A model of oxidation in pyritic mine wastes: part 2: comparison of numerical and approximate solutions

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Results are presented of a numerical solution to a set of equations which models oxidation in pyritic mine wastes under natural conditions. Oxidation proceeds at a moving front within the particles comprising the wastes. Properties predicted by the numerical solution are compared with results predicted by an approximate analytical solution. The accuracy and usefulness of the approximate analytical solution are discussed.

Key words: mathematical model, oxidation, pyritic mine wastes

Davis and Ritchie[1] have developed a model to describe the way in which oxidation proceeds in pyritic mine wastes under natural conditions. The model is based on physical processes that are consistent with observations of the physicochemical conditions within mine wastes undergoing oxidation and uses parameters which can be readily measured. The main impetus behind the development of such a model is the need to understand the way in which pollutants are generated in pyritic mine wastes and to develop tools for assessing the cost effectiveness of schemes to reduce the environmental impact of such mine wastes[2] during the operational and post-operational phases of mining.

The model assumes that the oxidation rate is limited by the rate of supply of oxygen to oxidation sites within the particles that make up the wastes. Oxygen is assumed to come from the atmosphere external to the wastes and to be transported to the oxidation sites by diffusion through the pore space of the wastes followed by diffusion into the particles. The other assumptions in the model predicate the formation of a reaction front in the particles that starts at the surface of the particle and moves inward until it reaches the centre. This 'shrinking core' description of the oxidation process in the particles has been used[3–6] in models that describe the extraction of metals from low grade ore by a heap leach process. Indeed, there are many similarities between the processes that go on in a heap leach and those going on inside a pile of pyritic mine waste. The major difference is that in a heap leach every attempt is made to speed up the oxidation process and ensure adequate supply of oxidant throughout the heap whereas in the natural system there is every likelihood that the oxidant supply is the rate limiting mechanism.

Moving boundary formulations such as the one arising in the present model have wide application in a number of fields; these include the freezing and thawing of food and ice, solidification and melting of metals, and many facets of chemical engineering. Some examples of these

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applications are discussed in more detail in recent conference proceedings;[7,8] a number of reviews of moving boundary models and solution procedures have also been published.[9–11] The solution of fully time-dependent moving boundary problems is inherently difficult owing to the nonlinearity introduced by the moving front. Analytical solutions are available for some planar problems[12] and many semi-analytical solutions have been developed for spherical and cylindrical geometries (e.g. Davis and Hill).[13] In general, however, solution of a moving boundary problem requires the application of numerical techniques. Where an approximate analytic solution exists, numerical solutions are invaluable for establishing the accuracy and effective range of applicability of the approximate solution.

This paper presents the results of a numerical solution to the model equations developed by Davis and Ritchie and compares them with results derived from an approximate analytical solution (AAS) of the model equations.[1] Apart from the intrinsic interest of providing a solution to a moving boundary problem, it is of interest to determine how accurately the AAS predicts various properties of the pyritic wastes and the extent to which this computationally simple solution is useful for predicting these properties.

The model equations and the AAS

The derivation of the equations that describe the present model of pyritic oxidation and details of the AAS are presented elsewhere.[1] However, some of the more important assumptions in the model together with some of the main equations and results are presented below.

The waste material was assumed to be a porous slab with the surface open to the atmosphere and the base impermeable to gas transport. Because the horizontal extent of the waste material under consideration is generally much greater than its height, the transport of oxygen through the pore space of the dump is considered to be one-dimensional. The model equations consisted of a coupled system of three partial differential equations linking the oxygen concentration within the pore space of the wastes, the oxygen concentration within the particles comprising the wastes and the position of the moving reaction front within the particles. Assumption of pseudo-steady state diffusion within the particles allowed an analytical expression to be found for $v(r,x,t)$, the dimensionless oxygen concentration within the particles:

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

Equation (1) enabled elimination of v from the other dimensionless equations, thus reducing the three partial differential equations to two:

$$\delta_1 \frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - \frac{3kuR}{1-R} \qquad 0<x<1 \tag{2}$$

$$\frac{\partial R}{\partial t} = \frac{-ku}{R(1-R)} \qquad 0<R<1 \tag{3}$$

while the boundary and initial conditions became:

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

$$u(x,0) = 0 \qquad R(x,0) = 1 \tag{5}$$

The symbols are the same as those used in Davis and Ritchie[1] and are defined in the nomenclature.

