Aqueous pyrite oxidation and the consequent formation of secondary minerals

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Chapter 3

Aqueous Pyrite Oxidation and the Consequent Formation of Secondary Iron Minerals

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ABSTRACT

The oxidation of pyrite in aqueous systems is a complex biogeochemical process involving several redox reactions and microbial catalysis. This paper reviews the kinetic data on pyrite oxidation, compares available data on the inorganic vs. microbial oxidative mechanisms and describes the occurrence of mineral products resulting from pyrite oxidation. Although oxygen is the overall oxidant, kinetic data suggests that ferric iron is the direct oxidant in acid systems and that temperature, pH, surface area, and the presence of iron and sulfur-oxidizing bacteria can greatly affect the rate of reaction. The vast amount of literature on the microbial and geochemical investigations on this subject have limited usefulness for understanding natural systems. Additional research is needed on the hydrologic, geologic and microbiologic characteristics of field sites where oxidation occurs. The acid water resulting from pyrite oxidation may precipitate a large suite of soluble and insoluble iron minerals depending on pH, degree of oxidation, moisture content, and solution composition.

INTRODUCTION

The oxidation of common sulfide minerals such as pyrite plays a key role in (a) the supergene alteration of ore deposits, (b) the formation of acid mine waters, (c) the formation of acid sulfate soils, (d) the source and distribution of dissolved sulfate in natural waters, (e) the source and distribution of heavy metals in the aquatic environment, and (f) the in situ solution mining and dump leaching of heavy metals for economic recovery. Pyrite oxidation is a complicated process which includes several types of oxidation-reduction reactions, hydrolysis and complex ion formation, solubility controls and kinetic effects. To interpret these reactions in

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Acid Sulfate Weathering.

natural aquatic systems requires the additional knowledge of microbial ecology, hydrology, and geology. It is not surprising that important aspects of this process are not clearly understood and many questions remain unresolved.

The overall process describing pyrite oxidation is commonly given by the following incongruent reaction:

$$FeS_{2(s)} + (15/4)\,O_{2(aq)} + (7/2)\,H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 2H_2SO_{4(aq)} \qquad [1]$$

in which pyrite and water, in the presence of oxygen, form insoluble ferric hydroxide and sulfuric acid. Although the ultimate driving force is atmospheric oxygen, the fundamental mechanism and the major rate-determining step(s) may not involve oxygen at all. Furthermore, many other iron minerals may form in addition to or instead of ferric hydroxide. In natural environments the relative importance of physical, chemical and microbiological factors may vary widely. This paper (1) reviews the known rates and suggested mechanisms for pyrite oxidation with some discussion of the effects of geology, hydrology, and climate and (2) describes the occurrence of hydrated iron sulfate and iron oxide minerals which result from pyrite oxidation. Illustrative examples are given from acid mine drainage studies because more research has been done in this area than any other. The conclusions, however, are just as applicable to acid sulfate soils.

Investigations on pyrite oxidation usually center on the question of whether an inorganic or microbiological mechanism is more important in controlling the rate of the oxidative process. The relative importance of these two mechanisms will dictate the preferred approach for "at-source" control of acid mine drainage and acid sulfate soil formation.

INORGANIC OXIDATION MECHANISMS

The oxidation and hydrolysis shown by reaction 1 involves the loss of 1 electron by iron, 14 electrons by sulfur, and the gain of 7½ electrons by oxygen per mole of pyrite. Also, 1 mole of iron is hydrolyzed and precipitated. Clearly, all of these changes cannot take place in one step. Kinetic studies and quantum mechanical calculations indicate that one-electron-transfer reactions are most likely to occur, two-electron reactions much less likely and more than two are highly unlikely (Basolo and Pearson, 1967). Furthermore, the oxidative half-cell reaction does not have to take place at the same rate as the reductive half-cell. A maximum of 22 electron transfer reactions are possible, and there may be the same number of possible rate-determining steps. More steps are possible if other oxidizing agents are considered. Experimental measurements on this heterogeneous system indicate that two electrons are frequently transferred and that all 22 steps do not need to be individually considered. The following discussion will begin with pyrite in aqueous solution and sequentially consider the loss of electrons from pyrite as well as the rates and mechanisms of oxidation whenever data are available.

Several investigators have shown that the first step in the breakdown of a sulfide in an aqueous solution is the dissolution of the metal and the oxidation of sulfide to neutral sulfur. High temperature (~ 100 to 200 C) metallurgical reactions consistently have the general stoichiometry:

$$MS_{(s)} \rightarrow M^{2+}_{(aq)} + S^{\circ}_{(s)} + 2e^{-} \qquad [2]$$

for a divalent metal, M (Burkin, 1966; Wadsworth, 1973). Using pyrite as an electrode, Sato (1960) made potentiometric measurements at 25 C which indicated the initial step for $pH \leq 3.0$ was:

$$FeS_{2(s)} \rightarrow Fe^{2+}_{(aq)} + S^{\circ}_{2} + 2e^{-} \qquad [3]$$

and this reaction was also found as a limiting condition in the experiments of Garrels and Thompson (1960). Current-potential measurements on pyrite by Biegler and Swift (1979) at 25 C and $pH \leq 3.0$ were interpreted as a combination of

$$FeS_2 + 8H_2O \rightarrow Fe^{3+} + 2SO_4^{2-} + 16H^{+} + 15e^{-} \qquad [4]$$

and

$$FeS_2 \rightarrow Fe^{3+} + 2S^{\circ} + 3e^{-} \qquad [5]$$

where reaction 5 is not an intermediate leading to reaction 4. In order to speed up the reaction rate, Biegler and Swift (1979) had to make these measurements at rather high potentials (0.95 to 1.4 V) which oxidized dissolved iron to the ferric state. Lower potentials were achieved by Bailey and Peters (1976) by increasing the temperature to 110 C, and in these experiments there were significant amounts of ferrous iron. All of these measurements were done in the absence of oxygen. In neutral to basic solutions Sato (1960) proposed the reaction:

$$FeS_{2(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + S^{\circ} + 3H^{+}_{(aq)} + 3e^{-} \qquad [6]$$

