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Mathematical modelling of rate-limiting mechanisms of pyritic oxidation in overburden dumps

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MATHEMATICAL MODELLING OF RATE-LIMITING MECHANISMS OF PYRITIC OXIDATION IN OVERBURDEN DUMPS

A thesis submitted in fulfilment of the requirements for the award of the degree of

DOCTOR OF PHILOSOPHY

from

THE UNIVERSITY OF WOLLONGONG

by

GREGORY BRUCE DAVIS, B.Sc, B.Math(Hons), W'gong

DEPARTMENT OF MATHEMATICS

1983
DECLARATION

This thesis is submitted to the University of Wollongong, N.S.W. and I declare that no part of it has been submitted for a higher degree to any other University or Institution.

GREGORY B. DAVIS
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ABSTRACT

The mining of valuable minerals often leads to major environmental pollution problems especially when pyritic material is associated with the orebody being mined. In this thesis mathematical equations are formulated which describe a "dual region" model of pyritic oxidation within a waste rock dump, where it is assumed that oxygen transport is the rate-limiting step in the oxidation process, and that oxygen transport to reaction sites occurs in two stages; bulk diffusion of oxygen from the atmosphere, at the top surface of the dump, through the pore space of the dump to particles within the dump, and then diffusional transport of oxygen from the surface of particles to oxidation sites within the particles.

A moving boundary (shrinking-core) formulation, describing transport and reaction processes within a single particle of the dump, is solved by a new analytic series solution technique involving a change of coordinates leading to a non-linear partial differential equation with fixed boundaries. Based on this analysis a pseudo-steady state assumption is made with respect to diffusion within the particles giving a simplified system of equations for the dump model.

The system of equations is solved both in an approximate analytic way and numerically. An approximate analytic result is obtained by solving a planar moving boundary formulation which in turn comes from approximation of the position of the moving reaction front within the particles of the dump. The position of the planar front within
the dump is given by a transcendental equation which is shown to collapse on the \( \frac{1}{2} \) classical planar moving boundary result when the particle size tends to zero. A combined Crank-Nicolson and Backward Euler discretisation of the system of equations is adopted for the numerical scheme. The approximate and numerical solutions are compared.

A particle size distribution is included in the model equations. A substantial difference is observed, in parameter prediction, between a dump assumed to be comprised of particles of a single or “average” size, and a dump when a range of particle sizes is accounted for.

Variables such as the total sulphate production rate, the position of the planar moving front within the dump, the oxygen concentration within the pore space of the dump and the heat source distribution, are evaluated and their dependence on other parameters in the model noted. Comparisons are made with both experimental measurements and with predictions of a simpler diffusion rate-limited model of pyritic oxidation. The present model is in much better qualitative agreement with experimental values than the simpler model. The model is also extended to assess the effectiveness of a rehabilitation strategy intended to reduce pollutant production within oxidising pyritic material.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>TITLE PAGE</th>
<th>DECLARATION</th>
<th>ACKNOWLEDGEMENTS</th>
<th>ABSTRACT</th>
<th>TABLE OF CONTENTS</th>
<th>NOTATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Page</td>
<td>ii</td>
<td>iii</td>
<td>iv</td>
<td>vi</td>
<td>viii</td>
</tr>
</tbody>
</table>

## CHAPTER 1. INTRODUCTION

1.1 General Introduction 1  
1.2 Scope of the Thesis 6

## CHAPTER 2. PHYSICAL LAYOUT OF RUM JUNGLE AND SIMPLE MODEL

2.1 Introduction 10  
2.2 The Rum Jungle Mine 10  
2.3 White's Overburden Dump 15  
2.4 Simple Model of White's Heap (Ritchie, 1977) 17