A number of parameters other than the pore space oxygen concentration are of interest as they too can be evaluated from experimental measurements. Such parameters include the spatial heat source distribution:

$$H(x,t) = \frac{k_1 u(x,t) R(x,t)}{[1 - R(x,t)]} \tag{6a}$$

which is obtained after using equation (3), and the total sulphate production rate integrated over the depth of the wastes:

$$S(t) = \frac{L\delta_s}{\delta}\int_0^1 H(x,t)\mathrm{d}x \tag{6b}$$

An approximate analytical solution was found for equations (2) to (5) by considering the quantity:

$$w(x,t) = \int_0^t u(x,\tau)\mathrm{d}\tau \tag{7}$$

Integrating equation (3) and using equations (5) and (7) yields:

$$2R^3 - 3R^2 + 1 - 6kw = 0 \qquad 0 \leqslant R \leqslant 1 \tag{8}$$

It is apparent from equation (8) that one can consider the evolution of the oxidation process in two time regions, $0 \leqslant t \leqslant t_c$ and $t \geqslant t_c$ where t_c is the time taken for the particles right at the surface of the wastes to be fully oxidized. Substituting $R = 0$ into equation (8) and using the first of the boundary conditions (4) in equation (7) yields:

$$t_c = 1/(6k) \tag{9}$$

It is also apparent from equation (8) that for $t > t_c$, the wastes can be divided into two regions defined by a planar moving front $X(t)$ which satisfies:

$$w(X(t),t) = 1/(6k) \tag{10}$$

In the region $0 \leqslant x \leqslant X(t)$, the particles are fully oxidized ($R = 0$) whereas in the region $X(t) \leqslant x \leqslant 1$, the particles are in all stages of oxidation ($0 < R < 1$).

The AAS followed from finding the solution to the upper bound $\overline{w}(x,t)$ of $w(x,t)$. The corresponding result for the oxygen concentration within the pore space can be written as:

$$\overline{u}(x,t) = \mathrm{e}^{-\beta' t}\operatorname{erfc}\left[\left(\frac{\delta_1}{t}\right)^{1/2}\frac{x}{2}\right] + \beta'\int_0^t \mathrm{e}^{-\beta'\tau}\operatorname{erfc}\left[\left(\frac{\delta_1}{\tau}\right)^{1/2}\frac{x}{2}\right]\mathrm{d}\tau \tag{11}$$

for $t \leqslant t_c$. When $t \geqslant t_c$ one has:

$$\bar{u}(x,t)=\begin{cases} 1-\dfrac{x}{X}\left[\dfrac{t-t_c-(X^2/2)}{t-(X^2/2)}\right] & 0\leqslant x\leqslant X(t) \\[2ex] \dfrac{t_c\cosh\sqrt{\beta}(1-x)}{[t-(X^2/2)]\cosh\sqrt{\beta}(1-X)} & X(t)\leqslant x\leqslant 1 \end{cases} \tag{12}$$

The position of the planar moving front $X(t)$ can be found from the transcendental equation:

$$t=t_c+\frac{X^2}{2}+t_c\sqrt{\beta}X\tanh(\sqrt{\beta}(1-X)) \tag{13}$$

The quantity t_d:

$$t_d=t_c+\tfrac{1}{2} \tag{14}$$

the time to oxidize fully all the pyritic material in the wastes, can be obtained by substituting $X(t) = 1$ into equation (13).

The numerical algorithm

Central differences in the space variable were used[14] to replace equations (2) and (3) by a system of coupled ordinary differential equations, which could be solved using the DIFSUB[15] package. The time steps the package was able to take were extremely small, because of the size of the derivatives when $R \simeq 1$, a situation which exists at some point in the dump at all times.

A special purpose integration scheme was written. This employed the well-known Crank–Nicolson formulation for the diffusion part of equation (2), combined with a backward Euler treatment of the loss term which avoids the singularity at $R = 1$ and maintains the stability of the Crank–Nicolson scheme.