based on potentiometric measurements. The neutral sulfur produced in reactions 5 and 6 would, at first, simply remain at the pyrite surface as part of the structure while ferrous ions leached out from the surrounding lattice sites. This sulfur-rich surface would eventually become unstable and do one of two things: (1) disrupt and reorganize into elemental sulfur (such as S_8 rings) or (2) disrupt into solution as dimers which would be highly unstable and would form sulfate rapidly in the presence of a strong oxidizing agent. Electrochemical measurements support these hypotheses (Peters, 1977; Biegler and Swift, 1979). Metal ions leach readily from sulfide minerals and for some the sulfur will remain behind in the original structure. This residual sulfur behaves like elemental sulfur in that it dissolves in carbon disulfide (Sullivan, 1930). There is evidence for both the presence and absence of elemental sulfur resulting from pyrite oxidation. Clark (1966) has cited several instances of pyrite-derived sulfur from coal seams. Presumably the organic matter retards the further oxidation of sulfur. Smith et al. (1968), and Stokes (1901) found that elemental sulfur was produced in the initial stages of oxidation using freshly-prepared pyrite, whereas samples conditioned by prior oxidation did not produce sulfur in the oxidation experiments. In highly oxidizing sulfide mineral deposits little or no sulfur is found (Kinkel et al., 1956; Nordstrom, unpublished data). However, Bergholm (1955) has documented the production of elemental sulfur from pyrite at low pH and in the presence of ferric iron. In Bergholm's experiments most of the sulfur coated the pyrite as elemental sulfur and retarded the oxidation. Brock et al. (1976) found that elemental sulfur did not reduce ferric iron at a pH of 1.6 and temperatures of 60 to 90 C. Decreasing temperature and decreasing pH both led to increased sulfur production at 100 to 130 C in the experiments of McKay and Halpern (1958). Also, McKay and Halpern (1958) have hypothesized two independent reactions of the same stoichiometry as Biegler and Swift (1979) which gives additional credance to the dual reaction paths, one leading to the production of sulfur and the other to sulfate. These observations suggest that the oxidation rate of free sulfur to sulfate relative to the oxidation rate of sulfide-sulfur to free sulfur determines whether free sulfur will occur or not. In turn, these rates will depend upon the transport rate of the oxidizing agents to the pyrite surface, the pH, and the temperature. The evidence cited indicates that these two rates are somewhat comparable but that sulfide to sulfur is faster.

The oxidizing agent in waters of neutral pH is oxygen since the only other likely oxidant, Fe^{3+}, is highly insoluble. The reduction of oxygen on pyrite proceeds through the following steps:

$$O_2 + e^- \rightarrow O_2^- \qquad [7]$$

$$O_2^- + 2H^+ + e^- \rightarrow H_2O_2 \qquad [8]$$

At pH values above 4, reaction 8 appears to be the rate-limiting step, whereas at lower pH values the rate is independent of pH and the limiting step is given by reaction 7 (Biegler et al., 1977). This conclusion is also verified by the rate data of Smith et al. (1968). The initial oxidation-reduction reaction of pyrite in water and oxygen results from combining reactions 3, 7, and 8:

$$FeS_{2(s)} + O_2 + 2H^+ \rightarrow Fe^{2+} + S_2^\circ + H_2O_2 \qquad [9]$$

Elemental sulfur formation is probably faster than peroxide formation for a system containing pure pyrite in solutions of neutral pH where diffusional processes are not rate-limiting. Therefore pyrite oxidation kinetics and sulfur formation depends upon the availability and rate of oxygen reduction. In soils and bedrock, the rate is probably related to the rate of oxygen infiltration.

The three products of reaction 9 are unstable and rapidly oxidized or decomposed. At neutral pH values ferrous iron oxidizes very rapidly according to the expression:

$$d[Fe(II)]/dt = k[Fe(II)][O_2]/[H^+]^2 \qquad [10]$$

(Ghosh, 1974; Singer and Stumm, 1968; Stumm and Lee, 1961). Brackets denote concentrations, k is the rate constant and t is the time. Equation [10] holds for pH values above 4.5 and for poorly buffered solutions. Ghosh (1974) pointed out that the oxidation rate increases with increasing carbonate alkalinity and that highly buffered waters may differ by more than an order of magnitude in their ferrous oxidation rates. In poorly buffered perchlorate solutions and at a pH of 7.0, the rate constant is about 10^2 day^{-1} by extrapolating the data of Singer and Stumm (1968). When sulfate is used instead of perchlorate the rate is different; Singer and Stumm (1968) found that the rate decreased, whereas Huffman and Davidson (1956) found the rate increased with increasing sulfate concentration. The discrepancy must be resolved by additional measurements over a wider range of concentrations.

A review of pyrite oxidation kinetics by Shumate et al. (1971) pointed out that the rate dependence on oxygen concentration differs somewhat between investigators. They reported a rate expression based on an adsorption equilibrium hypothesis:

$$r = (k[O_2])/(1 + K_1[O_2] + K_2[I]) \qquad [11]$$

where r is the rate of pyrite oxidation in micromoles pyrite per hour per gram of sample, k is the rate constant, K_1 is the adsorption equilibrium constant for oxygen on pyrite, K_2 is the adsorption constant for an inert gas, I, on pyrite. Equation [11] fits the data well but does not provide any insight into the electrochemical nature of the reaction mechanism.

Once the iron is oxidized it will hydrolyze and precipitate as ferric hydroxide:

$$Fe^{2+} + (5/2)\,H_2O + \tfrac{1}{4}O_2 \rightarrow Fe(OH)_{3(s)} + 2H^+ \qquad [12]$$

or, if the hydrogen peroxide produced by reaction 7 is the oxidizing agent:

$$Fe^{2+} + (1/2)\,H_2O_2 + 2H_2O \rightarrow Fe(OH)_{3(s)} + 2H^+ \qquad [13]$$

The presence of iron hydroxide on the surface of oxidizing pyrite has been observed by Baker (1972) using Mossbauer spectroscopy.

It is interesting to note that if the sulfur produced in reaction 3 did not further oxidize there would be no change in the pH of the solution since the protons consumed in reaction 9 exactly balance the protons produced in reaction 12 or 13:

$$FeS_{2(s)} + (3/4)\,O_2 + (3/2)\,H_2O \rightarrow Fe(OH)_{3(s)} + S_2^o \qquad [14]$$

When the sulfur is oxidized to sulfate, the pH drops:

$$S_2^o + 3O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+. \qquad [15]$$

Relatively little has been studied on the rates and mechanisms of reaction 15 with regard to pyrite oxidation, and this reaction could be an important rate-determining step in the initial weathering of pyrite to produce acid conditions from neutral solutions. Six electrons are transferred per sulfur atom, and the formation of several intermediate sulfur species such as thiosulfate, sulfite and polythionates are possible complicating factors. Sulfite, SO_3^{2-}, is not stable and rapidly oxidizes to sulfate in the presence of oxygen or any other oxidizing agent. Thiosulfate, $S_2O_3^{2-}$, is more stable at high pH than low pH and readily decomposes to elemental sulfur and sulfite (and hence to sulfate) in acid solutions. Polythionates are more stable than thiosulfate or sulfite, especially in acid media, but they too tend to breakdown by disproportionation to simpler species such as sulfur and sulfate. Thiosulfate can be oxidized by ferric iron to tetrathionate and the indication of thiosulfate formation on air-oxidized sulfides by Steger and Desjardins (1978) leads to the hypothesis that polythionates are important intermediates during aqueous pyrite oxidation in neutral to acidic solutions. This hypothesis is verified by the study of Nor and Tabatabai (1977) who reported that nearly all the dissolved sulfur present during the oxidation of elemental sulfur in soils was sulfate at a pH of 7.8, whereas tetrathionate was dominant at pH values of 5 to 6. Goldhaber (1977, personal communication) found tetrathionate and sulfate to be present in equal proportions from pyrite oxidation at a pH of 6 whereas thiosulfate was dominant at pH values of 8 and 9.

