

ing amounts of chlorophyll on ocean color presented by Ramsey (9). The change in shape with increasing chlorophyll is reflected in decreased mean slope of the spectra. Anomalies in the shape and amplitude of these spectra, and of some taken on other occasions, make it evident that other factors play a role that merits further investigation.

Our investigation shows that large differences occur in the spectra of the light backscattered from the ocean and that they can be recorded from aircraft. In the present instance, the slopes of the spectra correlate quite closely with differences in chlorophyll concentration. The discrepancies are believed to be due to difference in time within paired observations, to differences in surface reflection, to scattered air light, and to the presence in the water of material other than chlorophyll that affected the light selectively. If such interference can be eliminated, or identified and allowed for, spectrometric procedures from aircraft (and perhaps from satellites) will be of great value in the rapid investigation of oceanic conditions, including conditions important for biological productivity.

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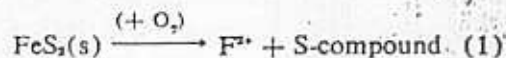
12 December 1969

Acidic Mine Drainage: The Rate-Determining Step

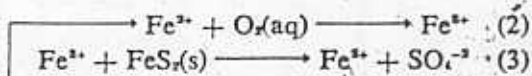
Abstract. *The rate-determining step in the oxidation of iron pyrite and the formation of acidity in streams associated with coal and copper mines is the oxidation of ferrous iron. Effective pollution abatement necessitates controlling this reaction.*

The oxidation of iron pyrite (FeS_2) and the release of acidity into waters draining through coal mines (1) can be represented by the following reaction sequence (2).

Initiator reaction:



Propagation cycle:



Fe^{2+} is released in the initiator reaction either by simple dissociation of the iron pyrite or by oxidation of the

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11. Microbial catalysis of the oxygenation of Fe^{2+} by the autotrophs *Thiobacillus ferrooxidans* and *Ferrobacillus ferrooxidans* has often been demonstrated in laboratory systems [M. P. Silverman and H. L. Ehrlich, *Advan. Appl. Microbiol.* **6**, 153 (1964)].
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17. We thank K. Spencer and G. Kutz for laboratory assistance, the Public Health Service for support of P. Singer, and the Federal Water Pollution Control Administration for supporting this research (PH 86-66-107). Present address: Department of Civil Engineering, University of Notre Dame, Notre Dame, Indiana 46556.

pyrite by oxygen (3). After the sequence has been initiated, a cycle is established in which Fe^{2+} is oxidized by oxygen to Fe^{3+} which is subsequently reduced by pyrite thereby generating additional Fe^{2+} and acidity. This model is similar to an earlier one proposed by Temple and Delchamps (4). We have studied, in our laboratory, the relative rates of the reactions that comprise the mine-water environment to ascertain which of the steps is rate-limiting in order to suggest measures that should be emphasized in the abatement of pollution by coal mine drainage.

Two possible oxidants for iron pyrite are available, namely oxygen and ferric iron (5). The reduction of Fe^{3+} by pyrite (Fig. 1) both in the presence and in the absence of oxygen (0.20 atm) showed no difference in the rate of the reaction (the parallelism exhibited by the two straight lines is indicative of equivalent reaction rates) or in the rate of change of soluble ferrous iron. The rate of the reaction is relatively rapid; for example, at pH 1, 50 minutes was required for the reduction of 50 percent of the initial ferric iron concentration by approximately 3 square meters of pyrite per liter of solution. In the absence of ferric iron, no oxidation of pyrite was observed even after 1 week. Further evidence for the slowness of reaction 1 is the fact that pyrite can be used as a reasonably inert electrochemical electrode (6, 7). Hence, the major oxidant of iron pyrite is ferric iron, as indicated in the propagation cycle.

The rate of oxidation of Fe^{2+} by oxygen in abiotic systems is shown in Fig. 2 to be a function of pH. These results were obtained in pH-buffered systems (using HClO_4 or CO_2 and HCO_3^-) under a constant partial pressure of oxygen and, at pH values greater than 4.5, were found to be compatible with the kinetic relationship (8)

$$-\frac{d[\text{Fe}^{2+}]}{dt} = k[\text{Fe}^{2+}][\text{O}_2][\text{OH}^-]^2 \quad (4)$$

where $k = 8.0 \times 10^{13} \text{ liter}^2 \text{ mole}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$ at 25°C . At pH values below 3.5, the reaction proceeds at a rate independent of pH, that is,

$$-\frac{d[\text{Fe}^{2+}]}{dt} = k'[\text{Fe}^{2+}][\text{O}_2] \quad (5)$$

where $k' = 1.0 \times 10^{-7} \text{ atm}^{-1} \text{ min}^{-1}$ at 25°C . The reaction has previously been reported to be first- or second-order with respect to Fe^{2+} , depending

