A model of oxidation in pyritic mine wastes: part 1 equations and approximate solution

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A set of equations is formulated to model the way in which oxidation proceeds in a mass of pyritic mine wastes. The model assumes that the oxidation rate is limited by the rate that oxygen is supplied to oxidation sites within the particles comprising the wastes. Oxygen supply is assumed to be by diffusion through the pore space of the wastes followed by diffusion into a moving reaction front within the particles. An approximation is made which simplifies the equations and paves the way for solution. A further approximation is made that allows an analytical solution to be constructed. The results predicted by this analytical solution are compared with the predictions of a simpler model.

Keywords: mathematical model, pyritic mine wastes, oxidation

Iron pyrites is a common mineral and is commonly associated with minerals of economic significance. As it oxidizes readily on exposure to air and water and as one of the oxidation products is sulphuric acid, increased acidity of ground and surface waters in the mine environs is a common consequence of mining activity. If other metal sulphides are present with the pyrites then solubilization of these metals will occur and trace metal pollution of water can be a further environmental problem. There are many examples of the deleterious effect that pyritic oxidation in mine wastes has had on water quality.[1]

While all these examples stem from mining activity in comparatively recent times it is worth recalling that Georgius Agricola wrote in his 16th century classic De Re Metallica[2], 'when the ores are washed, the water that has been used poisons the brooks and streams and either destroys the fish or drives them away.' One suspects that much of the 'poisons' stemmed from the products of pyritic oxidation. With growing concern for the maintenance of good water quality for aesthetic reasons and, more often, because good quality water is an important and increasingly rare resource there is a need to find cost effective ways to reduce pollution from old mines and to ensure an acceptably low environmental impact from new mines.

The solubilization of trace metals consequent on the oxidation of pyrites, while posing environmental problems, is being used increasingly for the extraction of metals in commercial quantities from low grade ores. Interest lies therefore, in identifying the rate limiting step governing the oxidation of pyritic ore. Much work has been done to assess the importance of physical, chemical and microbiological factors that affect the rate of leaching of metals.[3-10] However, there is little work reported in the literature quantifying the mechanisms

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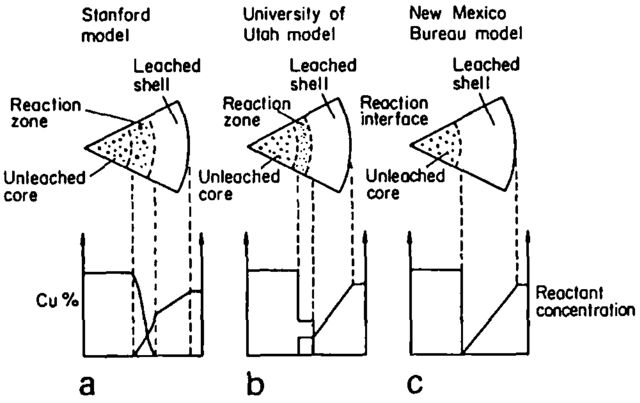

Figure 1 Three models for individual particle leaching after Roman[38]: (a)[12]; (b)[13]; (c)[14]

that control the rate of oxidation in mine wastes under natural weathering conditions. Hence there is a need for both field measurement and mathematical modelling of such processes.

A number of mathematical models have been developed over the last twenty years or so to describe the leaching process, the emphasis being on commercial production of copper from heap leach piles but with some work on the extraction of other metals such as nickel and uranium. The first of these models was due to Harris[11] who developed a model to describe leaching of copper from the piles of sulphide and oxide ore at the Rum Jungle mine site.

In the mid 1970s a number of models describing the extraction of minerals by heap and *in-situ* leaching were published. Three main types of model were proposed, each describing the leaching behaviour of the entire ore mass by focusing on the leaching behaviour of individual particles within the ore. The three types, which can be characterised by the models of Bartlett,[12] Braun *et al.*[13] and Roman *et al.*[14], differ primarily in the assumptions made about the rate of chemical reaction compared to the rate of reactant transport to the reaction site within the particles. *Figure 1* details the differences between the three models by showing a segment of a particle and illustrating graphically the change in concentration of copper and reactant with depth in the particle. All three models assume that the particles are spherical and describe the kinetics in terms of the inward radial diffusion of reactant driven by the chemical reaction within the particles.

Models describing heap leaching behaviour have also been proposed by others.[15–21] Cathles[21] extended the earlier model to include the effects of bacterial catalysis and, after calibration of the model on test dumps, its predictions were compared with results from large scale leaching experiments. The large scale tests confirmed the general validity of the model, however, detailed predictions were quite inaccurate in some circumstances. Subsequently, a two-dimensional model was proposed by Cathles and Schlitt[22] in an attempt to account for the lateral transport of heat and oxidant within leaching dumps.