Reaction 15 is the initial acid-producing reaction which can reduce the pH to about 4.5 where the rate of ferrous iron oxidation slows down significantly (Singer and Stumm, 1968) and ferric hydroxide is more soluble. Ferrous iron oxidation becomes independent of pH below a pH of 3 with a rate constant of $10^{-3.5}$ day^{-1}. For example, in a 9×10^{-4} *M* ferrous iron solution it takes about 5½ days to oxidize 1×10^{-5} moles at a pH of 2, a P_{O_2} of 0.2 atm and a temperature of 25 C.

As the ferric concentrations increase with the increased acidity, the role of ferric iron becomes more important as an oxidizing agent. Measurements by Garrels and Thompson (1960) and by Smith et al. (1968) have shown that pyrite is rapidly oxidized by ferric iron in the absence of oxygen and at low pH values according to the stoichiometry:

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad [16]$$

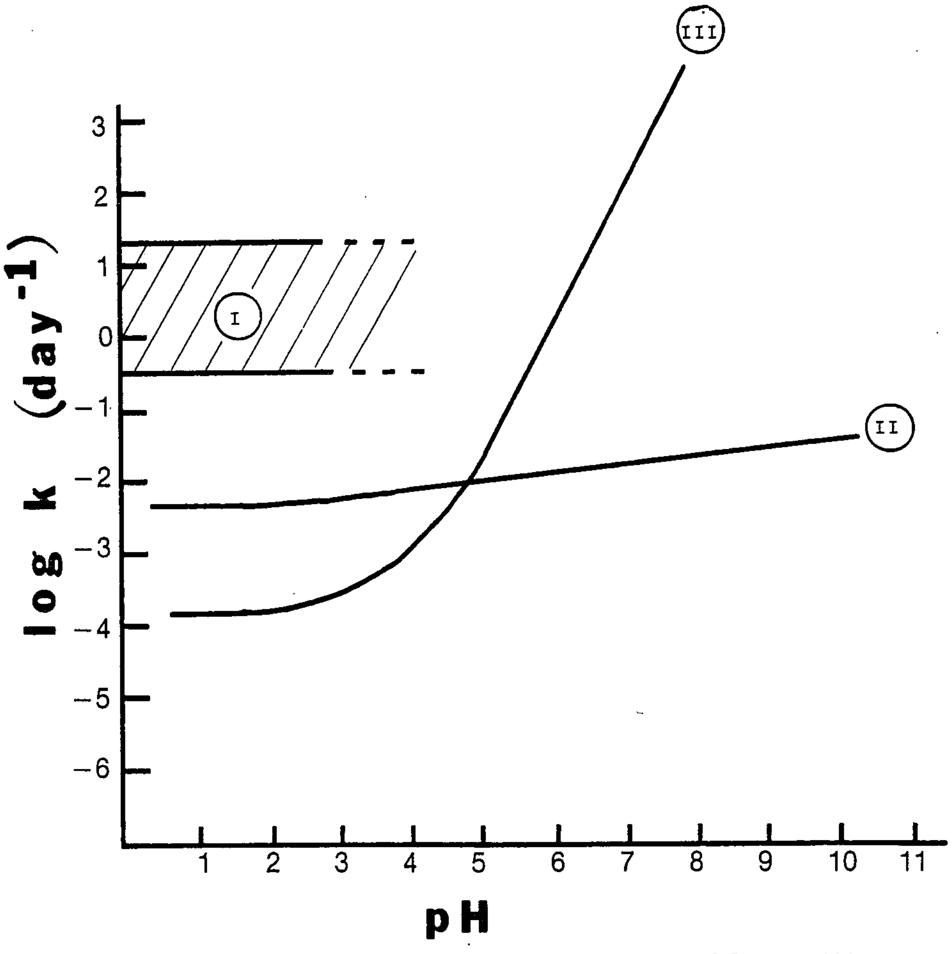
No residual sulfur was noted in these experiments which runs contrary to the work of earlier investigators such as Bergholm (1955). From the data of Garrels and Thompson (1960), 50% of a 2×10^{-3} m solution of ferric sulfate was reduced by pyrite in 5 hours. Singer and Stumm (1969) carred out similar experiments over a broader range of conditions and showed the first order dependence on both Fe^{3+} and FeS_2:

$$-d[Fe^{3+}]/dt = k[Fe^{3+}][FeS_2] \qquad [17]$$

where $[FeS_2]$ represents the molar concentration of pyrite. Singer and

Stumm (1969) calculated rate constants which ranged from 0.389 day^{-1} to 17.4 day^{-1} depending on the proportions of total Fe^{3+} and FeS_2 to the solution volume.

Figure 1 compares the oxidation rates of ferrous ion to ferric ion by oxygen (III), pyrite to acid ferrous sulfate solution by oxygen (II), and pyrite by ferric ion (I) as a function of pH. At low pH values (≤ 3.0) ferric iron oxidizes pyrite much more rapidly than oxygen and more rapidly than dissolved ferrous can be oxidized by oxygen. At neutral to alkaline pH values the rate of ferrous oxidation rises rapidly, but the dissolved ferric concentration also decreases greatly due to the precipitation of ferric hydroxide. The results of these studies support the contention that pyrite is initially oxidized by oxygen, and the pH consequently decreases depending on the rate of oxidation of sulfur to sulfate. When the pH de-



I $FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$
(data from Singer and Stumm, 1969)

II $FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$
(data from Smith, et al., 1969)

III $Fe^{2+} + 1/4 O_2 + H^+ \rightarrow Fe^{3+} + 1/2 H_2O$
(data from Singer and Stumm, 1968)

Fig. 1. Comparison of rate constants as a function of pH for I. The oxidation of pyrite by ferric iron, II. The oxidation of pyrite by oxygen and III. The oxidation of ferrous iron by oxygen.

creases to 4.5, ferric iron becomes more soluble and begins to act as an oxidizing agent, and below a pH of 3.0 it is the only important oxidizer of pyrite. The presence or absence of oxygen makes no difference to the oxidation rate by ferric iron (Singer and Stumm, 1969). Since pyrite can reduce ferric ion to ferrous faster than ferrous can be regenerated into ferric by oxygen, the pyrite will simply reduce all the ferric ions and then the reaction will stop. Thus, the ferrous to ferric oxidation has been called the rate-determining step in the production of acid mine drainage (Singer and Stumm, 1970). One of the strongest catalysts of this reaction is the iron-oxidizing bacterium, *T. ferrooxidans*, which is known to increase the ferrous oxidation rate by five to six orders of magnitude (Lacey and Lawson, 1970; Singer and Stumm, 1970; Nordstrom, 1976). This increase makes the ferrous oxidation rate, in the presence of the bacterium, comparable or slightly greater than the pyrite oxidation by ferric iron and thereby makes pyrite oxidation a rapid self-perpetuating process.

