
PFA	7.0 (0.4)	7.6 (0.1)	3.0 (0.2)	2.8 (0.3)	3.1 (0.2)

$mgH^+ \ l^{-1}$ (leachate)

	Day 55	120	202	251	298
Control	0.6 (0.5)	0.6 (0.0)	13 (14)	8.5 (5.3)	12 (4.9)
PFA	0.4 (0.2)	0.4 (0.0)	26 (18)	40 (29)	20 (11)

Results are presented as the mean of each group of four pots. The standard deviation for each group is in brackets.
pH of spoil not measured on days 55, 202 and 251.
* indicates a significant difference between the two groups on that day, using $\alpha = 0.05$.

Table A16 Analysis of PFA, Full-Lime Pots

$mgSO_4^{2-}$ in Leachate

	Day	55	120	202	251	298
Control		7.4 (0.7)	5.1 (1.4)	9.5 (17.1)	11.0 (1.4)	12.4 (1.7)
PFA		7.1 (1.1)	6.4 (1.8)	14.3 (5.3)	19.8 (7.1)	14.6 (2.8)

$mgFe\ l^{-1}$ (leachate)

	Day	55	120	202	251	298
Control		0.3 (0.1)	5.0 (1.6)	95 (130)	33 (23)	65 (17)
PFA		0.2 (0.1)	6.5 (1.8)	275 (260)	330 (345)	75 (65)

$mgAl\ l^{-1}$ (leachate)

	Day	55	120	202	251	298
Control		0	0	34 (28)	27 (19)	35 (16)
PFA		0	0	80 (47)	110 (65)	60 (36)

Table A16 Continued.

mgMn l^{-1} (leachate)

	Day	55	120	202	251	298
Control		0	0	0.8 (0.7)	0.8 (0.5)	1.3 (0.6)
PFA		0	0	1.5 (0.7)	2.9 (1.7)	2.7 (1.5)

mgSi l^{-1} (leachate)

	Day	55	120	202	251	298
Control		19 (1)	15 (5)	39 (9)	44 (5)	53 (13)
		*				
PFA		25 (4)	17 (5)	41 (7)	55 (12)	58 (13)

Dry Weight (mg) of Harvested Grass

	Day	55	120	202	251	298	All Harvests Added Together
Control		---	142 (175)	368 (187)	300 (112)	85 (25)	893 (369)
				*			*
PFA		---	160 (176)	773 (184)	480 (108)	120 (37)	1534 (348)

Grass not harvested at first leach (Day 55).

Table A16 Continued.

Si Concentration	Pot	Day 15	29	38	49	57	67
	1	9.2	8.7	7.0	6.4	6.3	6.5 (5.2)
2%	2	8.8	8.1	5.3	5.6	6.0	8.2 (6.3)
	3	8.9	7.5	6.6	6.4	6.1	6.6 (5.6)
	4	8.6	8.5	5.3	5.9	5.5	5.1 (2.2)
1%	5	7.9	9.0	6.5	5.6	5.6	5.6 (2.0)
	6	9.1	8.8	5.8	6.2	5.9	5.1 (2.9)
	7	7.9	5.0	5.2	6.4	5.6	3.0 (1.8)
0.1%	8	5.0	3.5	4.2	4.8	6.0	2.6 (2.0)
	9	4.5	3.0	2.8	3.5	3.8	2.3 (1.6)
	10	3.4	3.7	3.5	4.5	4.3	2.5 (2.3)
0	11	4.1	3.7	4.1	4.4	4.5	2.2 (2.4)
	12	2.8	2.7	3.4	3.9	4.0	2.5 (2.4)

pH of spoil, when measured, presented in brackets.

Table A17 pH of Leachates of Pots with Added Sodium Silicate Solution.

Si Concentration	Pot	Day 78	85	91
2%	1	6.0	4.3 (4.0)	3.0 (5.1)
	2	7.4	5.7 (5.1)	2.6 (4.9)
	3	5.8	3.3 (5.5)	2.4 (5.0)
1%	4	3.7	2.4 (2.6)	2.6 (2.7)
	5	4.8	2.6 (2.4)	2.4 (2.4)
	6	4.0	2.4 (2.6)	2.4 (2.5)
0.1%	7	2.2	2.2 (2.3)	2.4 (2.3)
	8	2.5	2.1 (2.4)	2.2 (2.3)
	9	2.2	2.1 (2.3)	2.2 (2.3)
0	10	2.5	2.2 (2.3)	2.2 (2.3)
	11	2.3	2.1 (2.3)	2.1 (2.2)
	12	2.4	2.1 (2.3)	2.1 (2.2)

Table A17 Continued.

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