In general the above models describe the leaching response of the entire heap by focusing on transport and reaction mechanisms within particles of the heap; the bulk transport mechanism which delivers oxidant from outside the heap to reaction sites within the heap, is often neglected as being unimportant, with the consequent assumption that the oxidant concentration surrounding each particle of the dump is constant. This greatly simplifies the mathematics involved. In some cases a bulk advective transport mechanism is included in the model. A number of these models have recently been reviewed and tested against the results from a series of leach column experiments.[23]

The assumption of constant oxidant concentration throughout the heap may well be valid in commercial leaching operations where liquor is circulated through the heaps but is less likely to be true for natural weathering processes in pyritic mine wastes. A model of natural oxidation in a pyritic waste rock dump was developed by Ritchie.[24] In this model the dump was assumed to be a homogeneous slab and it was further assumed that all the nutritional requirements for bacterial growth were freely available, that the oxidation reaction proceeded as fast as reactants were fed to the oxidation sites and that all the reactants for the oxidation of pyrites were also freely available except for oxygen. The oxygen supply rate was assumed to be limited by the rate that oxygen could diffuse through the pore space of the dump. This simple homogeneous model (SHM), which took no account of heterogeneity or microstructural phenomena within the dump predicted sulphate production rates that were consistent with observed values.

This paper formulates a model of pyritic oxidation in mine wastes that incorporates the assumptions of the simple model of Ritchie but couples the effect of transport of oxygen into the particles comprising the dump with transport through the pore space of the dump. A simplifying assumption is made which clears the way for numerical solution of the model equations that will be discussed in a companion paper. A further simplification allows an analytical solution to be found for the model equations which permits ready evaluation of a number of parameters such as pollutant production rates, oxygen concentration profiles and the rate of oxidation at different points within the wastes. Various general properties of the approximate analytical solution (AAS) are presented and their relationship to the solution of the simple model discussed.

The mathematical model

The model

The present model should apply to pyritic oxidation in a wide range of mine wastes but has been formulated against a background of observations on the waste rock dumps that have resulted from opencut mining of uranium orebodies at the now abandoned Rum Jungle uranium mine.[25] Both the physical and microbiological environments within these dumps has been investigated;[26–31] in particular Harries and Ritchie[29] have evaluated the rate of oxidation as a function of depth from estimates of the heat source distribution in White's dump, the largest of the waste rock dumps at the mine site, and have concluded that diffusion through the pore space of the dumps is an oxygen transport mechanism which can supply oxygen at a rate consistent with that required to explain the observed oxidation rates. The fact that the heat source (oxidation rate) is spatially distributed indicates that the SHM of Ritchie, which

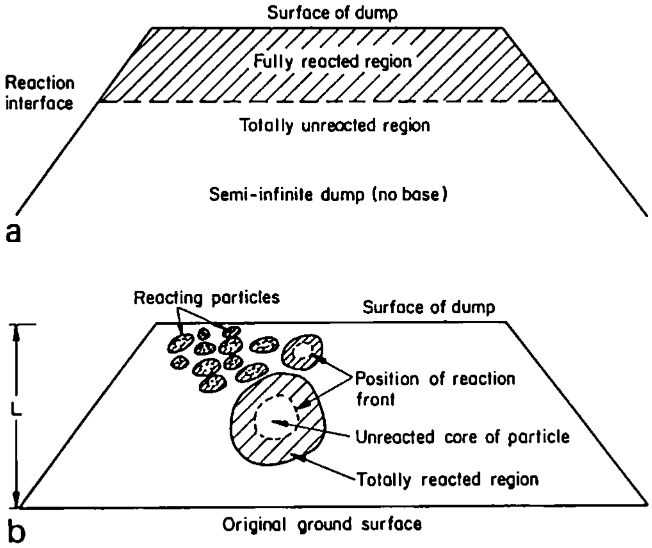

Figure 2 Schematic diagram of models describing pyritic oxidation within waste rock dumps: (a) simple homogeneous model;[24] (b) present proposed model

predicts a δ-function heat source distribution, is too simple. One assumption which is clearly suspect in the simple model is that all of the pyrites in the dump is equally accessible to the oxidation reaction. As it is reasonable to assume that pyrites on the surface of a particle is more accessible to oxidation than pyrites embedded deep within a particle, the present model makes the more realistic assumption that oxygen transport is a two-stage process, diffusion through the pore space of the dump followed by diffusion into reaction sites within the particles comprising the dump.

It is further assumed that the pyrites is evenly distributed throughout the particles and that the particles are spherical. A consequence of these assumptions is that there is a reaction front within each of the particles that starts at the surface of the particle and moves towards its centre; the region outside the front is wholly oxidized while the region on the inside remains unoxidized. A pictorial representation of the SHM compared with the present model is given in *Figure 2.*

From what is known of the bacteria that catalyse pyritic oxidation, it follows that the reaction proceeds in aqueous media. Hence wherever the reaction occurs one must assume that it does so within a water film. The model must therefore describe transport of oxygen from the dump pore space across this water film which is assumed to be at the surface of the particle.

The model equations

For simplicity it is assumed that all of the particles within the dump have the same size. The extension of the equations to model a dump having a distribution of particle sizes is straightforward.