Other factors which can affect the inorganic oxidation rate include temperature, surface area, the presence of impurities such as trace metals, and the presence of other minerals such as chalcopyrite, sphalerite, calcite, etc. These factors have been summarized by Shumate et al. (1971) and Clark (1966). Temperature causes the oxidation rate by oxygen to double for every 10 C rise. Pyrite can vary significantly in grain size and morphology. Pyrite in coal deposits has been found in at least six different forms, and the most reactive form is framboidal pyrite having pyrite crystals less than a micrometer in size (Caruccio, Geidell, and Sewell, 1976). The occurrence of framboidal pyrite has been used to estimate the acid-forming potential of coal mine refuse (Caruccio, 1975). Studies cited by Clark (1966) and Shumate et al. (1971) described "sulfur ball" pyrite as having surface areas about an order of magnitude greater than museum grade pyrite of the same diameter. Sulfur ball pyrite is assumed to be equivalent to "framboidal" pyrite.

The occurrence of trace metals appears to have no significant effect on the oxidation rate, but the co-existence of other sulfides such as chalcopyrite and sphalerite tends to decrease the oxidation rate. Sveshnikov and Dobychin (1956) pointed out that rates of metal release from different sulfides are related to their electrode potentials and that a mixture of sulfides releases more metals into solution and decreases the pH more than monomineralic samples. Pyrite greatly increases metal release from other sulfides while its own dissolution is reduced by galvanic protection. These phenomena have been used to explain oxidation and supergene enrichment in sulfide ore bodies by considering the mass of sulfides as a natural galvanic cell (Sveshnikov and Ryss, 1964; Thornber, 1975). The presence of relatively inert conductors such as graphite has also been proposed to speed up the oxidation rate by increasing the electron flow between the anodic and cathodic portions of an ore body (Cameron, 1979).

These additional factors may or may not be important depending upon the particular geological and climatological circumstances of the oxidizing pyrite. The surface area effect seems to be very important in the initial stages of acid sulfate production, but once the pH has decreased to

3 or less it would seem to be less important. On the other hand, bacterial oxidation could be the single most important factor over the whole range of pH of natural waters.

MICROBIAL OXIDATION MECHANISMS

There are at least two well-established facts of microbial ecology: (1) microbes are ubiquitous on this planet, existing under a wide range of natural conditions (Kushner, 1978) and (2) microbes catalyze many reactions including those related to the formation and oxidation of sulfide ore deposits (Kuznetsov et al., 1963; Zajic, 1969). Very few microorganisms have been studied as much as the sulfur-oxidizing genus, *Thiobacillus*. This bacterium utilizes some form of sulfur as an energy source and reduces CO_2 for a carbon source and is therefore termed chemoautotrophic. Three species of *Thiobacillus* have been isolated from acid mine wastes: *T. ferrooxidans* which oxidizes ferrous iron and pyrite as well as sulfur, *T. thiooxidans* which oxidizes only sulfur and pyrite, and *T. acidophilus* which is a facultative autotroph (grows on either inorganic or organic substrates, Guay and Silver, 1975) oxidizing sulfur but not ferrous iron. *Thiobacillus acidophilus* cannot oxidize pyrite unless it is in a mixed culture. These bacteria are acidophilic with optimal growth conditions around a pH of 2 to 3, although they can survive up to pH values as high as 6 and 7.

The importance of *Thiobacillis* in pyrite oxidation and the mechanism of microbial attack has long been a controversial issue. *Thiobacillus ferrooxidans* has been implicated as an essential catalyst in the production of acid mine waters because (1) it can usually be isolated from acid mine waters; (2) it actively accelerates pyrite oxidation in lab experiments; and (3) it can speed up the oxidation of dissolved ferrous ions by five to six orders of magnitude over the inorganic rate, thereby providing a way of rapidly regenerating ferric ions in acid solutions. Direct evidence for microbial growth in the deeper portions of the unsaturated zone, however, has not been demonstrated. Growth may occur in the surface layer of a soil but some skepticism has been raised about the possibility of growth deeper in the subsurface such as in underground mines or in coal refuse piles. Kleinmann (1979) and Kleinman and Crerar (1979) have refuted these criticisms in an oxidation study of pyritic coals and overburden where they simulated the well-oxygenated surface layer, the unsaturated zone above the water table and the saturated zone below the water table. They found that *T. ferrooxidans* catalyzed pyrite oxidation in the unsaturated zone for a few days following rainfall infiltrations as well as in the surface layer.

There has been considerable discussion about the mechanism of microbial pyrite oxidation. *Thiobacillus ferrooxidans* can rapidly generate ferric ions from ferrous ions in acidic media; pyrite is then directly and inorganically oxidized by ferric iron. This process has been named the "indirect contact" mechanism. Some investigators (Bryner and Jameson, 1958; Beck and Brown, 1968) have questioned this mechanism and have proposed that the bacterium makes direct contact with the pyrite crystals and oxidizes them through enzymatic pathways. The bacterial population on the pyrite surface is much greater than in solution (Tuovinen and Kelly, 1972), and it seems that *T. thiooxidans* oxidizes elemental sulfur by direct contact. Thus, a direct contact mechanism has been suggested for the microbial oxidation of pyrite. This mechanism is also indicated by studies on the oxidation of non-ferrous sulfides such as sphalerite, chalcocite, and covellite in the presence of *T. ferrooxidans* (Silver and Torma, 1974; Duncan and Walden, 1972; Nielson and Beck, 1972) where iron is not present in the system. Silverman (1967) attempted to determine which mechanism was more important, and he concluded that both mechanisms were operating concurrently. However, in every experiment the bacteria were allowed to make direct contact with the pyrite grains, and in the experiments without bacteria he failed to measure and compare the reaction rates. A series of critical experiments were carried by Arkesteyn (1979) in which he not only demonstrated the direct contact mechanism but also showed that the rate of pyrite and elemental sulfur oxidation at a pH of 5.0 was faster than the oxidation rate of ferrous iron, all in the presence of *T. ferrooxidans.* In addition, when Arkesteyn (1979) separated the bacteria from pyrite by a dialysis bag the oxidation rate decreased. These results confirmed other sets of experiments in which he individually inhibited the oxidation of ferrous iron or sulfur by the organism without stopping the oxidation process.

A further point that tends to confuse the whole microbial picture is the ability of *T. thiooxidans* and *Sulfolobus acidocaldarius* (a thermophilic sulfur and iron-oxidizing bacterium) to reduce ferric iron during the aerobic oxidation of elemental sulfur (Brock and Gustafson, 1976). *Thiobaccillus ferrooxidans* also reduces ferric iron during sulfur oxidation under anaerobic conditions while utilizing the oxidized iron as an energy source. These data have very important implications concerning our understanding of sulfide mineral oxidation in subsurface environments such as in tailings piles, water-logged soils, and sulfide mineralization located below the water table. First, it must be recognized that these iron and sulfur-oxidizing bacteria are facultative with respect to their oxygen requirements. Clearly the presence of a suitable electron acceptor such as ferric ion will do just as well as oxygen. Thus, we can expect pyrite oxidation to continue by microbial activity under low or even undetectable oxygen concentrations. No one, however, has determined if the microorganisms catalyze the anaerobic oxidation process. If they do, then clearly mine sealing and flooding is an inappropriate method of preventing acid mine drainage from abandoned mines.

