A Model for Pyritic Systems

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Introduction

The formation of acid mine drainage has been a subject of intense study for many years, and there have been extensive attempts to secure abatement in particular instances by such practices as mine sealing, establishing cover on spoil banks, and drainage control. It is becoming increasingly evident, however, that much of the consideration given to acid mine drainage formation and abatement has been taken out of context. In many instances, the problem has either been oversimplified, or assumed to be too complex to be handled by other than gross empirical approaches. This has resulted in difficulty in defining the rate controlling factors in specific mine drainage situations, and in both lack of communication and the accumulation of conflicting data. As a result, there appears to be a widespread element of doubt concerning the general feasibility of abatement of mine drainage pollution at the source, as an alternative to treatment. It may be that effective at-source abatement will be applicable to only a minor fraction of existing and future points of acid generation. It is just as likely, however, that through a more thorough understanding of pyritic systems,* economical abatement procedures can be developed which will eliminate the necessity of an interminable treatment program in the majority of cases. Further, it will provide a basis for more effective planning of mining operations with respect to optimizing abatement at the source.

The authors do not feel that the questions concerning at-source abatement versus drainage treatment can be answered on the basis of existing information. We strongly contend, however, that the time and expense required to arrive at these answers can be greatly reduced if the individuals, disciplines, and agencies associated with and/or dependent on mine drainage research and demonstration efforts can achieve a common basis for intensive and critical discussion. It is apparent that there are a host of widely held concepts concerning the nature of pyritic systems which differ primarily in emphasis on one or another aspect of the system. We have all experienced the frustration of argumentive discussions culminating in the realization that both parties were essentially in agreement from the first, or worse, in the realization that effective communication was not established at all.

The purpose of this paper is to present a model for the conceptualization of pyritic systems. The model draws principally on the type of descriptive framework commonly used in chemical engineering systems, and is neither new nor

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* The term pyritic systems, as used in this paper, refers to the occurrence of pyrite in field situations; e.g.; gob piles, strip pits, spoil banks, and underground mines.

controversial. Rather, it is merely a restatement, in the context of pyritic systems, of the fundamental principles which describe virtually any reaction system. The model is intended to identify and provide a framework for integration of the numerous factors which determine the rate of acid release from any type of pyritic system associated with mining activity. It is hoped that this model will spark an increased level of critical discussion among those persons associated with acid mine drainage.

Rate versus Equilibrium and Rate Process Interdependencies

The acid mine drainage problem is essentially a rate problem, in which we are concerned ultimately with the rate at which products of pyrite oxidation (especially H^+, iron (Fe^{++} and Fe^{+++}), and $SO_4^{=}$) are released to receiving waters. Although thermodynamic considerations define the reactions which can occur in a given system, they do not define the rates at which they will proceed. Analysis of the rate of pollutant production requires the further delineation of the rate processes, which include:(a) rate of transport of reactants to the points of reaction, (b) rate of the reactions themselves, or reaction kinetics and (c) rate of transport of the products away from the points of reaction. Pyritic systems fall in the category of heterogeneous reaction systems, since the overall reactions involve gas, liquid, and solid phases. In any heterogeneous system there is, in general, a definite interdependency between the various rate processes. Often, one of the rate processes will be a rate limiting step in the overall sequence, and control of this specific rate process represents a potentially efficient means of controlling the rate of production of the system. The interdependency of rate processes will be discussed in more detail below.

Rate Processes in Pyritic Systems

The oxidation of pyritic materials associated with coal and other mined minerals has often been described by the following equations:

$$FeS_{2(s)} + 3\,1/2\,O_2 + H_2O \rightarrow Fe^{++} + 2SO_4^{=} + 2H^{+} \;\ldots\ldots\; (1)$$

$$Fe^{++} + 1/4O_2 + H^{+} \rightleftharpoons Fe^{+++} + 1/2H_2O \;\ldots\ldots\ldots\; (2)$$

$$Fe^{+++} + 3H_2O \rightarrow \underline{Fe(OH)_3}\downarrow + 3H^{+} \;\ldots\ldots\ldots\; (3)$$

As these are familiar to all involved in acid mine drainage work, it is convenient to outline the model in relation to these equations. It must be remembered that these are gross stochiometric equations, and although they indicate initial reactants and final products, they in no way indicate either the mechanisms of reaction or intermediate products which may be formed, but which may cancel out of the overall equations. It is significant that they do not define reaction kinetics, nor do they define the locations within a given system where the indicated reactions take place. It is likely that the simplicity of these reactions as they are popularly written may in itself be a factor in the tendency toward oversimplification in the analysis of pyritic oxidation systems.