The mass balance of oxygen within the pore space of the dump is governed by bulk diffusion and can be written in dimensionless form as:

$$\delta_1 \frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - q \qquad 0 < x < 1 \tag{1}$$

while within the particles, the oxygen concentration between the surface of the particle and the moving reaction front is given by:

$$\delta_2 \frac{\partial v}{\partial t} = \frac{\partial^2 v}{\partial r^2} + \frac{2\partial v}{r\partial r} \qquad R(x,t) < r < 1 \tag{2}$$

where the boundary conditions are:

$$u(0,t) = 1 \qquad \frac{\partial u}{\partial x}(1,t) = 0 \tag{3}$$

$$v(1,x,t) = u(x,t) \qquad v(R(x,t),x,t) = 0 \tag{4}$$

$$\frac{\partial v}{\partial r}(R(x,t),x,t) = -k_2 \frac{\partial R}{\partial t}(x,t) \tag{5}$$

and the initial conditions are:

$$u(x,0) = 1 \qquad R(x,0) = 1 \tag{6}$$

Consider now the loss term q in equation (1). As previously indicated, since water is necessary for both the oxidation of pyrites, and the bacteria that catalyse the reaction, the oxidation sites within the particles are assumed to be in an aqueous phase. Also since the particles of the dump are assumed to be spherical and to all have the same size, then the loss term is:

$$q^*(x^*,t^*) = \nu D_2 4\pi a^2 \frac{\partial v^*}{\partial r^*}(a,x^*,t^*) \tag{7}$$

A dimensionless factor could also be introduced into equation (7) to take account of the fact that the effective surface area of a spherical particle is different to an actual particle of the dump owing to the non-sphericity or convolution of the particle surface. For perfectly spherical particles the constant ν can be given as:

$$\nu = \frac{3(1-p)}{4\pi a^3} \tag{8}$$

which leads to an expression for q in dimensionless form:

$$q = k_1 \frac{\partial v}{\partial r}(1,x,t) \tag{9}$$

The boundary conditions (3) state that at the top surface of the dump the pore space oxygen concentration is that of oxygen in the atmosphere and that there is no gas flow through the bottom surface of the dump. The conditions (4) invoke Henry's law to relate oxygen concentrations at the outer surface of the particle to the pore space oxygen concentrations and state that oxygen concentrations are zero at the reaction front within the particle while condition (5) follows from mass balance at the reaction front. More detail is given elsewhere.[32] From physical considerations one can impose the extra condition:

$$\frac{\partial v}{\partial r} = 0 \tag{10}$$

when $R = 0$ for any x and t.

It should be emphasized that the boundary condition $v(1,x,t) = u(x,t)$ is due solely to the assumption that the transport processes on both sides of the gas–liquid interface are diffusional. The postulation of an advective transport term within the pore space of the dump would necessitate a flux type (radiation type) boundary condition, involving a mass transfer coefficient (e.g., Bird *et al.*).[33]

Table 1 Values or range of values for parameters that appear in model

Parameter	Value or range of values	Source of data
D_1	6.72×10^{-6} m^2 s^{-1}	Ritchie[24]
D_2	2.6×10^{-9} m^2 s^{-1}	Perry[37]
p	0.4	Ritchie[24]
u_o	0.265 kg m^{-3}	
L	18 m	Davy[25]
a	0.1–20 cm	
ε	1.746	
ρ_s	16.7–167.0 kg m^{-3}	Davy[25]
γ	0.03	Davis[36]

Equations (1)–(10) now define a physically reasonable model describing oxygen diffusion and reaction within mine wastes. Estimates of values for the parameters that appear in the model equations are given in *Table 1*.

The time derivative in equation (2) is now neglected because δ_2 is small (from *Table 1* for moderate values of a, $\delta_2 \sim 10^{-6}$). A pseudo-steady state approximation for the particles of the dump is also supported by the analysis and discussion of Davis and Hill.[34] Solving the steady state equivalent of equation (2) using the boundary conditions (4), then yields an explicit expression for $v(r,x,t)$ in terms of $u(x,t)$ and $R(x,t)$ as:

$$v(r,x,t) = \frac{u(x,t)}{[1 - R(x,t)]}\left(1 - \frac{R(x,t)}{r}\right),\quad R \leqslant r \leqslant 1 \tag{11}$$

Substitution of (11) into equations (5) and (9) enables one to eliminate $v(r,x,t)$ from the system of equation, which now reads as:

$$\delta_1 \frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - 3k\frac{uR}{1 - \mathrm{R}} \quad 0 < x < 1 \tag{12}$$

$$\frac{\partial R}{\partial t} = -\frac{ku}{R(1-R)} \quad 0 < R < 1 \tag{13}$$

with the boundary and initial conditions given simply as:

$$u(0,t) = 1 \qquad \frac{\partial u}{\partial x}(1,t) = 0 \tag{14}$$

$$u(x,0) = 0 \qquad R(x,0) = 1 \tag{15}$$

Output parameters such as the heat source distribution and the total sulphate production rate are of particular interest since experimental data pertaining to both these quantities are available for comparison with model results.[29] Also, the heat source distribution is a useful estimate of the oxidation rate of pyrites within waste material while the total sulphate production rate is a measure of the pollution load presented to the environs of the mine site by waste rock dumps.