Another source of controversy is the possible role of microorganisms in the initial stages of pyrite oxidation. *Thiobaccillus ferrooxidans* can play an active role once the pH has decreased to 4 to 4.5. How does a neutral soil or ground water initially become acid from pyrite oxidation? One possibility is the inorganic oxidation by molecular oxygen, but this mechanism is quite slow. It is more likely that the initial step is microbially catalyzed by some of the heterotrophs and/or autotrophs which occur in the soil horizon and are known to metabolize inorganic sulfur compounds (Roy and Trudinger, 1970). Walsh and Mitchell (1972a, 1972b) have proposed that *Metallogenium*, an acid-tolerant iron-oxidizing bacterium, initiates a pH-dependent succession of bacteria. Metallogenium optimally oxidizes iron between pH values of 3.5 and 5. Once *Metallogenium* brings the pH down to about 4 then *T. ferrooxidans* takes over and reduces the pH to below 4. In his studies on simulated coal refuse environments, Kleinman (1979) found that (1) inoculation with and without *Metallogenium* made no difference in the rate of initial acidification and (2) *T. ferrooxidans* not only survives at pH values up to 7, but it also initiates pyrite oxidation to provide the acidity and ferrous ions. It should be kept in mind that although the bulk solution phase may have a neutral pH, the pH right at the surface of a pyrite grain may be considerably less and may be the site location of viable *Thiobacilli.* He suggested that in the initial stage of oxidation the direct contact mechanism was probably more important since ferric ions are too low in concentration. Several other species of *Thiobacillus* are also capable of performing the same function as initiator (Sokolova and Karavaiko, 1968; Zajic, 1969) provided that free sulfur is available from the pyrite. Arkesteyn (1980) found that the presence of *T. thiooxidans*, *thioparus*, *intermedius*, and *perametabolis* does not increase the pyrite oxidation rate over sterile blanks when starting at pH values of 6.0. There seems to be a slight enhancement of the rate when Arkesteyn (1980) used *T. ferrooxidans* but not by an amount greater than the experimental uncertainty. These data seem contrary to his experiments carried out at pH 5.0 in which microbial catalysis by direct contact was evident. In addition, new evidence summarized by Kelly et al. (1979) indicates that several other bacteria are important in pyrite oxidation and that mixed cultures can be more effective in oxidizing pyrite than single species cultures. Arkesteyn (1980) was also unable to isolate *Metallogenium* from some acid sulfate soils. The conclusion from all these investigations is that the initiation of pyrite oxidation in soils or sulfide refuse piles probably occurs more rapidly by microbial catalysis than by a purely inorganic mechanism and that *T. ferrooxidans* and possibly other microorganisms which normally inhabitat the soil environment may catalyze these reactions. The potential role of *Thiobacilli* species in initiating pyrite oxidation is another area of research worthy of further investigation. The importance of the microbial vs. the inorganic mechanisms for the initiation step is still subject to controversy.

If the rate-determining steps are controlled primarily by *T. ferrooxidans*, then the oxidation rate depends upon the factors controlling the bacterial growth kinetics such as the availability of oxidizing agents, carbon dioxide, and nutrients. Periodic rainwater infiltration provides the oxygen and carbon dioxide requirements in the unsaturated subsurface (Tuovinen and Kelly, 1972; Kleinmann, 1979). Regular flushing not only provides the needed aeration, but it transports oxidation products away from the reaction zone so that fresh pyrite surfaces are exposed. Nutrient requirements (such as nitrate and phosphate) for *T. ferrooxidans* are not limiting to growth because extremely small concentrations are quite sufficient for growth. *Thiobaccillus ferrooxidans* grows in the absence of any added N compound, and it has been suggested that it may fix atmospheric N_2 (Tuovinen and Kelly, 1972). Nitrogen fixation has recently been demonstrated by Mackintosh (1978). Trace quantities of phosphate and Mg are sufficient for growth. Sulfate is a requirement for iron oxidation (Lazaroff, 1963), but it does not limit growth because it is always available as an oxidation product. Since the only important limiting factors are oxygen and carbon dioxide, it follows that no growth occurs below the oxygenated water table. Kleinman (1979) confirmed that there is no significant growth in saturated environments, and field observations have shown that when deep coal mines are flooded by mine sealing techniques there is usually a significant, albeit incomplete, reduction of acidity (Foreman, 1972). Complete inhibition of the oxidation process may never be possible because of the availability of ferric iron as an alternate oxidizing agent.

Microbial catalysis of pyrite oxidation is an established fact, and the reaction rate may be primarily determined by the growth kinetics of *T. ferrooxidans*. However, recent data from Silver (1978) demonstrates that the DNA base composition of *T. ferrooxidans* can vary depending on the substrate used for growth. *Thiobaccillus ferrooxidans* may be a heterogeneous culture and other bacteria, as yet unidentified, may be more crucial to the oxidation process. Alternatively, mixed cultures may have symbiotic relationships which could produce different oxidation rates than those obtained from pure cultures adapted to specific media. In addition to oxygen or ferric iron concentrations or pH, rates should also be expressed in terms of environmental factors such as hydrologic flow path, residence time, pyrite surface area, temperature, climatic patterns, and soil properties if they are to be applied to actual field situations.

ENVIRONMENTAL INFLUENCES

Pyrite oxidation investigators have emphasized the rate-determining step in a very complex heterogeneous system. The results indicate that the governing factor is the growth kinetics of iron and sulfur-oxidizing bacteria, chiefly *T. ferrooxidans*. Laboratory studies on batch or continuous cultures (chemostat cultures), however, are not appropriate simulations of natural systems. They are useful in obtaining rate data, comparing rates and deriving mechanisms, but our understanding of natural systems also requires knowledge of cyclic processes such as seasonal, diurnal, and rainstorm influences. These processes strongly influence reactions by regulating temperature, pH, oxygen, water and nutrient availability. Additional information on microbial ecology and the environmental factors which influence growth are needed to determine the rate at which pyrite oxidizes under natural conditions. Unfortunately, very little work has been done in this area, and few field studies contain quantitative data on the microbiology, mineralogy, geology, hydrology, and climate.