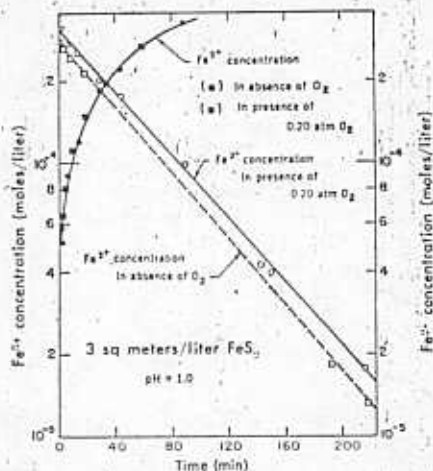


Fig. 1. Reduction of ferric iron and increase in dissolved ferrous iron in the presence and absence of oxygen.

upon the ionic medium (9); in the presence of ligands which form relatively strong complexes with Fe^{3+} (pyrophosphate, fluoride, and dihydrogen phosphate), the rate is first order in $[\text{Fe}^{2+}]$; for ligands of moderate strength (sulfate and chloride) and for perchlorate (10), the reaction rate is dependent upon $[\text{Fe}^{2+}]^2$. The actual rates of the reaction, however, are of the same order of magnitude as those reported here in the lower pH range. The half-time of the reaction in this acidic pH region is approximately 1000 days, reflecting the slowness of the oxygenation reaction when compared with the rapid oxidation of pyrite by ferric iron. Since reaction 2 is significantly slower than reaction 1, the oxidation of Fe^{2+} by oxygen appears to

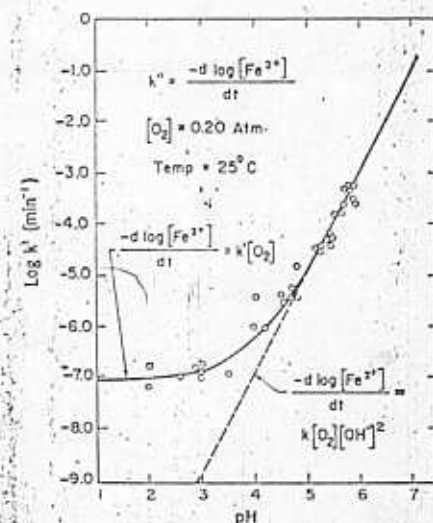


Fig. 2. Oxygenation rate of ferrous iron as a function of pH in abiotic systems.

be the rate-limiting step in the propagation cycle. It is irrelevant in this model whether pyrite or marcasite, the orthorhombic polymorph of FeS_2 , is considered as the sulfide source; reaction 2 continues to be the rate-controlling reaction.

Field investigations of the oxidation of Fe^{2+} in natural mine drainage waters were conducted in the bituminous coal region near Elkins, West Virginia. Observations of the rate of this reaction in these acidic streams (at pH values close to 3) showed it to proceed considerably more rapidly than the laboratory studies at pH 3 predicted.

Many agents indigenous to these natural mine streams have been cited in the literature, in various circumstances, as displaying catalytic properties in the oxidation of Fe^{2+} by oxygen. The catalytic effects of sulfate, iron(III), copper(II), manganese(II), aluminum(III), charcoal, iron pyrite, clay particles and their idealized counterparts, alumina and silica, and microorganisms were investigated and compared in synthetic mine waters in our laboratory. Of these, microorganisms (11) appeared to exhibit the greatest effect in accelerating the oxygenation of Fe^{2+} . Comparisons between the rates of oxidation of Fe^{2+} under sterile conditions after inoculation with untreated and with sterilized natural mine water showed that microbial mediation accelerates the reaction by a factor larger than 10^6 .

If the reaction scheme describing the oxidation of pyrite and the formation of acidity (reactions 1 to 3) is considered, it appears that the oxygenation of Fe^{2+} is the rate-determining step and that in natural acidic systems the reaction is greatly accelerated by microbial mediation. A similar mechanism is probably applicable to acidic leaching processes in other mines, such as copper mines, where iron is also invariably present. If so, copper sulfides are oxidized by ferric iron and the resultant ferrous iron is reoxygenated, again with the aid of microorganisms, to form additional iron(III).

The solution to the problem of acidic mine drainage, therefore, appears to be dependent upon methods of controlling the oxidation of Fe^{2+} . Proposals for such control fall into two classes: thermodynamic control and kinetic control.

Thermodynamic control requires the total elimination of oxygen and the maintenance of reducing conditions

within the mine. Total exclusion of oxygen through mine-sealing programs (12, 13) is economically and technologically unfeasible, owing to the many fractures and faults in the mine wall. Partial elimination of oxygen is inconsequential, for the microorganisms involved are microaerophilic and can survive at reduced oxygen tensions. The flooding of mines to hydrologically isolate the system (14) is an effective means of sealing the mine, but only for mines below the groundwater table. The introduction of organic material in order to reduce iron(III) and sulfate chemically (15) requires the continual addition of the reducing agent and the elimination of oxygen to maintain iron and sulfur in their reduced states.