The heat output, in watts per cubic metre, can be simply expressed as:

$$H(x^*,t^*) = -\frac{\partial\delta\rho_s}{(1-p)} 4\pi R^{*2} \frac{\partial R^*}{\partial t^*}$$

Using the dimensionless variables and equation (13), the heat source distribution takes the form:

$$H(x,t) = \frac{k_3 u(x,t) R(x,t)}{1 - R(x,t)} \tag{16}$$

The sulphate production rate integrated over the total depth of the dump is written as:

$$S(t) = \frac{L\delta_s}{\delta}\int_0^1 H(x,t)\mathrm{d}x \tag{17}$$

Approximate analytical solution

Before proceeding to the approximate analytical solution (AAS) it should be noted that equations (12)–(15) can be simplified further. Observe that equation (13) can be written as:

$$\frac{\partial(R^3)}{\partial t} = -3k\frac{uR}{1-R} \tag{18}$$

and therefore equation (12) can be rewritten as:

$$\delta_1 \frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} + \frac{\partial(R^3)}{\partial t} \tag{19}$$

Now if one lets:

$$w(x,t) = \int_0^t \acute{u}(x,\tau)\partial\tau \tag{20}$$

equations (13) and (19) can be integrated once with respect to time, using initial conditions (15) to give:

$$\delta_1 \frac{\partial w}{\partial t}(x,t) = \frac{\partial^2 w}{\partial x^2}(x,t) - [1 - R^3(x,t)] \tag{21}$$

$$3R^2(x,t) - 2R^3(x,t) - 1 + 6kw(x,t) = 0$$
$$0 \leqslant R(x,t) \leqslant 1 \tag{22}$$

whilst the boundary and initial conditions on $w(x,t)$ become:

$$w(0,t) = t \tag{23}$$

$$\frac{\partial w}{\partial x}(1,t) = 0 \tag{24}$$

$$\frac{\partial w}{\partial t}(x,0) = 0 \tag{25}$$

In this section, approximate results are developed from the form of the equations given by equations (21) and (22). If the oxygen concentration surrounding the particles within the dump were to be held constant, then equation (22) would be recognizable as the pseudo-steady state result for a diffusion-controlled shrinking-core model of a single reacting particle,[35] since in this case $w(x,t)$ simplifies to $w(x,t) = t$.

Although equations (21) and (22) are valid for $0 \leqslant R(x,t) \leqslant 1$, once $R(x,t) = 0$ anywhere in the dump the equation to be solved becomes:

$$\delta_1 \frac{\partial w}{\partial t}(x,t) = \frac{\partial^2 w}{\partial x^2}(x,t) - 1 \tag{26}$$

$R(x,t) = 0$ holds whenever the particles in that region of the dump are fully oxidized. Equation (22) allows one to quantify where this changeover occurs since if one sets $R(x,t) = 0$ one obtains:

$$w(X,t) = \frac{1}{6k} \tag{27}$$

where one defines $X = X(t)$ as the position of a planar moving interface within the body of the dump above which all particles have finished reacting ($R(x,t) = 0$), whilst between $x = X(t)$ and the base of the dump particles are at all stages of oxidation ($R(x,t) \neq 0$). Equation (27) indicates that whenever $w(x,t)$, at any point x and time t, reaches $(6k)^{-1}$ then the particles at that point $x = X(t)$, are fully reacted.

Note that the time for the particles at the surface of the dump to fully react, can be written simply (since $w(0,t) = t$) as:

$$t_c = \frac{1}{6k} \tag{28}$$

Therefore for $t \leqslant t_c$, equations (21) and (22) are valid throughout the dump, while for $t > t_c$ one is led to consider two regions within the dump separated by a planar moving interface $X(t)$. For $t > t_c$, in the region where $R(x,t) = 0(w(x,t) \geqslant t_c)$, one is required to solve equation (26) subject to equation (23). In the region of the dump where $R(x,t) \neq 0(w(x,t) < t_c)$, one must solve equations (21) and (22) subject to (24). The matching condition for the two region solution is given by equation (27).

A consequence of the pseudo-steady state simplification is that the particles of the model dump no longer absorb oxygen once the particle has finished reacting. This can be seen by substituting $R(x,t) = 0$ in equation (11) from which it becomes apparent that $v(r,x,t) = u(x,t)$ throughout the particle as soon as $R(x,t) = 0$. In reality if the time dependence in the particles is retained then there is a time delay between complete reaction of the particle and complete saturation of the particle with oxygen. It can be shown, however, that for a range of parameter values of practical interest the pseudo-steady approach is quite accurate, since the oxygen volume difference and time delay between complete reaction and saturation is very small.[34]

A solution can now be obtained for $w(x,t)$ which from physical reasoning is an upper bound solution; also found are the corresponding expressions for $u(x,t)$ and $R(x,t)$. It should be noted from the outset that even though one can find an upper bound for $w(x,t)$, this gives no guarantee that $u(x,t) = (\partial w/\partial t)$ is an upper or lower bound.

For $0 \leqslant R(x,t) \leqslant 1$, and starting with the inequality $R^2(x,t) \geqslant R^3(x,t)$, it is easily shown that:

$$2R^3 - 3R^2 + 1 \leqslant 1 - R^3 \tag{29}$$

Using equation (22) one can write equation (29) as:

$$6kw \leqslant 1 - R^3 \tag{30}$$

for all R and w such that $0 \leqslant R \leqslant 1$ and $0 \leqslant w \leqslant t_c$. Therefore, by replacing the loss term $(1 - R^3)$, in equation (21), with $6kw$, one is then required to solve the equation:

$$\delta_1 \frac{\partial w}{\partial t}(x,t) = \frac{\partial^2 w}{\partial x^2}(x,t) - \beta w(x,t) \tag{31}$$

subject to equation (23).