Referring initially to equation (1), we might rewrite this equation as:

$$FeS_{2(s)} + \text{electron acceptor} \rightarrow Fe^{++} + 2S^{+6} + \text{reduced electron acceptor} \;\ldots\ldots\; (4)$$

This oxidation-reduction reaction provides for the oxidation of $FeS_2(_s)$ *, but does not imply that O_2 is a necessary electron acceptor or oxidizing agent. For example, it has been widely demonstrated that Fe^{+++} can be the oxidizing agent, in which case we could rewrite this oxidation reaction as :

$$FeS_2(_s) + 14Fe^{+++} + 8H_2O \rightarrow 15Fe^{++} + 2SO_4^{=} + 16H^{+} \quad . . . (5)$$

The 14 Fe^{+++} ions in equation (5) would have to come from the oxidation of Fe^{++} iron formed by the previous oxidation of $FeS_2(_s)$. Rewriting equation (2) to provide the required 14 Fe^{+++} ion gives:

$$14Fe^{++} + 3\ 1/2O_2 + 14H^{+} \rightleftharpoons 14Fe^{+++} + 7H_2O \quad . . . . (6)$$

Adding equations (5) and (6) gives:

$$FeS_2(_s) + 3\ 1/2O_2 + H_2O \rightarrow Fe^{++} + 2SO_4^{=} + 2H^{+}$$

or the same net reaction as given in equation (1).

In any case, unless there is a continuous source of Fe^{++} entering from outside the system, 3 1/2 moles of O_2 must be provided, at some point in the system, for each mole of $FeS_2(_s)$ put into solution. That is, oxygen can be regarded as the ultimate electron acceptor, within the context of the above reactions. For purposes of simplifying the presentation in this paper, oxygen will be regarded as taking part directly in the oxidation reaction. This in no way precludes the application of the model concept to the more complex and potentially very important case of pyrite oxidation by reaction with Fe^{+++} ions.

Taking equation (1) to represent the initial oxidation of pyrite, then equation (2) and (3) represent the eventual oxidation of Fe^{++} to Fe^{+++}, and the precipitation of $Fe(OH)_3(_s)$. These two steps may occur within the pyritic system, or in the receiving water, depending on environmental conditions and on residence time of the products of equation (1) within the bounds of the system.

The rate processes to be accounted for, then, are the reaction rates of the reactions shown in equations (1) through (3), the rate of transport of oxygen and water to the site of pyrite oxidation, and the rate of transport of the dissolved products of equation (1) away from the site, and eventually to the receiving water. In a high humidity environment, the water can be assumed to be present at the site, either as liquid water or water vapor, and thus will not be discussed in connection with reactant transport. Liquid water flow is of paramount importance in the dissolution and transport of products, however.

Description of a Pyritic System

Certain characteristics common to all pyritic systems can be summarized, which provide further definition of the factors to be included in any system model. These are:

(a) The reaction is heterogeneous, involving the reaction of crystalline (FeS_2) with oxygen in water. The initial reaction site is the pyrite surface, and it is the environment at this surface which determines the kinetics of the oxidation.

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* In this paper, pyrite oxidation is taken to mean the type of reaction shown in equation (4), and does not include the subsequent oxidation of ferrous iron, leading to the precipitation of ferric iron, as shown in equations (2) and (3).

reaction. This rate may be expressed in kinetic terms as a function of the concentrations of reacting species, and of factors having a catalytic effect on the rate. The 'concentration' of FeS_2 is the number of reactive sites per unit area of pyrite, while other chemical species may be represented in conventional concentration terms.

(b) A calculation of the solubility of oxygen in water, together with a consideration of the stochiometry of equations (1) through (3) and the acid and iron concentrations commonly observed in mine drainages, shows that it is possible for only a trace of the oxygen required to have entered the system in the form of dissolved oxygen. Therefore, oxygen transport must be predominantly in the gas phase (1). This fact has far-reaching implications, one of the most important of which is the fact that pyrite undergoing oxidation cannot be covered by more than a thin film of water, due to the resistance to oxygen transport in water. One must look, then, to the factors controlling gas phase oxygen transport for a description of this major and indespensible link in the overall reaction train.

(c) 'Dry' pyrite will undergo oxidation at a rate similar to that observed for pyrite in water saturated with oxygen, as long as the relative humidity is near 100% (2). The products of oxidation are sufficiently hygroscopic to cause water to condense from the surrounding water vapor, resulting in an adsorbed liquid of high acid and salt content.

