

# THE RELEVANCE OF THE INTRINSIC OXIDATION RATE TO THE EVOLUTION OF POLLUTED DRAINAGE FROM A PYRITIC WASTE ROCK DUMP<sup>1</sup>

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**Abstract:** We have developed a simple model of the oxidation of pyrite in a waste rock dump, in which the oxidation proceeds through the dump in a series of steps. The model is used to examine the sensitivity of the overall oxidation rate to the intrinsic oxidation rate (IOR) of the pyrite. For values of IOR below a critical value, the overall oxidation rate proceeds at a constant rate until all the pyrite is consumed. The rate is proportional to the IOR and the total time to oxidize the dump is inversely proportional to it. At the other end of the scale, for an infinitely high IOR, the overall oxidation rate decreases smoothly in time from a high value. The time for complete oxidation is the same as for the critical IOR value. There remains a range of intermediate IOR values, for which the overall oxidation rate decreases in a stepwise manner. This range provides the transition from the critical IOR value (effectively one step) to the infinite IOR case (effectively an infinite number of steps). With this model the time dependence of the overall oxidation rate approaches the rate calculated for infinite IOR at quite modest values of IOR. The simple model is supported by a finite-difference calculation which gives the evolution of sulfate in the dump drainage, as well as the overall oxidation rate.

**Additional Key Words:** pyrite oxidation, acid mine drainage, mathematical model.

## Introduction

Mathematical modeling of the progress of oxidation in waste rock dumps containing pyritic material is a powerful aid to understanding and predicting the overall behavior of the process. A basic parameter required for a model is the rate of oxygen consumption at each point in the dump. We have called this rate the intrinsic oxidation rate or IOR. This is the rate at which the reaction will proceed in that particular waste rock, under the physical, chemical, and microbiological conditions that apply. It might be expected that the IOR would be a critical factor in the overall dump oxidation rate. Our aim is to examine this expectation. We need a suitable mathematical model to achieve this aim, and therefore identification of such a model becomes a secondary aim of this paper.

There have been two main approaches in treating the IOR in dump oxidation models. Ritchie (1977) based a simple one dimensional model on the assumption that the oxidation rate is very fast compared with the rates of oxygen diffusion (the Simple Heap Model). Oxidation therefore occurs in an infinitely thin reaction front, which proceeds downwards through the dump as the pyrite is consumed. Using methods developed by Crank (1956), Ritchie derived a useful set of formulae describing the gross features of dump oxidation. However, clearly this model cannot be used for the present work as the parameter we wish to vary, the IOR, is assumed to be infinitely fast.

In the other class of model the aim is to treat the IOR more realistically by various means (Cathles and Schlitt, 1980, Davis and Ritchie, 1986 and 1987, Jaynes et al. 1984, Pantelis and Ritchie, 1992). The IOR has been described both by the shrinking core model and by various empirical expressions; both approaches require numerical solution. This class of model of oxidation in dumps has proved very successful. The fact that numerical methods are required for their solution permits two dimensional treatment and allows the inclusion of features such as gas convection and dump inhomogeneity. This degree of complexity is not appropriate to our present aim. We will neglect convection,

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which is limited to the edges of waste dumps, since in typical waste rock dumps the edges are a small fraction of the total dump volume (Harries and Ritchie, 1990). A one dimensional model is therefore adequate, and the insight gained from an analytical model is attractive.

In this paper we develop a model similar to Ritchie's Simple Heap Model, but which is not limited to an infinitely high IOR. In this model it is assumed that the IOR has a finite value wherever both oxygen and pyrite have concentrations greater than zero. Simple formulae are derived that give insight into the basic features of dump oxidation. We apply these formulae to explore the significance of the IOR to overall dump oxidation rates. Finally a simple one dimensional numerical model is used to support the results of the analytical model. The numerical model includes the rate of water infiltration and is used to find the behavior of pollutant load in the dump drainage.

### Constant Intrinsic Oxidation Rate Model

A simple assumption for the basis of a dump oxidation model is that the IOR is independent of oxygen and sulfur concentrations, provided that neither is zero. This assumption has some experimental support, as it has been shown in laboratory measurements (Liu et al. 1987) that the rate is constant for oxygen concentrations from 20% (atmospheric) to 1% to 2%. Only below about 1% or so does the rate begin to drop significantly. Similar results, under certain circumstances, have been reported by Hammack and Watzlaf (1990).

Assuming the dump is homogeneous, with diffusion coefficient  $D$ , it can be shown that oxygen will initially penetrate a distance  $x_1$ , given by

$$\Delta x_1 = \sqrt{\frac{2DC_o}{S'}} \quad (1)$$

where  $C_o$  is the atmospheric oxygen concentration and  $S'$  is the IOR.