Reviews on the microbiology of acid mine waters (Lundgren et al., 1972; Nordstrom, 1977) cite many papers containing species identification but none describing the relative proportions of species. Dugan et al. (1970a, 1970b) and Nordstrom (1977) have described acid slime streamers which contain an abundance of both motile and nonmotile bacilli (see color Plate 1A). The slime-excreting bacterium has not been isolated and its function in acid mine waters is not known. Natural acid sulfate waters contain mixed cultures of many species and several families of microorganisms whose growth rates may be quite different from lab growth rates with single species. An example of the interdependency of mixed cultures is a study by Arkesteyn (1980b)[2] on the association of *T. ferrooxidans* and *T. acidophilus.* Apparently *T. ferrooxidans* cannot grow in the presence of many common organic compounds without the presence of *T. acidophilus* which can utilize those compounds as an energy source. It is also interesting to note that *T. acidophilus* was present in approximately equal numbers as *T. ferrooxidans* in all the cultures which Arkesteyn (1980b)[2] examined.

A study has been made on the dissolved ferrous ion oxidation rate in a mountainous stream containing acid mine wastes (Nordstrom, 1976, 1977). The rate was found to be nearly identical to that determined for optimal growth of *T. ferrooxidans* in 9K culture media. The data indicates that the bacteria are growing at optimal rates in this dynamic aqueous environment because iron oxidation can be directly related to cell population growth (Silverman and Lundgren, 1959). After a rainstorm, the oxidation rates in the stream decreases significantly due to dilution and to the flushing effect of high flow. This study is at least one example of the role which climate and hydrology can play.

The geologic structure and composition of the rock strata are very important to the development of acid mine waters. Hollyday and McKenzie (1973) have shown how the positioning of carbonate strata with respect to oxidizing pyritic coals and shales can reduce the production of acid waters. Parizek and Tarr (1972) give an excellent account of several hydrogeologic techniques which can be used to reduce or prevent acid mine drainage. These techniques include diverting water flow away from the pyritic layers by pumping and diverting water through carbonate strata so that they develop high alkalinity before infiltrating pyritic strata. Geidel and Caruccio (1977) have further investigated the rate of alkalinity accumulation compared to acid accumulation by water infiltration through limestones, sandstones, and shales. Their results demonstrate that more frequent infiltration tends to reduce acid development. When longer dry periods are permitted there is a continual buildup of pyrite oxidation products (soluble sulfate salts) which cause higher acidity in the leachates when the next rainfall occurs. Alkalinity production, however, tends to level off with time. These conclusions are contrary to the work of Kleinman (1979) and Kleinman and Crerar (1979) who showed that the activity of *T. ferrooxidans* and the acidity production decrease if the dry intervals between infiltrations are increased. The processes occurring during infiltration are extremely important, and more research on short-term and seasonal variability is needed.

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[2] Arkesteyn, G. J. M. W. 1980b. *Thiobacillus acidophilus*: a study of its presence in *Thiobacillus ferrooxidans* cultures. Unpublished manuscript.

OXIDATION PRODUCTS: THE FORMATION OF HYDRATED IRON MINERALS

A large number of iron minerals may be found in acid, unsaturated pyrite-rich soils, on sulfide mine dumps, and on the surfaces of exposed sulfide ores and pyritic shales. These minerals have a wide range of properties from very insoluble iron hydroxides to very soluble iron sulfate hydrates. The more soluble sulfates are most commonly formed during dry periods as evaporation promotes the rise of subsurface waters to the uppermost soil surfaces by capillary action. As these waters reach the upper portions of the soil, they become progressively more concentrated and finally precipitate various salts in an efflorescence. This phenomenon is quite comparable to the buildup of efflorescent crusts associated with closed basin lakes in arid environments (Eugster and Jones, 1979). The formation of these efflorescent iron sulfates is an important intermediate step preceding the precipitation of the more common insoluble iron minerals such as goethite and jarosite.

Hydrated ferrous sulfate minerals frequently occur on the surface of weathering pyrite where moisture is present. When conditions become sufficiently dry, the dissolved ferrous and sulfate ions produced by reaction 14 first reach saturation with respect to melanterite, $FeSO_4 \cdot 7H_2O$. Under continued dryness, melanterite dehydrates to either rozenite, $FeSO_4 \cdot 4H_2O$, or szomolnokite, $FeSO_4 \cdot H_2O$. The mineral ferrohexahydrite, $FeSO_4 \cdot 6H_2O$, is much less common and has a very limited stability. The pentahydrate, siderotil, requires copper in its structure to be stable. If these minerals are still in contact with soil water or humid air and warm temperatures, they oxidize to copiapite, $Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20\,H_2O$ (see color Plate 4C) which can be stable for long periods of time when protected from rainfall or flowing water. Copiapite may contain several other divalent and trivalent metals substituted into the ferrous and ferric sites. It also has a very yellow color making it difficult to distinguish from sulfur. From the author's experience this mineral is one of the most abundant minerals found on sulfide mine tailings and on oxidizing sulfide ore minerals.

The transformation to copiapite may proceed according to the reaction:

$$5FeSO_4 \cdot 7H_2O + O_2 + H_2SO_4 \rightarrow Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O + 15H_2O \qquad [18]$$

which indicates that lower pH values as well as partial oxidation is required. Copiapite may precipitate directly from acid sulfate waters, but no field evidence for this has yet been found. Copiapite overgrowths on melanterite, however, have been observed (Nordstrom and Dagenhart, 1978) and a specimen from Shasta County, California (Nordstrom, 1977) has been reproduced in color Plate 1B. The bulk of the specimen is cuprian melanterite (blue). Small amounts of rozenite occur as a white

Overall Stoichiometry

$$FeS_2 + 15/4O_2 + 7/2H_2O \longrightarrow Fe(OH)_3 + 2H_2SO_4$$

	ACID MEDIA (pH≤3)	SLIGHTLY ACID TO BASIC MEDIA (pH≥4)
initiation phase	$\begin{cases} FeS_2 \rightarrow Fe^{2+} + S_2 + 2e^- \\ O_2 + e^- \rightarrow O_2^- \end{cases}$	$\begin{cases} FeS_2 + 3H_2O \rightarrow Fe(OH)_3 + S_2 + 3H^+ + 3e^- \\ O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \end{cases}$

acid-generating phase: $S_2 + 3O_2 + 2H_2O \longrightarrow 2SO_4^{2-} + 4H^+$

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

Fig. 2. The major steps during the course of pyrite oxidation.

frosting and the small yellow crystals are copiapite. The sulfate hydrate coquimbite, $Fe_2(SO_4)_3 \cdot 9H_2O$, is intimately associated with copiapite in oxidizing sulfide deposits. Melanterite, rozenite, szomolnokite, and copiapite are probably the most abundant efflorescences associated with oxidizing coal deposits (Nuhfer, 1967).[3] All of these sulfates are highly soluble and may be at least partially responsible for the increased acidity and dissolved solids load in receiving streams during rainstorm events (Nordstrom and Dagenhart, 1978).