Therefore one can write the upper bound solution $\overline{w}(x,t)$ as:

$$w(x,t) = \begin{cases} w_1(x,t) & t \leqslant t_c \\ \left.\begin{matrix} w_2(x,t),\ 0 \leqslant x \leqslant X(t) \\ w_3(x,t),\ X(t) \leqslant x \leqslant 1 \end{matrix}\right\} & t \geqslant t_c \end{cases} \tag{32}$$

where $w_1(x,t)$ is the solution of equation (31) subject to equations (23)–(25), $w_2(x,t)$ is the solution of equation (26) subject to equations (23) and (27), and $w_3(x,t)$ is the solution of equation (31) subject to equations (24) and (27), while the initial conditions on $w_2(x,t)$ and $w_3(x,t)$ are given by:

$$w_2(x,t_c) = w_3(x,t_c) = w_1(x,t_c) \tag{33}$$

In solving for $w_1(x,t)$ one considers equations (31), (23), and (25), but substitutes the condition:

$$w(x,t) \text{ is finite as } x \to \infty \tag{34}$$

for the boundary condition (24). The dump is now considered to be a semi-infinite slab, which lead to a relatively simple result describing the transient development of the solution from $t = 0$ through to $t = t_c$. The change of boundary condition from (24) to (34) is a reasonable one since for moderately sized particles ($\leqslant$10 mm) t_c is small and for small times the solution for $w_1(x,t)$ is relatively unaffected by the bottom boundary condition, because in the small time span, where w_1 is valid, little oxygen has time to reach the base of the dump. The result for $w_1(x,t)$ is therefore:

$$w_1(x,t) = \int_0^t [1 + \beta'(t - \tau)]\mathrm{e}^{-\beta'\tau} \operatorname{erfc}\left(\frac{\sqrt{\delta_1}x}{2\sqrt{\tau}}\right)\mathrm{d}\tau \tag{35}$$

Equation (35) may also be considered reasonable for larger particles (~10 mm) if t_c is short compared to the reactive lifetime of the dump. However, it is clearly not applicable for, say, 100 mm particles, where t_c is of the order of hundreds of years since this is of the same order as the time taken to oxidize the whole dump, as predicted by the simple homogeneous semi-infinite slab model of Ritchie.[24] In considering a dump comprised of 100 mm sized particles the more complicated infinite series result, using boundary condition (24), would therefore be required.

Since δ_1 is small the pseudo-steady state result for $w_1(x,t)$ could also have been used instead of equation (35), however, it does not adequately depict the transient stages of the model solution. Indeed, since $w_1(x,t)$ for the pseudo-steady state is then only a linear function of time (from solving the steady state equation (31) subject to equations (23), and (24)) the oxygen profile from equation (20) becomes constant in time and therefore could not possibly describe the small time behaviour of the oxidizing dump.

Solutions can be constructed for $w_2(x,t)$ and $w_3(x,t)$. Unlike $w_1(x,t)$, quasi-steady state results are thought to be acceptable for $w_2(x,t)$ and $w_3(x,t)$. Experience with diffusion-controlled moving boundary problems[34] indicates that the pseudo- or quasi-steady state result, whether for spherical, cylindrical or planar geometry, is a useful estimate of the response of the fully time dependent system. This is especially so for gas–solid reactions.[35] The non-trivial and useful nature of the solution can be tied to the time dependence associated with the moving interface.

Under the assumption of quasi-steady state, the solutions for $w_2(x,t)$ and $w_3(x,t)$ are:

$$w_2(x,t) = \frac{x^2}{2} + t - \frac{x}{X(t)}\left[\frac{X(t)^2}{2} + t - t_c\right] \tag{36}$$

$$w_3(x,t) = \frac{t_c \cosh \sqrt{\beta}(1-x)}{\cosh \sqrt{\beta}(1 - X(t))} \tag{37}$$

The solution $w_2(x,t)$ is quadratic in x and not necessarily linear in time since $X(t)$ appears in the expression. Also, since the oxygen profile is the time derivative of $w(x,t)$, it can be seen, from equation (36), that the oxygen profile is linear in x for the quasi-steady approximation as is expected for planar moving boundary problems (e.g., Crank).[32] The solution for $w_3(x,t)$ depends on time only through its functional dependence on $X(t)$.

The solutions $w_2(x,t)$ and $w_3(x,t)$, given by equations (36) and (37), depend explicitly on the position of the planar moving boundary $X(t)$ which, at this stage, is still unknown. One therefore requires an extra boundary condition at the moving front $X(t)$. In the classical planar moving boundary problem[32] the boundary condition at the moving front arises from the assumption that the chemical reaction takes place only at the moving front. In the present problem the reaction proceeds in particles dispersed throughout the dump below the moving front $X(t)$. Therefore, it can be stated that the mass flux of oxygen across the moving front from both sides is equal, that is the gradient at $x = X(t)$ is assumed to be continuous. Hence:

$$\frac{\partial w_2}{\partial x}(X(t),t) = \frac{\partial w_3}{\partial x}(X(t),t) \tag{38}$$

Substituting equations (36) and (37) into (38) gives a transcendental equation for $X(t)$, namely:

$$t = t_c + \frac{X^2}{2} + t_c\sqrt{\beta}X \tanh \sqrt{\beta}(1 - X) \tag{39}$$