The solution algorithm is as follows:

(i) Estimate the starting values for the new values R_j^{i+1} using:

$$R_j^{i+1}=2R_j^i-R_j^{i-1} \tag{15}$$

(ii) Solve for u_j^{i+1} using the tridiagonal system:

$$\begin{aligned}&\frac{-\Delta t}{2(\Delta x)^2}(u_{j+1}^{i+1}+u_{j-1}^{i+1})\\ &\quad+u_j^{i+1}\left[\delta_1+\frac{\Delta t}{(\Delta x)^2}+\frac{3\Delta t k R_j^{i+1}}{(1-R_j^{i+1})}\right]\\ &\quad=\frac{\Delta t}{2(\Delta x)^2}(u_{j+1}^i+u_{j-1}^i)+u_j^i\left(\delta_1-\frac{\Delta t}{(\Delta x)^2}\right)\end{aligned} \tag{16}$$

(iii) Solve for R_j^{i+1}, the cubic obtained by integrating (3):

$$\begin{aligned}&(\tfrac{1}{2}R_j^{i+1^2}-\tfrac{1}{3}R_j^{i+1^3})-(\tfrac{1}{2}R_j^{i^2}-\tfrac{1}{3}R_j^{i^3})\\ &\quad=-\frac{k\Delta t}{2}(u_j^{i+1}+u_j^i)\end{aligned} \tag{17}$$

(iv) Iterate (ii) and (iii) until converged. Further details of the numerical scheme and the solution algorithm are given by Davis.[17]

Despite the nonlinearity in the implicit time integrations, the special routine ran 600 times faster for similar accuracy. To obtain acceptable resolution for parameters such as the heat source distribution, a mesh interval of $\frac{1}{2}$m was adequate when the particle size was about 10 mm or so but it had to be reduced to $\frac{1}{16}$m when the particle size was $\simeq$1 mm. Hence, except when the particle size was very large ($t_c \sim t_d$), the time required for a calculation in which the particle size was small was greater than when the particle size was large.

The results presented were obtained on the AAEC's IBM 3033S central computer at Lucas Heights and the initial development of the program was undertaken on the UNIVAC 1106 computer at the University of Wollongong.

Comparison of the numerical solution, the SHM solution and the AAS

The AAS allows simple and easy evaluation of a number of properties including the oxygen concentration, heat source distribution, and position of the planar moving front. It also allows ready assessment of the sensitivity of these properties to changes in the values of parameters in the model such as porosity, diffusion coefficients, and pyrites content. Hence, use of the AAS can provide insight into the manner in which oxidation proceeds in the wastes; in particular, it can provide insight into the parameters that govern the rate of oxidation of the wastes. However, it is useful only if it provides reasonably accurate estimates of the various properties. It is therefore important to compare predictions of the AAS with those of the more accurate numerical solution.

In obtaining the results in the comparison below, the values of such parameters as pyrites content (3%), diffusion coefficient ($D = 6.72 \times 10^{-6}\,\mathrm{m^2\,s^{-1}}$), porosity (40%) and height of the wastes (18 m) are those appropriate to White's waste rock dump at the Rum Jungle mine site in the Northern Territory of Australia. Details of White's dump and the history of the Rum Jungle mine have been given in Davy.[18] To obtain a proper comparison of the three solutions, it is necessary to limit the numerical solution to the case in which the wastes are assumed to be composed of particles of just one size.

One prediction of the AAS is that, below a certain particle size, the sulphate production rate, integrated over the depth of the wastes, is largely independent of the particle size for most of the lifetime of oxidation in the wastes. The production rate should also be close to that predicted by the simple homogeneous model (SHM) of Ritchie.[1,19] *Figure 1* shows that this is indeed the case for particle sizes smaller than a few millimetres but for particles of 10 mm the AAS increasingly underestimates $S(t)$ at times greater than about half the lifetime of oxidation in the wastes. Other results show that the larger the particle size the larger is the discrepancy and the earlier the time at which the discrepancy appears. Clearly and interestingly the SHM provides an excellent estimate of the total sulphate production rate over much of the lifetime of the oxidation process. It should be noted that for large particle sizes, the AAS also underestimates the total time-integrated sulphate production.