In accordance with the constant IOR model, this zone will oxidize uniformly throughout until all the sulfur is used. Thereupon the zone becomes inert and the oxygen diffuses through it to form a new oxidation zone below. It is easy to show that, for the range of IOR of interest here, the time taken for the oxygen to attain this new pseudo-steady state is short compared with the time taken to oxidize a zone; the transition time is therefore ignored in this model, and the oxidation proceeds in a series of steps. This approximation is backed up by the results of the numerical modeling that appear below.

The thickness of the subsequent steps progressively reduces owing to the increasing thickness of inert material above. The following general expression can be derived for the thickness of the  $n$ th zone:

$$\Delta x_n = \sqrt{\frac{2C_o D}{S'}} [\sqrt{n} - \sqrt{n-1}] \quad (2)$$

The time,  $t_s$ , for the pyrite in a zone to oxidize fully is given by the ratio of the density of sulfur,  $\rho_{rs}$ , to the IOR, with a stoichiometric factor,  $\epsilon$ , which relates the consumption of sulfur to the consumption of oxygen. The time for each step to oxidize is the same for all steps and is given by

$$t_s = \frac{\epsilon \rho_{rs}}{S'} \quad (3)$$

The overall oxidation rate is given by

$$R = S^i \Delta x_n = \sqrt{2S^i C_o D} \left[ \sqrt{n} - \sqrt{n-1} \right] \quad (4)$$

and the position of the  $n$ th step by

$$x_n = \sqrt{n} \sqrt{2C_o D / S^i} . \quad (5)$$

The dump height is denoted by  $L$ ; then if  $x_n < L$  and  $x_{n+1} > L$  the oxidation within the dump takes  $n+1$  steps; the time to oxidize the dump,  $t_d$ , is

$$t_d = (n+1) t_s = (n+1) \frac{\epsilon \rho_{rs}}{S^i} . \quad (6)$$

### Relationship between IOR and overall dump oxidation rate

We now use these formulae to look at how the IOR affects the overall oxidation rate of the dump.

#### Low IOR

For a sufficiently low value of IOR the thickness of the first zone will be limited by the dump height,  $L$ . In this case the dump will oxidize in one step and the overall oxidation rate will be proportional to the IOR. The critical value of IOR for this behavior is easy to establish by putting  $x_1=L$  into equation 1. In terms of a nondimensional IOR ( $S$ ), the criterion for the dump oxidation rate to be proportional to the value of the IOR is

$$S = \frac{S^i L^2}{C_o D} < 2 . \quad (7)$$

The time for complete oxidation will obviously be inversely proportional to the IOR. For the critical value  $S=2$  the time to oxidize all the pyrite in the dump is

$$t_d^0 = \frac{\epsilon \rho_{rs} L^2}{2C_o D} . \quad (8)$$

#### High IOR

The thickness of the steps is small for large IOR (equation 2) and the time to oxidize each step is small (equation 3). Therefore after a relatively short time, with a small fraction of the dump oxidized, the value of  $n$  will be large. In equation 4 we therefore approximate  $\sqrt{n} - \sqrt{n-1} = 1/2\sqrt{n}$  and use the relationship implied in equation 6 that  $n = S^i t / \epsilon \rho_{rs}$  to give the overall oxidation rate for high IOR as

$$R = \sqrt{\frac{C_o D \epsilon \rho_{rs}}{2t}} . \quad (9)$$

Thus, for high values of IOR, the overall oxidation rate is independent of IOR. This formula is the same as derived by Ritchie's Simple Heap Model referred to above. The time to oxidize all the material in the dump is the same as for the critical value  $S=2$ , given in equation 8.

## Intermediate IOR

The strength of the Step Model is that it can be used to examine the cases between the high and low IOR limit. In particular it can be used to quantify the value of 'high IOR'. The intermediate IOR case is of practical interest, as for many dumps the values of  $D$  and the IOR are such that the thickness of the oxidation zone is 5m or so, and the number of oxidation steps is around 3 or 4. The time duration of all steps is the same, given by equation 3 and the overall oxidation rate remains constant for the duration of a step. The time to oxidize all the material in the dump oscillates between two limits with varying IOR, the lower limit being the critical value  $t_d^0$  (from equation 8) and the upper limit being twice the lower; this oscillatory behavior arises because a step whose thickness is limited by dump bottom takes as long to oxidize as a full step. The time to totally oxidize the pyrite in the dump returns to the value given in equation 8 for all cases where the number of full length steps is a integer.