As the iron becomes fully oxidized in acid mine waters it eventually reaches saturation with respect to either ferrihydrite[4] or jarosite, $KFe_3(SO_4)_2(OH)_6$. Jarosite is stable at lower pH values than ferric hydroxide (Brown, 1971). Both of these minerals have been observed as precipitates in acid mine drainage (Nordstrom et al., 1979) but are not stable for more than a season. Color Plate 2A shows a bright yellow deposit of jarosite precipitation from acid mine water. Fresh precipitates of iron in acid mine drainage which produce the so-called "yellow boy" may in fact be jarosite. As jarosite weathers or is exposed to dilute waters with higher pH, it will gradually decompose to ferrihydrite or goethite. Mine tailings may often be in equilibrium with both jarosite and ferrihydrite thereby providing a buffer system (Miller, 1979). Miller (1979) has estimated the pH of this buffer as 3.19 (±0.17). Studies on acid mine drainage environments suggest that the soluble hydrated sulfates form during periods of dry weather near the vicinity of oxidizing pyrite in unsaturated soil horizons. Ferrihydrite, goethite, and jarosite are spatially distributed further away from the pyrite and commonly form by precipitation from aqueous systems such as the saturated zone or in receiving streams as in Plate 2A.

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[3] Nuhfer, E. B. 1967. Efflorescent minerals associated with coal. M.S. Thesis. West Virginia University, Morgantown. 74 p.

[4] I have adopted the mineral name "ferrihydrite" here in place of ferric hydroxide, whether amorphous or otherwise, following the recommendation of Schwertman and Taylor (1977) and Schwertman (1979).

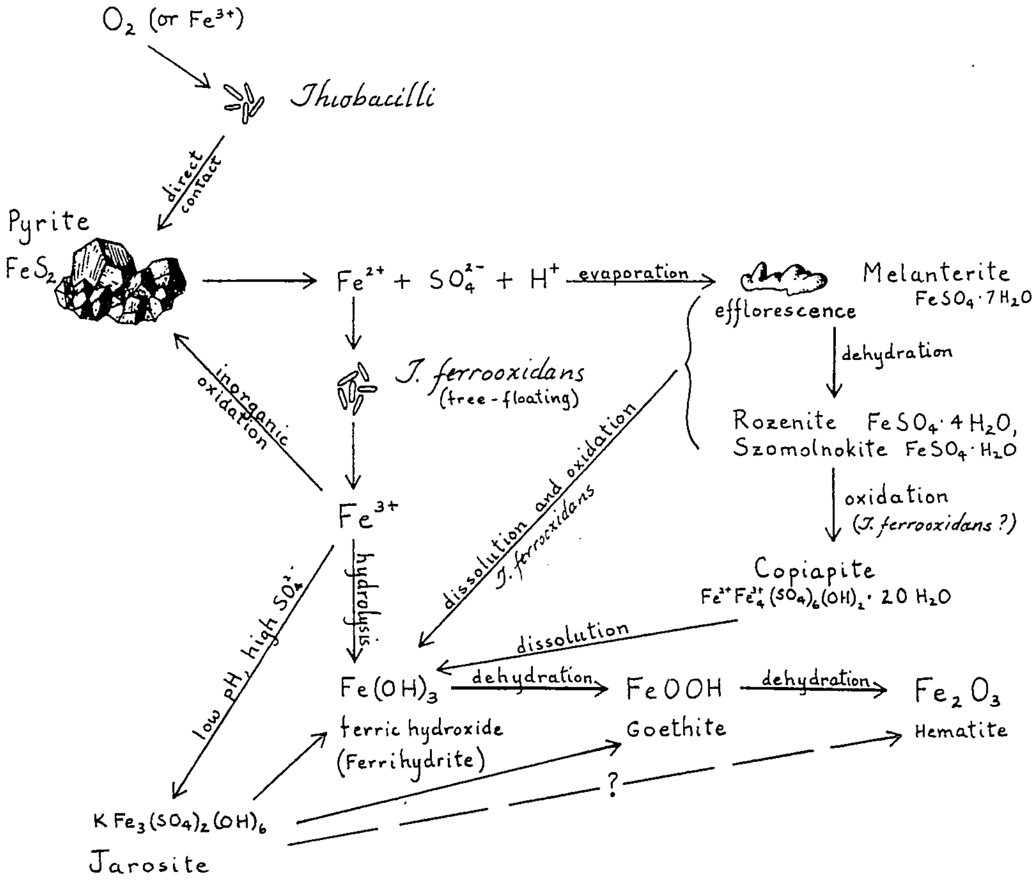

Fig. 3. The overall sequence of mineral reactions for pyrite oxidation showing the relationships between oxidizing agents, catalysts, and mineral products.

SUMMARY

The oxidation of pyrite involves many electron transfer reactions with the consequent reduction of oxygen in an aqueous environment and ultimately produces ferric iron, sulfate, and high acidity. The key reactions are summarized in Fig. 2 where the inorganic rate-limiting steps are pH dependent for values greater than 4.0. Below a pH of 3.0 the oxidation rates are independent of pH. The transition zone of pH $= 3$ to 4 includes both steps. The first step is the initiation phase in which elemental sulfur and ferrous iron are produced. At the higher pH values ferrous iron is oxidized to ferric hydroxide. The acid-generating phase in which sulfuric acid is produced from elemental sulfur follows next. Actual accumulation of sulfur may depend upon the concentration and availability of oxidizing agents such as sulfur-oxidizing bacteria. Once sufficient acid has been generated (pH < 3.0), ferric iron rapidly continues the oxidation of pyrite (catalytic phase). The most important catalyst is the iron-oxidizing bacterium, *T. ferrooxidans*, which greatly speeds up the oxidation of ferrous to ferric thereby regenerating the supply of ferric irons in solution. The scheme presented here is similar to the reaction sequence suggested by

Kleinmann (1979). The oxidation products include several possible iron sulfate, iron oxide, and iron hydroxide minerals whose genesis depends upon water content, degree of oxidation, and time. The grand sequence of reactants, products, and catalysts for pyrite oxidation is shown in the schematic illustration of Fig. 3. This picture attempts to tie together the roles played by (1) the oxidizing agents ferric iron and oxygen, (2) the catalyzing agent *T. ferrooxidans* which utilizes oxygen for respiration, and (3) the mineral products.