Davis and Ritchie[1] have shown that the use of the AAS to evaluate $S(t)$ gives rise to the expression:

$$S(t)=\frac{L\delta_s k_3}{\delta}\frac{1}{\beta\sqrt{\beta}(t-X^2/2)}F(\alpha) \tag{18}$$

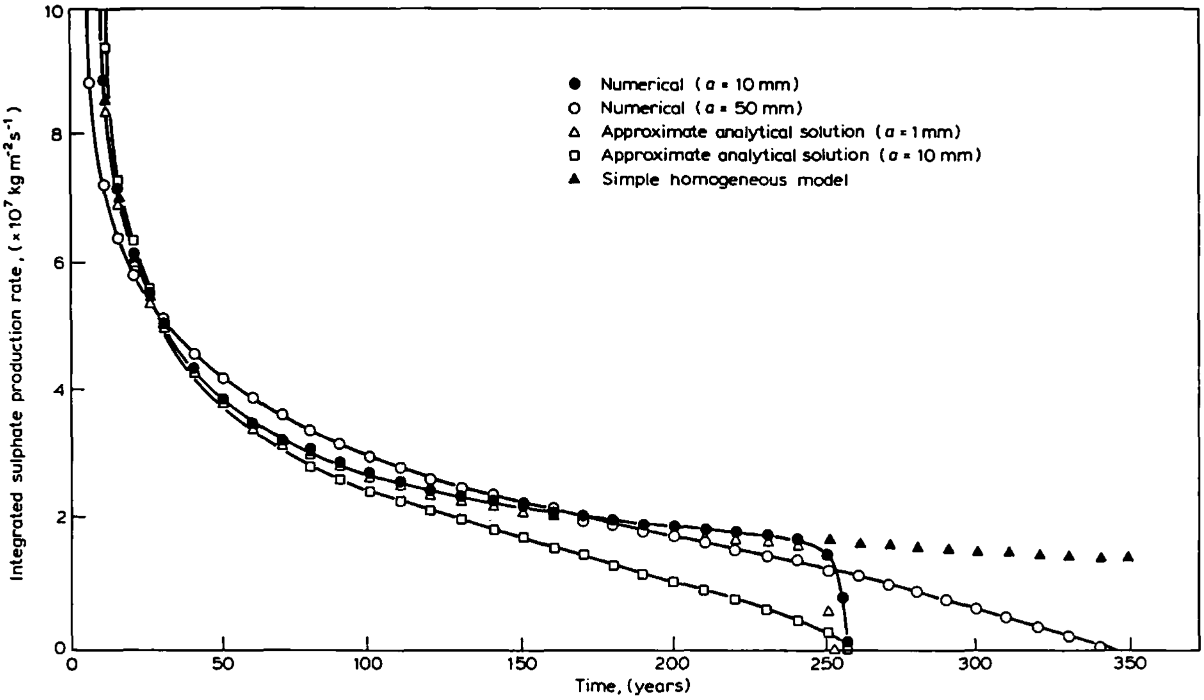

Figure 1 Total sulphate production rate as a function of time after creation of wastes

where:

$$\alpha = 1/\cosh \sqrt{\beta}(1 - X) \tag{19}$$

When β is very large, that is when the wastes are many metres deep and composed of particles of radius less than a few centimetres, α is very small provided that $X(t)$ is not close to unity, that is if oxidation of the wastes is not close to completion. It is easy to show that for α vanishingly small $F(\alpha) \to 2$ and one obtains the approximate result:[1]

$$S(t) \doteqdot \frac{L\delta_s k_3}{\delta} \frac{2}{\beta\sqrt{\beta}(t - X^2/2)}$$

$$\doteqdot \frac{L\delta_s \rho_s}{\tau_4} \frac{1}{\sqrt{2t - t_c}} \tag{20}$$

Davis and Ritchie used this equation to conclude that $S(t)$ evaluated using the AAS is largely independent of particle size for small particles. However, it is easy to show that $F(\alpha)$ can be expressed as:

$$F(\alpha) = 2 + C_1\alpha^{1/2} + C_2\alpha + C_3\alpha^{3/2} \ldots \tag{21}$$

where $C_1 = -2.07$. Truncation in equation (21) after two terms and substitution in equation (18) explains why $S(t)$ predicted by the AAS decreases with increasing time and increasing particle size.