One is, however, more interested in finding the approximate solution to $u(x,t)$, the oxygen concentration in the pore spaces of the dump. Using equation (20), one obtains from equation (35) that for $t \leqslant t_c$:

$$\bar{u}(x,t) = \mathrm{e}^{-\beta' t} \operatorname{erfc}\left(\frac{\sqrt{\delta_1}x}{2\sqrt{t}}\right) + \beta' \int_0^t \mathrm{e}^{-\beta'\tau} \operatorname{erfc}\left(\frac{\sqrt{\delta_1}x}{2\sqrt{\tau}}\right) \mathrm{d}\tau \tag{40}$$

For $t \geqslant t_c$ one has from equation (36) that:

$$\bar{u}(x,t) = 1 - \frac{x}{X^2}\left\{\left[\frac{X^2}{2} - (t - t_c)\right]\dot{X} + X\right\} \tag{41}$$

for $0 \leqslant x \leqslant X(t)$, and from (37) one obtains:

$$u(x,t) = t_c \sqrt{\beta}\dot{X} \tanh \sqrt{\beta}(1 - X) \frac{\cosh \sqrt{\beta}(1-x)}{\cosh \sqrt{\beta}(1-X)} \tag{42}$$

for $X(t) \leqslant x \leqslant 1$ where $\dot{X}(t) = \mathrm{d}X(t)/\mathrm{d}t$. An expression for $\dot{X}(t)$ can be obtained by differentiating equation (39) with respect to time, and noting that $t_c\beta = 1$, to give:

$$\dot{X}(t) = \frac{t_c X}{[t - t_c - (X^2/2)]\,[t - (X^2/2]} \tag{43}$$

from which, for $t \geqslant t_c$,

$$\bar{u}(x,t) = 1 - \frac{x}{X}\left[\frac{t - t_c - (X^2/2)}{t - (X^2/2)}\right] \qquad 0 \leqslant x \leqslant X(t) \tag{44}$$

$$\bar{u}(x,t) = \frac{t_c \cosh \sqrt{\beta}(1-x)}{[t - (X^2/2)] \cosh \sqrt{\beta}(1-X)} \qquad X(t) \leqslant x \leqslant 1 \tag{45}$$

Results and discussion

Some general properties of the AAS

A number of observations can be made concerning the motion of the moving interface $X(t)$.

Firstly, if one sets $X(t) = 1$, in equation (39), that is the moving front is allowed to reach the bottom of the dump one obtains an expression for the reactive lifetime of the waste rock dump, given by:

$$t_d = \tfrac{1}{2} + t_c \tag{46}$$

The time t_d consists precisely of the time to oxidize completely the particle at the surface of the dump (t_c) together with the time for the moving front $X(t)$ to travel the full depth of the dump. The SHM of Ritchie[24] gives rise to the classical moving boundary solution:

$$t_d = \tfrac{1}{2} \tag{47}$$

Hence the approximate upper bound solution indicates that the more complex model equations have introduced a delay in the oxidation process down the dump which consists of the time taken by the surface particle to react fully. From the definition of t_c it can also be seen as $a \to 0$ then $t_c \to 0$, and equation (46) collapses onto the classical result (47).

For $X(t) \sim 0$, that is $t \sim t_c$, it follows from equation (39) that:

$$\dot{X}(t_c) = \frac{1}{(\theta\sqrt{t_c})} \tag{48}$$

where $\theta = \tanh \sqrt{\beta}$. Therefore, the moving front has a finite velocity at $X(t) = 0 (a \neq 0)$, unlike the classical solution where the initial velocity is infinite. However, in the limit as $a \to 0$, equation (48) also gives an infinite velocity.

For $X(t) \sim 1$

$$X(t) = 1 - [1 - 2(t - t_c)]^{1/2} \tag{49}$$

$$\dot{X}(t) = [1 - 2(t - t_c)]^{-1/2} \tag{50}$$

As $X(t) \to 1$, that is $t \to t_d$, it follows from equation (46) that the velocity $\dot{X}(t)$ becomes infinite. The occurrence of an infinite velocity at $X(t) = 1$ is shown in Davis[36] to be solely a property of the finite depth of the dump.

Finally, the oxygen concentration at $X(t)$ is given by:

$$\bar{u}(X(t),t) = [1 + \sqrt{\beta}X(t) \tanh \sqrt{\beta}(1 - X(t))]^{-1} \tag{51}$$

where equations (45) and (39) have been used. It can be seen from equation (51) that at $X = 1$, $\bar{u} = 1$ indicating that the instant the planar moving front reaches the base of the dump the pore space attains its maximum oxygen concentration. This is a trait common to steady state solutions of many different moving boundary problems and has been discussed previously.

Figure 3 shows the position of the planar moving front in a dump as a function of time for different sized particles. The position of the reaction front predicted by the SHM is also shown. It can be seen that the curves all have a similar shape but are shifted by an amount that increases with increasing particle size. The reason for this becomes apparent when one considers the situation when β is large, which is so when the wastes are some tens of metres deep and the particle size is less than a few centimetres in radius. In this case the transcendental equation for $X(t)$ takes the form:

$$t = t_c + \sqrt{\beta}t_cX + \frac{X^2}{2} \tag{52}$$

$$X(t) = \sqrt{2t - t_c} - \sqrt{t_c} \tag{53}$$

When β is large, $t_c = 1/\beta$ is small and for $t_c \leqslant t \leqslant \frac{1}{2} + t_c X(t)$ is given approximately by $\sqrt{2t}$. Hence apart from the delay time t_c, $X(t)$ does not depend on the particle size over much of the time range of interest and has the same time dependence as the reaction front predicted by the SHM. In the particular case when $X(t)$ is close to unity it is given approximately by equation (49) which again shows that $X(t)$ is largely independent of particle size when t_c is small.