(d) Kinetic studies have shown that desorption of oxidation products does not influence oxidation rate of pyrite (in presence of water). (2) Thus, reaction rate is independent of the rate of transport of products away from the region of pyrite oxidation.

(e) In general, the reaction is not associated with pyrite exposed directly to the outside atmosphere, but instead with pyrite 'buried' within some type of porous structure.

Figure 1 shows an idealized example of a pyritic system, incorporating the major characteristics discussed thus far.

Interface A might be the ground surface in the case of a gob-pile, or the wall surface in an underground mine. The pyrite surface at C is buried at a distance L in the surrounding permeable material (e.g., coal, shale, etc.), and is covered by a film of water of thickness X. It should be noted that the term permeable media, as used here,does not imply a homogeneous permeability. It is likely that permeability to both oxygen and water is due largely to specific channels, such as cracks, partings, etc.

The boundary D marks the upper boundary of a region saturated with water, such as a saturated ground water flow region. Although products of pyrite oxidation might seep down to this region, and then be carried out of the system, pyrite buried in this region will not undergo significant oxidation, due to the resistance to diffusion of oxygen or any other electron acceptor in an unmixed (non-turbulent) volume of water. The distance and nature of water seepage from the point of oxidation to an area of active flow will determine the lag time between oxidation and appearance of products in the drainage.

Rate of Pyrite Oxidation:

Having defined the nature of this sample element of a large pyritic system, an expression can be developed to relate the rate at which the pyrite oxidation reaction proceeds to the system characteristics. This expression must be a function of the oxygen concentration at surface A, the mechanism of oxygen transport to the pyrite surface, and the kinetics of the oxidation reaction. For the purpose of discussion, it will be assumed that oxygen transport through the permeable media is by diffusion only. However, it should be noted that convective transport is very likely to be a major factor in oxygen transport in pyritic systems, due to the breathing action induced by atmospheric pressure fluctuations. Referring to Figure 1, let it be assumed that the oxygen concentration at the boundary A is c_1, that the oxygen concentration at the pyrite surface is c_3, and that the rate processes are proceeding under steady state conditions. Working with a unit area of pyrite,

$$r_r = k_1 c_3^n \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

r_r = rate of reaction (moles O_2/hr consumed)
k_1 = reaction rate constant
n = empirical constant

To simplify this example, it will be assumed that $n = 1$. At steady state,

$$r_r = r_{t1} = r_{t2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

r_{t_1} = rate of O_2 transport through porous media (moles O_2/hr)
r_{t_2} = rate of O_2 transport through water film (moles O_2/hr)

further, $$r_{t_1} = \frac{D_1}{L}(c_1 - c_2) \quad \text{and} \quad r_{t_2} = \frac{D_2}{X}(c_2 - c_3) \quad \ldots\ldots\ldots (9)$$

where D_1 = Diffusivity of O_2 through the permeable media
D_2 = Diffusivity of O_2 through the water
L = Length of diffusion path through porous media
X = Length of diffusion path through water film
c_2 = O_2 conc. at porous media - water film interface

rearranging euqations (8) and (9),

$$c_1 - c_2 = \frac{L}{D_1} r_{t_1} = \frac{L}{D_1} r_r \quad \ldots\ldots\ldots\ldots\ldots (10a)$$

$$c_2 - c_3 = \frac{X}{D_2} r_{t_2} = \frac{X}{D_2} r_r \quad \ldots\ldots\ldots\ldots\ldots (10b)$$

adding equations (10a) and (10b)

$$c_1 - c_3 = r_r \left(\frac{L}{D_1} + \frac{X}{D_2}\right)$$

and $$r_r = \frac{1}{\frac{L}{D_1} + \frac{X}{D_2}} (c_1 - c_2) \quad \ldots\ldots\ldots\ldots\ldots (11)$$

Note that for a given value of $c_1 - c_3$ (the overall driving force for oxygen transfer), an increase in L or X or a decrease in D_1 or D_2 will lead to a decrease in r_r. However, for a given reaction site in a given system, L, X, D_1, and D_2 will be constant and equation (11) can be rewritten as

$$r_r = k_m (c_1 - c_3) \quad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

where k_m is the overall mass transfer coefficient for the system. Combining equations (7) and (12) (with n = 1 in equation (7))

$$k_1 c_3 = k_m (c_1 - c_3) \quad \text{or} \quad c_3 = \frac{k_m}{k_1 + k_m} c_1 \; . \; . \; . \; . \; . \; . \; . \; (13)$$

This gives the oxygen concentration at the pyrite surface in terms of the concentration of oxygen at boundary A, the mass transport characteristics of the system (k_m) and the kinetic rate constant (k_1).