Figure 2 shows the heat source distribution about 25 years after creation of the waste dump, for a dump comprised of 1 mm sized particles and of 10 mm particles. The curves for AAS and the numerical solution are similar in shape, the distributions peaking at approximately the same position and close to the position of the δ-function predicted by the SHM. The peak height predicted by the AAS is, however, about a factor of two lower than that of the exact solution and the AAS predicts a higher heat production rate (oxidation rate) at depth than the numerical solution. The height of the δ-function from the SHM solution in *Figure 2* should

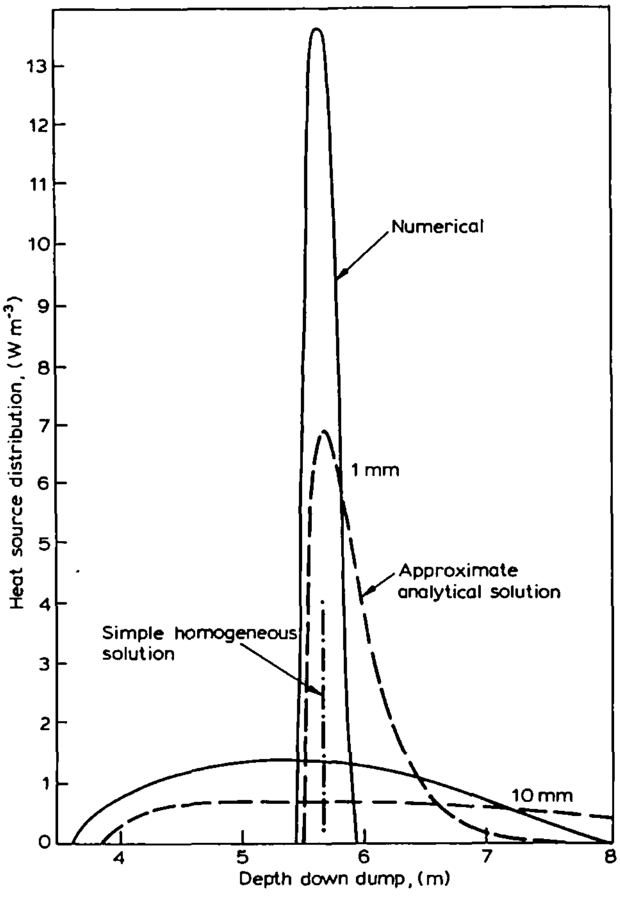

Figure 2 Spatial heat source distribution: comparison of approximate analytical solution, simple homogeneous model and numerical results

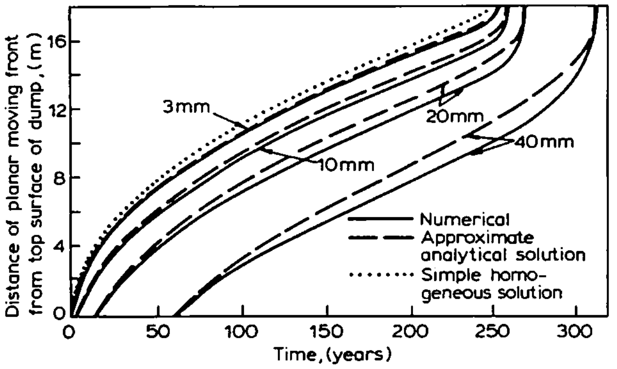

Figure 3 Distance of planar moving front from top surface of wastes as a function of time: comparison of approximate analytical solution, simple homogeneous model and numerical results

more properly be compared with the integrated heat production rate that can be derived from *Figure 1*. It is also clear from *Figure 2* that as the particle size becomes vanishingly small, the heat source distribution predicted by both the AAS and the numerical solution collapses onto that of the SHM solution.