The behavior of the overall oxidation rate with time is shown in figure 1 for three values of IOR. The magnitude of the overall oxidation rate is given by equation 4 and the time metric by equation 3. The parameters used for the calculation are shown in table 1. It can be seen that over the long term the general behavior for the three cases is similar. For practical purposes, for the dump parameters used here, it is clear that if the value of the IOR is  $5 \times 10^{-8}$   $\text{kg}(\text{O}_2)/\text{m}^3/\text{s}$  or greater it is not necessary to know its value to describe the evolution of overall dump oxidation rates, and as shown below, pollution load. With an IOR of  $10^{-8}$   $\text{kg}(\text{O}_2)/\text{m}^3/\text{s}$ , however, the different step sizes do make a very significant difference to the overall oxidation rate over the first 80 years. The figure also illustrates the variation in the time for oxidation of all the pyrite with different IOR values, due to the interaction of the step size with the dump height.

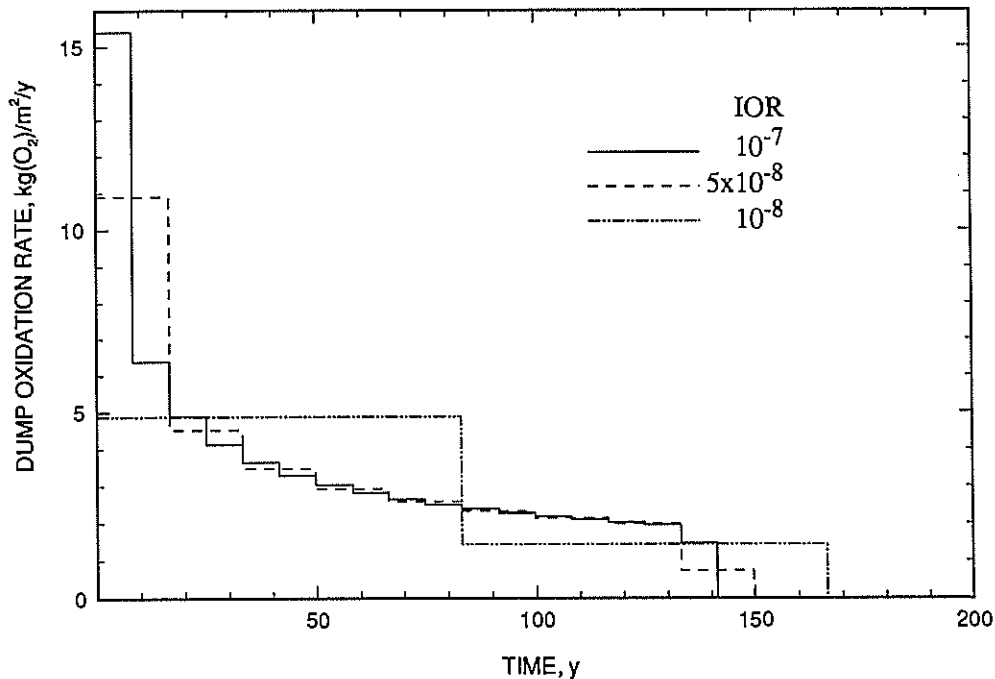


Figure 1. Overall dump oxidation rate as a function of time calculated by step model for three values of IOR.

The timescales for the oxidation of single steps can be appreciated from figure 1, namely in the range from 10 to 80 years. The time for oxidation of all the pyrite in the dump is about 150 years.

Table 1. Parameters used for dump model

Dump height L (m).....	20
Stoichiometric factor $\epsilon$ (mass $O_2$ /mass S).....	1.75
Stoichiometric factor (mass $SO_4$ /mass $O_2$ ).....	1.14
Bulk density of oxidizable sulfur $\rho_{rs}$ ( $kg/m^3$ ).....	15
Oxygen concentration in atmosphere $C_0$ ( $kg/m^3$ )....	0.265
Oxygen diffusion coefficient in dump D ( $m^2/s$ ).....	$4.5 \times 10^{-6}$
Water infiltration rate (m/y).....	0.5
Volumetric water content of dump material.....	0.1
Intrinsic oxidation rate $S'$ ( $kg(O_2)/m^3/s$ ).....	$10^{-8} - 10^{-7}$

### Time Evolution of Pollutants in Drainage

With pyrite oxidation we now include the transport of sulfate, the principal pollutant formed by oxidation, by water infiltrating the dump. We use a finite difference code to solve the time dependent gas diffusion equation and the pollutant transport equations. The water is assumed to move at a uniform rate vertically carrying sulfate from the point of production to the base. Two examples are shown in figure 2.