Rearranging eq. (13),

$$k_1 c_3 = \frac{k_1 k_m}{k_1 + k_m} c_1 = \frac{1}{1/k_m + 1/k_1} c_1$$

$$r_r = \frac{1}{1/k_m + 1/k_1} c_1$$

Thus, the rate of oxidation can be expressed as a function of k_m, k_1, and the concentration of oxygen at the outside atmospheric boundary of the system c_1.

This is analogous to a simple electrical circuit with two resistances, R_1, and R_2, in series. In this case,

$$I = \frac{1}{R_1 + R_2} E$$

where I = current flow

E = potential drop.

In looking at the problem in the manner shown above, it is not necessary to assume a first order reaction as in eq. (7), nor is it necessary to assume a single site with single values of L and X. The model can be expanded to fit complex situations, with the major limitation at this time being valid data on the factors determining mass transport and kinetics.

For example, k_m is a function, in general, of the scale of the system, and the factors determining both molecular diffusion and cnnvective transport (breathing) of oxygen. Similarly, k_1 is a function of oxygen, ferrous, and ferric ion concentrations at the pyrite surface, the nature and surface area of the exposed pyrite, and catalytic factors such as bacterial activity. All of these factors must by incorporated in a description of the reaction system.

In any specific case, either mass transport or kinetics might be the rate determining factor, depending on the relative values of k_1 and k_m. For example, as above, let $r_t = k_m (c_1 - c_3)$, and $r_r = k_1 c_3$. As before, $r_r = r_t$, and the simultaneous solution of the expressions for r_t and r_r will yield the rate of transport (or of reaction) and the concentration of oxygen at the pyrite surface which will be maintained at steady state. This solution, which was carried out analytically above, can also be demonstrated graphically, as shown in Figure 2. Three cases are shown: CaseA$_1$, $k_1 \approx k_m$; Case B, $k_1 <<< k_m$; and Case C, $k_1 >>> k_m$.

In Case A, it is seen that a change in either k_1 or k_m will yield a significant change in the steady state reaction rate : that is, both are rate controlling. In Case B, the steady state reaction rate is very sensitive to changes in k_1, but is insensitive to changes in k_m: thus, the reaction kinetics are rate controlling. To control acid formation at the source, attention should be given to the identification and control of the rate controlling step, which may well vary from one situation to another. It is the ultimate effect of such procedures as mine sealing on the rate controlling step which is of importance.

Rate of Acid Release:

Just as reaction rates can be modeled rationally, so also can product release rates be modeled. Referring to Figure 1, products of oxidation will move away from the site by either diffusion or convection, depending on whether the water film on the pyrite is moving or stagnant. If there is no water film, the products will remain at the site. The rate and frequency with which the products are removed from the system will depend on the mechanism of transport away from the site, and the proximity of regions of active water flow. As the position of regions of active flow change (e.g., ground water levels, or percolating drainage from precipitation). they may flush out products held at or near the site of pyrite oxidation. It is significant to note that changing positions of flow channels may 'flood out' oxidation sites, temporarily decreasing the rate of acid formation, but at this same time, the rate of removal of oxidation products from the system may be at a maximum value. The overall process of product removal can be represented mathematically by established expressions describing mass transport and ground water flow. The primary factor to bear in mind is the fact that the distance from the site to a region of active water flow is variable with time, and related to seasonal changes in flow patterns. The 'lag time' of product removal may be considerable (1) and the overall retention time of oxidation products will be a factor in the determination of the Fe^{++}/Fe^{+++} ratio in the system's effluent.

Value of Model

It is believed that through the descriptions of pyrite oxidation systems in the context of the model outlined here, the discussion of such systems can be classified,and problems of communication can be considerably lessened. Several points warrent particular emphasis at this time. In planning and executing laboratory investigations, due consideration must be given to the problem of extrapolating laboratory data to field conditions. For example, in studying reaction kinetics, it should be recognized that water in the immediate vicinity of pyrite oxidation sites will be extremely high in both hydrogen ion and salt content. This may have a very direct bearing on the conditions to be simulated in experiments dealing with microbial catalysis of pyrite oxidation. Second, in the application of bacterial agents or agents intended to block the oxidation reaction, it is likely that they must be applied in the vapor phase, (following the oxygen transport paths) since liquid phase applications are not likely to come in contact with the majority of oxidation sites. Finally, in demonstration efforts such as mine sealing, due consideration should be given to the lag time between oxidation and the appearance of oxidation products in the drainage. Also, every possible attempt should be made to directly measure environmental conditions well within the interior of a given system. Observed overall abatement effects must be broken down into specific effects on specific rate processes, if the results of a demonstration program are to be correctly interpreted with the intention of yielding generally applicable results.