The position of the planar front is shown in *Figure 3* as a function of time for a waste rock dump comprised of various sized particles. In all cases, the curves for the AAS and for the numerical solution have similar shapes and coincide both at the point when the moving front appears at the surface of the waste dump and when the front reaches the base of the dump. The AAS curve always lies above the 'exact' curve with the greatest difference occurring when $X(t)$ is about halfway down the dump, the difference increasing with increasing particle size. For example, for a dump comprised of 40 mm particles, which is rather an extreme case, the AAS prediction is that the planar front will reach a point about halfway down an 18 m high dump some 25 years earlier than is predicted by the numerical solution.

It is of considerable practical significance that the AAS predicts accurately the lifetime of oxidation within the waste dump since this parameter $t_d = t_c + \frac{1}{2}$ is readily evaluated. In contrast, evaluation of the lifetime of pyritic oxidation using the numerical solution requires the calculation to be run for the whole lifetime of oxidation in the wastes, a necessarily time-consuming process. Hence the utility of the AAS is particularly marked when there is a need to assess the most important parameters for determining the potency and longevity of the environmental impact of a particular dump.

For completeness, the position of the reaction front predicted by the SHM is also included in *Figure 3*. As has been discussed elsewhere,[1] the SHM cannot predict the time shift t_c, which is a feature of the other curves in *Figure 3*, and hence it underestimates the time taken to oxidize the material in the wastes. Moreover, the reaction front in the SHM represents the boundary in the wastes which separates fully oxidized material from unoxidized material, whereas in the present model the planar moving front is the boundary between that portion of the wastes in which particles are fully reacted ($R = 0$) and that in which the particles are in all stages of oxidation. However, the position of the planar moving front does provide some measure of the extent to which the material of the wastes has been oxidized. This is particularly so when the particle size is small. Indeed, as the particle size goes to zero, the value for $X(t)$ predicted by the AAS becomes indistinguishable from that predicted by the numerical solution and both collapse towards the reaction front of the SHM.

As indicated above, the position of the planar moving front predicted by the AAS is further from the surface of the wastes at any particular time in the oxidation process than the position predicted by the numerical solution. Notwithstanding, the oxygen concentration for $t > t_c$ predicted by the numerical solution is closer to a linear function of distance for a greater distance from the surface than that predicted by the AAS. This can be seen in *Figure 4* where the numerical solution results for a particule size of 20 mm are close to linear down to a depth of about 4 m but the AAS oxygen concentration profile, although linear as far as the planar moving front at 1.8 m is clearly nonlinear at greater depths. It can also be seen in *Figure 4* that near the surface the AAS oxygen concentrations for 20 mm particles lie below those for the numerical solution before crossing at a point about 4 m from the surface and thereafter lying above the exact result. This result is typical, the crossover point being closer to the surface the larger the particle size.

Because of the scale of *Figure 4*, it appears that the oxygen concentration profiles predicted by the numerical solution are coincident with each other towards the surface of the wastes and coincident with the profile predicted by the SHM; examination at a finer scale shows that when the planar front has moved away from the top surface, the flux at the surface increases with particle size. It is apparent that at these times the SHM somewhat underestimates the oxygen flux into the wastes. It is interesting to consider whether the flux at the surface tends to a limiting value as the particle size tends to infinity. It should be noted that for particle sizes much larger than about 200 mm the simplifying assumption that the time dependence of diffusion within the particles can be ignored (δ_2 small; $\delta_2 \ll \delta_1$; Davis and Ritchie)[1] may no longer be valid.

Conclusions

A numerical scheme has been developed and implemented to solve the system of equations developed to model oxidation of pyritic material in mine wastes. The system is a coupled system of partial differential equations involving a moving boundary formulation. The numerical scheme allows rapid and accurate evaluation

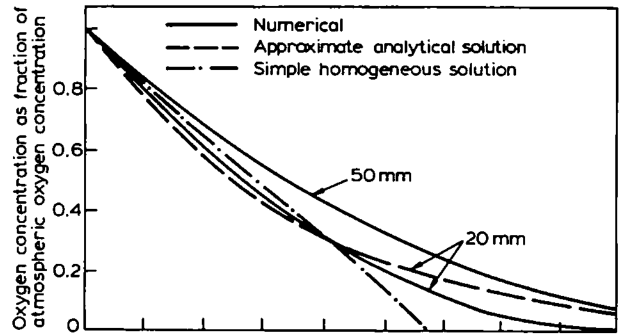

Figure 4 Dimensionless oxygen concentration as a function of distance from surface of wastes 26 years after creation of wastes: comparison of approximate analytical solution, simple homogeneous model and numerical results

of a number of properties of interest within the oxidizing waste material over the complete lifetime of the oxidation process. This lifetime is typically of the order of several hundreds of years.