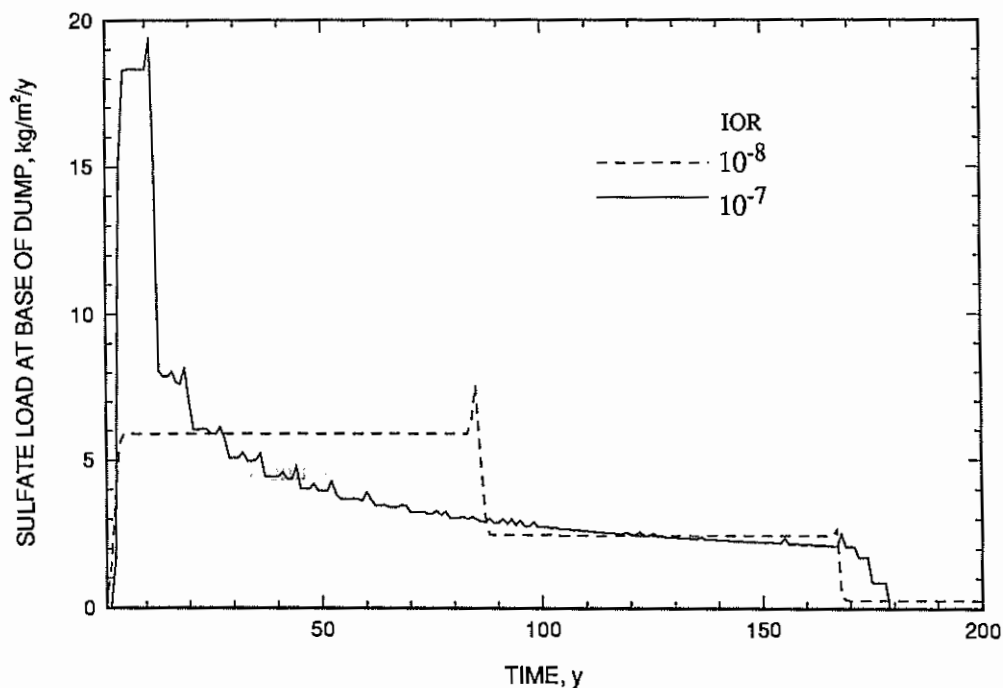


Figure 2. Time dependence of sulfate load at the base of the dump, calculated for two values of IOR

The parameters used are the same as for the analytical model and are shown in table 1. The time evolution of the pollution load at the dump base follows the oxidation rates calculated in the previous section quite closely, allowing for the time delays caused by the relatively slow water velocity.

Small spikes appear on the load curves at the end of each step. These occur because at the completion of oxidation of a step the oxygen quickly penetrates the material below and sulfate generation commences there. This sulfate is added to that in the water which is still proceeding downwards from the previous zone. This result is a consequence of the simplifying assumptions built into the model, namely the step function behavior of the IOR with both oxygen and sulfur concentration and the homogeneity in the dump composition that a one dimensional model entails. Clearly in practice, where these idealizations would not apply, one would not expect to see these spikes.

### Conclusions

A simple analytical model for the oxidation of pyrite in waste rock dumps has been developed, which allows the question of the effect of the intrinsic oxidation rate on overall oxidation within the dump to be examined. The oxidation takes place in zones that become progressively deeper as the material above becomes inert after complete oxidation. The thickness of the zones is the crucial parameter. For low values of IOR the zones are thick and the overall oxidation rate and the pollutant load are comparatively low and remain constant for long periods of time. As the IOR increases, the thickness of the zones decrease and the overall oxidation rate is initially high, but decreases rapidly over the period of 10 - 20 years. Once the IOR is high enough to cause oxidation to take place in say 10 steps its value ceases to be very significant, as the difference between oxidizing the dump in 10 steps and an infinite number is not great.

The paper relates to waste rock dumps that are commonly encountered in mining operations, namely about 20m high, with lateral dimensions at least 10 times greater than this. The material has a diffusion coefficient for oxygen of the order of  $5 \times 10^{-6} \text{ m}^2/\text{s}$ . If the IOR is greater than about  $5 \times 10^{-8}$  for this range of dump parameters, its value becomes unimportant to the time progression of the overall dump oxidation rate or the pollution load in the drainage. The simple oxidation model used here shows that it is only at low values of IOR that its value has practical importance. For values below the critical value, for which the dump oxidizes in one step, it is of crucial importance, as the overall oxidation rate is directly proportional to its value and the total time to completely oxidize all the pyrite in the dump is inversely proportional to its value.

A simple one dimensional finite difference code was used to justify the approximation that the time for the oxygen concentration profile to move from one pseudo-steady state to another could be ignored. This model was also used to show the time evolution of a pollutant generated by pyrite oxidation and appearing at the base of the dump as a result of water transport. Apart from some time delays and spikes in the load caused by the overlapping of pollutants from adjacent oxidation zones, the load at the base follows the overall oxidation rate closely.

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