Acknowledgement

The financial support of the Federal Water Pollution Control Administration, through Research Grant 1-WP-01328-01 , is gratefully acknowledged.

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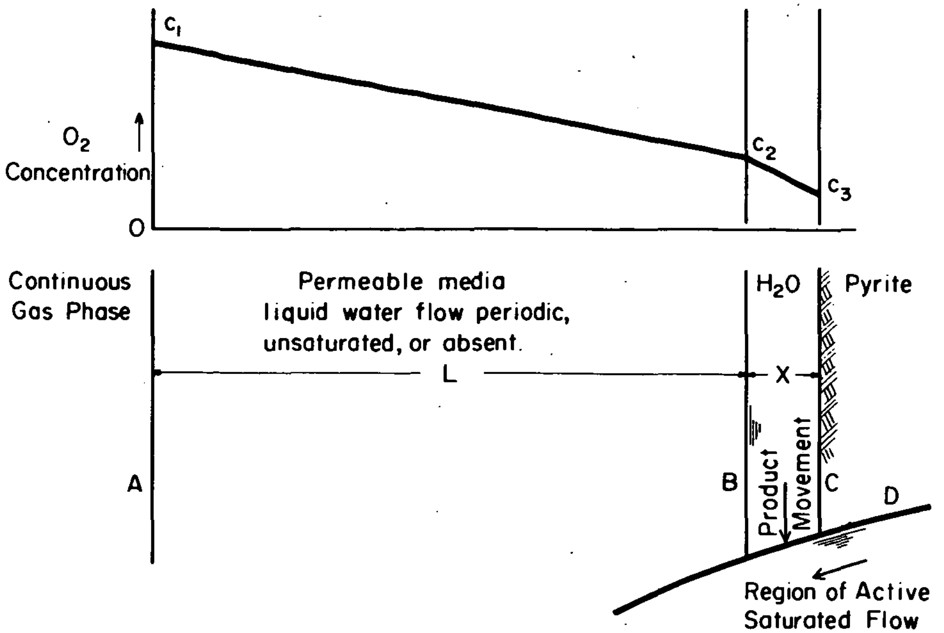

Figure I

Generalized Element of Pyritic System

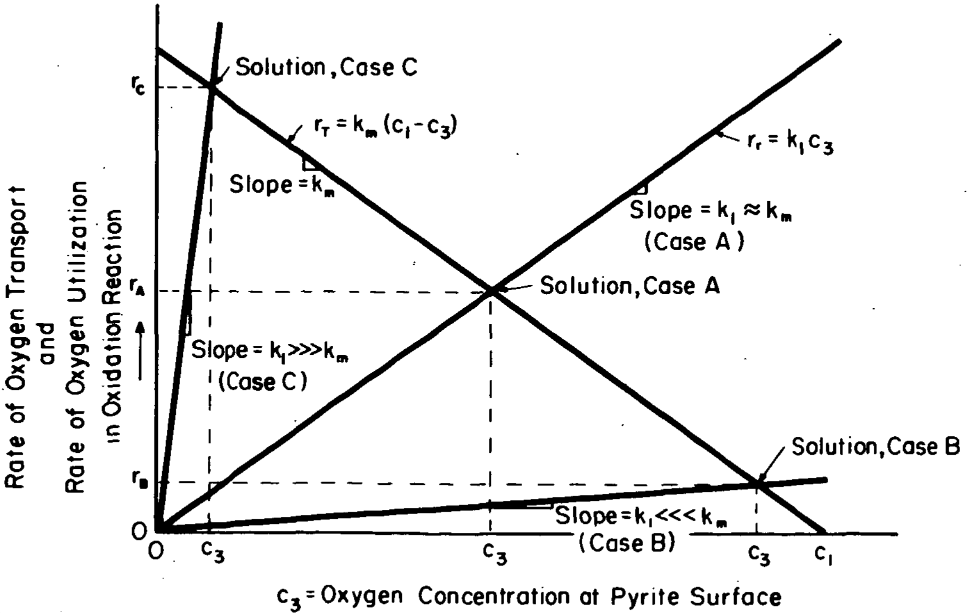

Figure 2

Solution of Steady State Rate Process Equation