Other parameters of interest

In general one is interested in the behaviour of parameters such as the oxygen concentration, heat source distribution and total sulphate production at times much greater than the time taken to oxidize the particle at the surface, that is $t \gg t_c$. In this time regime and β large the AAS for the oxygen concentration is given approximately by:

$$u(x,t) = 1 - x\frac{\sqrt{\beta}}{[1 + \sqrt{\beta}X]}$$
$$0 \leqslant x \leqslant X(t) \tag{54}$$

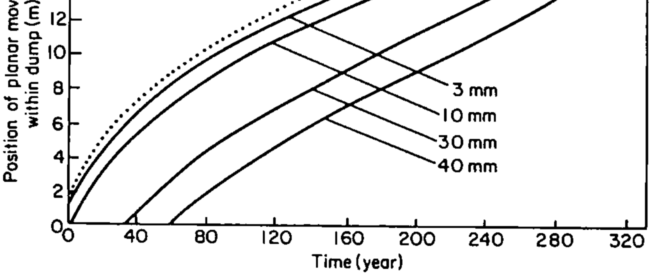

Figure 3 Distance of planar moving front from top surface of dump as function of time: approximate solution, ... simple model

$$u(x,t) = \frac{\exp(-\sqrt{\beta}(x - X))}{[1 + \sqrt{\beta}X]}$$
$$X(t) \leqslant x \leqslant 1 \tag{55}$$

It is clear that for $0 \leqslant x \leqslant X(t)$, which is the region where the particles are fully oxidized the oxygen concentration decreases linearly with distance as is predicted by the SHM but the oxygen concentration at the planar front is not zero. This is in contradistinction to the SHM. In the region below the planar front the oxygen concentration which is identically zero in the SHM, decreases exponentially. For $\sqrt{\beta}X \gg 1$, which is true for large β and $t > t_c$, the gradient of the oxygen concentration will be close to that predicted by the SHM.

Using equations (16), (22), (37) and (45) the heat source distribution can be written as:

$$H(x,t) = \frac{k_3}{\beta}\frac{1}{[t - (X^2/2)]}R(1 - R)(1 + 2R) \tag{56}$$

It is at once obvious from equation (56) that the maximum in the heat source distribution, H_m, always occurs at the same value of R independent of other parameters in the model. This value, $R_m = 0.608$, allows easy evaluation of the distance from the surface at which the maximum occurs. This point x_m and H_m are given to good approximation when β is large by:

$$H_m = \frac{0.528k_3}{1 + \sqrt{\beta}X} \tag{57}$$

$$x_m = X(t) + 1.08\sqrt{t_c} \tag{58}$$

As the particle size goes to zero, the peak in the heat source distribution occurs closer to the planar front and, in the limit, the heat source distribution is the δ-function predicted by the SHM.

Equations (22), (37) and (45) can be used with equation (56) to express the total sulphate production rate $S(t)$ as:

$$S(t) = \frac{L\delta_s k_3}{\delta}\frac{1}{\beta\sqrt{\beta}[t - (X^2/2)]}\cdot$$
$$-\int_0^{R_t}\frac{6R^2(1 - R)^2(1 + 2R)\mathrm{d}R}{[(1 - R)^4(1 + 2R)^2 - \cosh^{-2}\sqrt{\beta}(1 - X)]} \tag{59}$$

where R_t is given by:

$$1 - 3R_t^2 + 2R_t^3 = [\cosh\sqrt{\beta}(1 - X)]^{-1} \tag{60}$$

When β is large, the integral in equation (59) can be approximated by

$$\int_0^1 6R^2\mathrm{d}R = 2 \tag{61}$$

$$S(t) = \frac{L\delta_s\rho_s}{\tau_4}\frac{1}{\sqrt{2t - t_c}} \tag{62}$$

Since for a dump of a given depth and porosity, a large value of β implies a small value of particle size, it follows from equation (62) that below a certain particle size the sulphate production rate is largely independent of particle size over most of the time span of interest. If, further we neglect t_c compared to t, then the production rate predicted from equation (62) is the same as that predicted by the SHM.

Conclusions

The mathematical model presented is a physically realistic model of the way that oxidation proceeds in pyritic mine wastes under natural conditions. It is based on physical processes which are consistent with observations of physicochemical conditions within mine wastes undergoing pyritic oxidation. All the parameters that are used in the model can be readily measured; there is no need to 'calibrate' the model. The model equations as presented are those for wastes assumed to consist of particles all of the one size but can easily be extended to cover the real situation where there is a range of particle sizes in the wastes. This point will be covered in a companion paper.

The approximate analytical solution (AAS) to the model equations is an upper bound on $w(x,t)$ which is effectively the time averaged oxygen concentration within the mass of wastes. It is not necessarily an upper bound solution for the oxygen concentration. However, parameters such as the oxygen concentration and the heat source distribution evaluated using the AAS all tend to the form predicted by the simple homogeneous model (SHM) as the particle size becomes vanishingly small. This is the behaviour expected and gives confidence in the utility of the AAS. The accuracy of these various parameters evaluated using the AAS compared to their evaluation using a more exact numerical solution to the model equations is also the subject of a separate paper.