A comparison of results obtained using the more exact numerical scheme with those obtained from an approximate analytical solution (AAS) indicated that the AAS is generally very useful. In particular it produces accurate estimates for 'integral' quantities such as the lifetime of the oxidation process in the wastes and the total sulphate production rate, with the proviso that in the latter case the particle size is not too large. These are useful measures of the magnitude and longevity of the environmental impact presented by the wastes. Hence the AAS is a convenient method for quantifying the likely effectiveness of modifications to some of the properties of the wastes such as porosities, pyritic densities and so on, in attempts to reduce the environmental impact of such pyritic wastes.

The AAS predicts 'differential' quantities such as the oxygen concentration and the heat source distribution with less accuracy. This is not seen as a major failing since these quantities are most likely to be used in a comparison between experimental measurements and predictions of the model to estimate the extent to which the model adequately describes the oxidation process within pyritic wastes. In this situation the limitation of the AAS to the case where there is only one particle size in the wastes is likely to be more restrictive than any numerical limitations.

The AAS is still useful in that, given that its numerical accuracy is reasonable and that it allows easy and rapid evaluation of different properties, it provides insight into the relative importance of the various mechanisms that play a part in the oxidation process.

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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 ($W m^{-3}$)
$k = \frac{k_1}{3} = \frac{1}{k_2}$	
$k_1 = \frac{3\gamma D_2(1-p)L^2}{(D_1 a^2)}$	
$k_2 = \frac{\tau_3}{\tau_4}$	
$k_3 = \frac{3\delta\rho_s k}{\tau_4}$	
L	height of dump (m)
p	porosity of dump (dimensionless)
$r = \frac{r^*}{a}$	dimensionless radial distance
r^*	radial distance within a particle (m)
$R(x,t) = \frac{R^*}{a}$	dimensionless position of reaction front
$R^*(x^*,t^*)$	position of moving reaction front within particle (m)
$S(t)$	integrated sulphate production rate ($kg\, m^{-2} s^{-1}$)
$t = \frac{t^*}{\tau_4}$	dimensionless time
t^*	time (s)
t_c	dimensionless time to react particle at surface of dump
t_d	dimensionless time to fully oxidize dump
$u(x,t) = \frac{u^*}{u_0}$	dimensionless oxygen concentration
$u^*(x^*,t^*)$	oxygen concentration within pore space of dump ($kg\, m^{-3}$)
$\bar{u}(x,t)$	dimensionless oxygen concentration corresponding to $\bar{w}(x,t)$
u_0	concentration of oxygen at surface of dump (concentration of oxygen in air) ($kg\, m^{-3}$)
$v(r,x,t) = \frac{v^*}{\gamma u_0}$	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 (7)
$\bar{w}(x,t)$	upper bound solution for $w(x,t)$
$x = \frac{x^*}{L}$	dimensionless spatial coordinate
x^*	vertical spatial coordinate (m)
$X(t) = \frac{X^*}{L}$	dimensionless position of planar moving front
$X^*(t^*)$	position of planar moving front within dump (m)
$\beta = 6k$	
$\beta' = \frac{\beta}{\delta_1}$	
γ	a proportionality constant encompassing both Henry's law and gas law
δ	heat produced from oxidation reaction per mass of sulphur oxidized ($J\, kg^{-1}$)
$\delta_1 = \frac{\tau_1}{\tau_4}$	
$\delta_2 = \frac{\tau_2}{\tau_4}$	
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
ρ_s	density of sulphur within dump ($kg\, m^{-3}$)
$\tau_1 = \frac{pL^2}{D_1}$	
$\tau_2 = \frac{a^2}{D_2}$	

$$\tau_3 = \frac{\varepsilon \rho_s a^2}{[\gamma u_0 D_2(1-p)]}$$

$$\tau_4 = \frac{L^2 \varepsilon \rho_s}{(D_1 u_0)}$$

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