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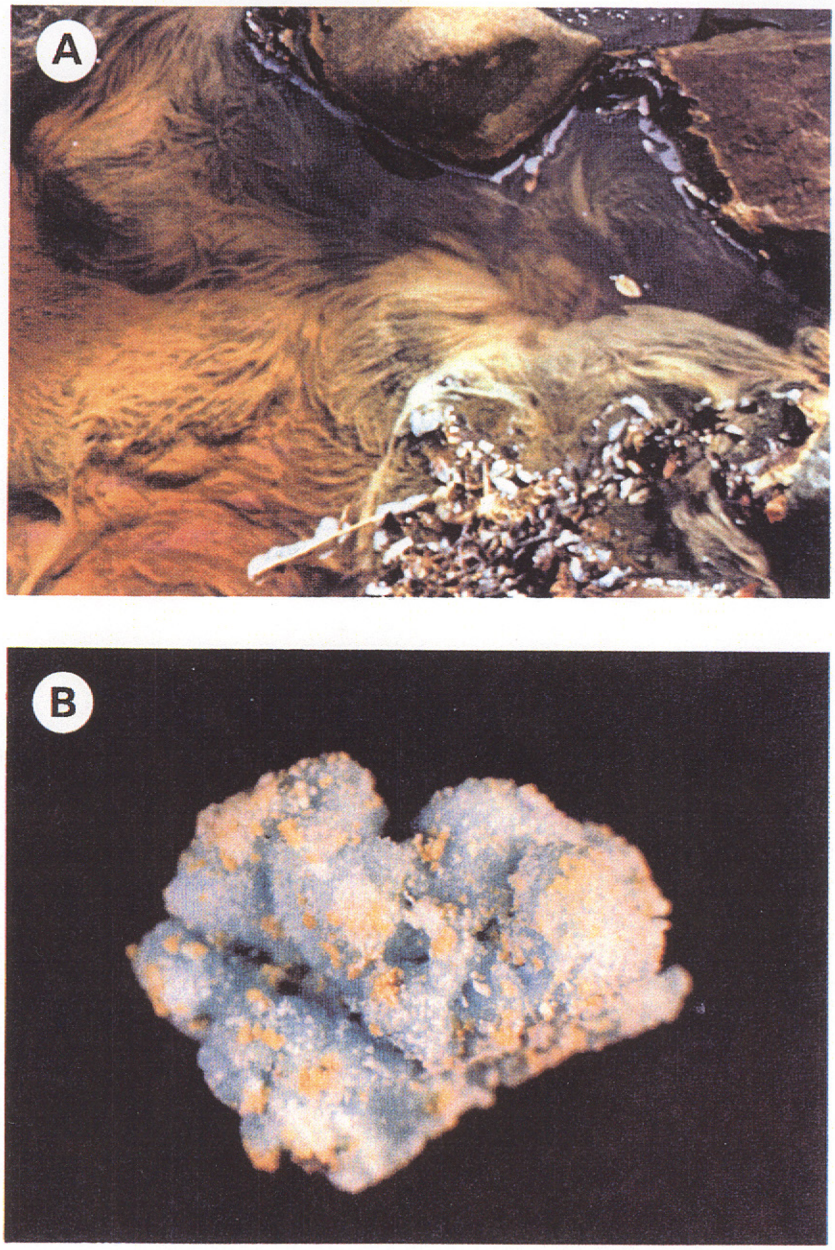

Plate 1. A. Slime-excreting bacteria growing along the stream bottom of a creek containing acid mine drainage in Shasta Co., California. These "acid slime streamers" contain very dense populations of bacilli enmeshed in a fibrillar polymer network similar to those found by Dugan, MacMillan and Pfister (1970a). Distance lengthwise across area shown by photo is about 0.8 m (See Chapter 3). Plate 1. B. Specimen of efflorescent growth containing copiapite (yellow) overgrowths on rozenite (white) which has dehydrated from cuprian melanterite (blue). This specimen measures about 1 cm across. (See Chapter 3).

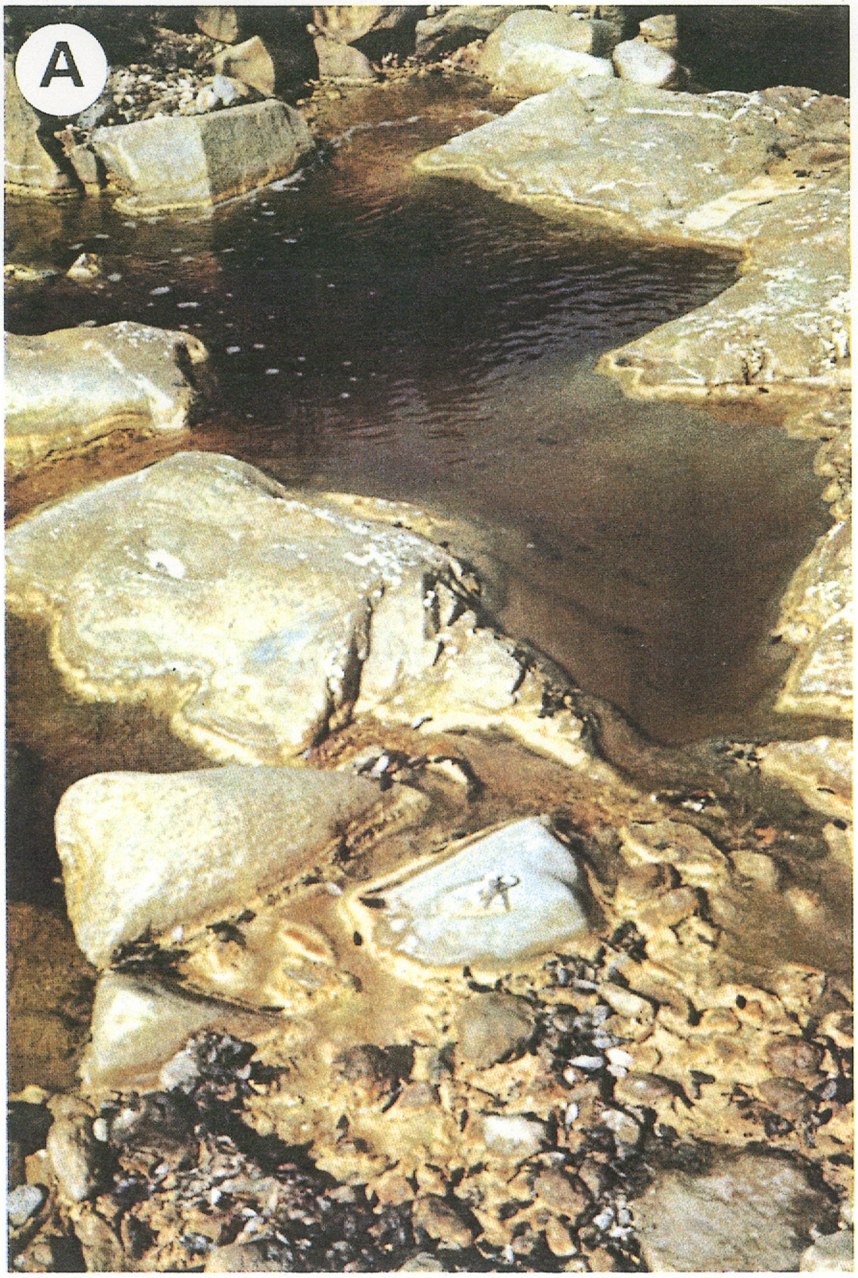

Plate 2. A. Jarosite (yellow) precipitation from an acid mine water (pH 2) in Shasta Co., California. Grey color on stream bed is a coating of bacterial slime. Scale is provided by a ring of keys in center foreground. (See Chapter 3). Plate 2. B. Face of lignite surface mine showing oxidized (about upper 1/5 of exposed soil-geologic column) and reduced zones of the pre-mining column. (See Chapter 10).