The AAS allows ready evaluation of parameters such as the oxygen concentration and heat source distribution, as functions of time and distance from the surface of the wastes, and the position of the planar front as a function of time. The evaluation of the position of the reaction front within the particles is less trivial (as it involves the solution of a cubic equation) but is still straightforward. Hence the AAS can be used to provide valuable insight into the processes going on within a mass of pyritic wastes and help quantify the relative importance of transport of oxygen by diffusion in the pore space as opposed to diffusion in the particles as rate limiting steps.

The AAS also allows ready evaluation of the time it takes for the oxidation of all the material in the mass of wastes and hence how long a particular mass of pyritic wastes is likely to present a source of pollution to the environment. Using the results of the AAS it is easy to see how the lifetime of the oxidation process depends on parameters such as the pyrites concentration, diffusion coefficients, depths of the wastes, particle size and so on. Also of interest is the fact that for particles below a certain size the sulphate production rate summed over the whole mass of the oxidizing wastes is largely independent of the size of the particles comprising the wastes over much of the lifetime of the oxidation process. Indeed the total sulphate production rate predicted by the AAS under these conditions is close to that predicted by the SHM. It will be interesting to see if a more exact solution to the present model equations shows that the AAS and SHM provide good estimates of the total sulphate production rate as this is a useful indicator of the potency of the wastes as a pollution source. Ready evaluation of this parameter and the extent to which its magnitude depends on parameters describing the physical form of the wastes is a useful tool for assessing the relative effectiveness of schemes to reduce the magnitude of the pollution source by effectively changing the physical form of the wastes or part of the wastes.

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Nomenclature

a	radius of particle (m)
D_1	diffusion coefficient of oxygen in pore space of dump ($m^2 s^{-1}$)
D_2	diffusion coefficient of oxygen in water ($m^2 s^{-1}$)
$H(x,t)$	heat source distribution ($W m^{-3}$)
$k = k_1/3 = 1/k_2$	
$k_1 = 3\gamma D_2(1-p)L^2/(D_1 a^2)$	
$k_2 = \tau_3/\tau_4$	
$k_3 = 3\delta\rho_s k/\tau_4$	
L	height of dump (m)
p	porosity of dump (dimensionless)
$q^*(x^*,t^*)$	rate of volume loss of oxygen from pore spaces ($kg m^{-3} s^{-1}$)
$r = r^*/a$	dimensionless radial distance
r^*	radial distance within a particle (m)
$R(x,t) = R^*/a$	dimensionless position of reaction front
$R^*(x^*,t^*)$	position of moving reaction front within particle (m)
$S(t)$	integrated sulphate production rate ($kg m^{-2} s^{-1}$)
$t = t^*/\tau_4$	dimensionless time
t^*	time (s)
t_c	dimensionless time to react particle at surface of dump
t_d	dimensionless time to fully oxidize dump
$u(x,t) = u^*/u_o$	dimensionless oxygen concentration
$u^*(x^*,t^*)$	oxygen concentration within pore space of dump ($kg m^{-3}$)
$\overline{u}(x,t)$	dimensionless oxygen concentration corresponding to $\overline{w}(x,t)$
u_o	concentration of oxygen at surface of dump (concentration of oxygen in air) ($kg m^{-3}$)
$v(r,x,t) = v^*/\gamma u_o$	dimensionless oxygen concentration within particles of dump
$v^*(r^*,x^*,t^*)$	concentration of oxygen within a particle within dump ($kg m^{-3}$)
$w(x,t)$	defined by equation (20)
$\overline{w}(x,t)$	upper bound solution for $w(x,t)$
$w_1(x,t)$	upper bound solution for $t \leqslant t_c$
$w_2(x,t)$	upper bound solution for $t \geqslant t_c$ and $0 \leqslant x \leqslant X(t)$
$w_3(x,t)$	upper bound solution for $t \geqslant t_c$ and $X(t) \leqslant x \leqslant 1$
$x = x^*/L$	dimensionless spatial coordinate
x^*	vertical spatial coordinate(m)

$X(t) = X^*/L$	dimensionless position of planar moving front
$X^*(t^*)$	position of planar moving front within dump (m)
$\beta = 6k$	
$\beta' = \beta/\delta_1$	
γ	a proportionality constant encompassing both Henry's law and gas law
δ	heat produced from oxidation reaction per mass of sulphur oxidized ($\mathrm{J\,kg^{-1}}$)
$\delta_1 = \tau_1/\tau_4$	
$\delta_2 = \tau_2/\tau_4$	
δ_s	mass of SO_4 produced per mass of sulphur consumed by chemical reaction
ε	mass of oxygen used per mass of sulphur in oxidation reaction
$\theta = \tanh\sqrt{\beta}$	
ν	number of particles per unit volume of dump ($\mathrm{m^{-3}}$)
ρ_s	density of sulphur within dump ($\mathrm{kg\,m^{-3}}$)
$\tau_1 = pL^2/D_1$	
$\tau_2 = a^2/D_2$	
$\tau_3 = \varepsilon\rho_s a^2/[\gamma u_o D_2(1-p)]$	
$\tau_4 = L^2\varepsilon\rho_s/(D_1 u_o)$	

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