Kinetic control requires suppression of the catalytic agent responsible for the rapid oxidation of ferrous iron. The application of bactericides (16) should be a successful means of coping with the problem. Such application necessitates injection of the bactericidal agent into the system at a suitable location where the entire influent water can be treated. Strip (surface) mines and coal refuse piles are especially amenable to such treatment.

Treatment of acidic mine drainage requires control of the cycle by which such acid discharges arise. Effective measures must be directed toward inhibiting the catalytic oxidation of Fe^{2+} : in the absence of such catalysis, the oxygenation rate of Fe^{2+} is too slow to be of any consequence in the formation of acidity in natural mine systems.

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References and Notes

- For general description of problem, refer to *Proceedings of Symposium of Coal Mine Drainage Research, 2nd, May 1968* (Mellon Institute, Pittsburgh, 1968).
- The exact stoichiometric equations are
 $FeS_2(s) + 7/2 O_2(aq) + H_2O = Fe^{2+}, Fe^{3+} + 2SO_4^{2-} + 2H^+$
 $Fe^{2+} + 1/4 O_2(aq) + H^+ = Fe^{3+} + 1/2 H_2O$
 $Fe^{2+} + 3H_2O = Fe(OH)_3(s) + 3H^+$
 $FeS_2(s) + 14Fe^{2+} + 8H_2O = 15Fe^{3+} + 2SO_4^{2-} + 16H^+$
- This reaction may be interpreted as an electrochemical corrosion reaction where the reduction of H^+ , H_2O , or O_2 is accompanied by the oxidation of FeS_2 .
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 - We thank K. Spencer and G. Kunz for laboratory assistance, the Public Health Service for support of P. Singer, and the Federal Water Pollution Control Administration for supporting this research (PH 86-66-107).
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Viscosity of the Atlantic Ocean Bottom

Abstract. Two profiles across the Mid-Atlantic Ridge were analyzed to determine viscosity values. Viscous creeping of bottom features due to gravitational stress was assumed, as was sea floor spreading at a rate of 2 centimeters per year. Values obtained agreed well with previous results obtained on the Fennoscandian Uplift, despite great differences in the horizontal dimensions of the bottom relief.

When rocks are subject to stress, they tend to deform. The rate of deformation is a complicated function of the stress tensor which is not yet fully understood (1). There is evidence (2), however, that over long periods the rate of deformation may be proportional to the applied stress to a first-order approximation. This principle permits us to apply the theory of viscous flow to geodynamics.

Viscous flow theory was first applied by Haskell (3) in his work on the Fennoscandian Uplift, and Crittenden (4) later applied it to the Lake Bonneville Uplift. Haskell obtained a value of the order of 10^{22} poises for the viscosity of the asthenosphere, whereas Crittenden derived a value of the order of 10^{21} poises. More recently (5) it has been observed that systems of different horizontal dimensions yield different viscosity values, and a variation of viscosity with depth has been advocated as an explanation.

We assume the simple Newtonian viscosity but use a different clock to determine the rate of deformation. Heezen (6) noticed that in east-west profiles across the Mid-Atlantic Ridge the bottom relief is more pronounced near the Central Rift Valley than toward the continents (6). Although many mechanisms could explain this decrease in relief, the decrease may also be due to the viscous creeping of the bottom features under gravitational stress. Since the sea floor is spreading away from the Central Rift Valley at a fairly constant rate of about 2 cm/year, the features farther from the Rift Valley are older and consequently have had more time to compensate.

By using this model and applying classical hydrodynamics to the ridge (7), we obtain the following equation for the characteristic decay time of topographic relief:

$$\tau = 4\pi\eta/\rho g\lambda \quad (1)$$

where τ is the decay time, η is the viscosity of the rock, ρ is the density con-

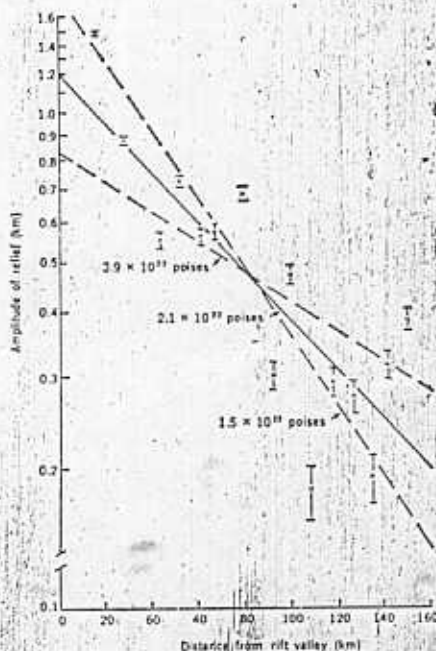


Fig. 1. Decrease in the amplitude of the relief of the Mid-Atlantic Ridge as a function of the distance from the rift valley [data from Heezen (6)]. Vertical bars indicate the uncertainty in the measurement of the amplitude from the profile. The solid line is the least-squares fit for the viscosity, and the dashed lines indicate the one standard deviation variance in the viscosity.