## CHAPTER 3. LITERATURE SURVEY

3.1 Introduction 20  
3.2 Heap Leaching Models 21  
3.3 Dual Region Models 28  
3.4 Summary 36

## CHAPTER 4. THE MATHEMATICAL MODEL

4.1 Introduction 39  
4.2 The Model Equations 41  
4.3 Parameters in the Model 49  
4.4 A Moving Boundary Problem for a Particle of the Dump 52  
4.5 Approximate Dimensionless Model 60  
4.6 Heat Source Distribution and Sulphate Production Rate 64  
4.7 The Particle Size Distribution 67

## CHAPTER 5. APPROXIMATE SOLUTIONS

5.1 Introduction 72  
5.2 Approximate Upper Bound Solution 75  
5.3 Approximate Lower Bound Solution 86

## CHAPTER 6. NUMERICAL RESULTS AND COMPARISONS

6.1 Introduction 90  
6.2 The Numerical Method 91  
6.3 Approximate, Numerical and Simple Model Solutions 97  
6.4 Sensitivity of the Model to Parameter Changes 107  
6.5 Import of the Particle Size Distribution 112
NOTATION

\( a \)  
radius of the particle (m)

\( a_0 \)  
minimum size of radius considered in the particle size distribution (m)

\( a_n \)  
maximum size of radius considered in the particle size distribution (m)

\( A,B \)  
arbitrary constants

\( A_n(x) \)  
coefficients of series expansion (4.4.13)

\( C_n \)  
coefficients in the series solution (5.3.1)

\( D_0 \)  
diffusion coefficient for oxygen corresponding to the low porosity zone of the dump (m^2s^{-1})

\( D_1 \)  
diffusion coefficient of oxygen in the pore space of the dump (m^2s^{-1})

\( D_2 \)  
diffusion coefficient of oxygen in water (m^2s^{-1})

\( D_i k'_i k''_i(i=1,2) \)  
measures of the porosity, permeability, compressibility and size of the rock, and the viscosity and compressibility of the liquid (Chapter 3 only)

\( D'_i(i=1,2) \)  
constants depending on properties of the rock and the liquid

\( D'_1 = D'_1/p_1 \)  
defined by equation (5.3.4)

\( f(x) \)  
defined by equation (5.3.4)

\( H \)  
Henry's law constant (kgm^{-1}s^{-2})

\( H(x,t) \)  
heat source distribution (Wm^{-3})

\( H_c(t) \)  
cumulative total heat production of the dump (Jm^{-2})

\( H_T(t) \)  
total heat production of the dump (Wm^{-2})

\( i,j,k \)  
integers when used as subscripts or superscripts or in summations

\( k = k_1/3 = 1/k_2 \)

\( k_1 = 3\gamma d_2(1-p_1)L^2/(D_1a^2) \)

\( k_2 = \tau_3/\tau_4 \)

\( k_3 = 3\delta_2 k/\tau_4 \)
constant given by equation (4.7.9)

\[ k' = 3a^2k \]

height of the dump (m)

\[ L \]

total mass of particle sample (kg)

\[ M_0 \]

molecular weight of oxygen (kg)

\[ M_1 \]

molecular weight of water (kg)

\[ n \]

integer

\[ n_0 \]

number of moles of oxygen (mol)

\[ n_1 \]

number of moles of water (mol)

\[ N \]

final node point in numerical scheme

\[ N(a)da \]

number of particles of radius between \( a \) and \( a+da \) in a sample of mass \( M \) (dimensionless)

\[ P_0 \]

partial pressure of oxygen in air \( (\text{kgm}^{-1}\text{s}^{-2}) \)

\[ p \]

porosity of the dump (dimensionless)

\[ P_1 \]

pressure associated with the fissure system

\[ P_2 \]

pressure associated with the porous matrix blocks

\[ q^*(x^*,t^*) \]

rate of volume loss of oxygen from the pore spaces \( (\text{kgm}^{-3}\text{s}^{-1}) \)

\[ r = r^*/a \]

dimensionless radial distance

\[ r^* \]

radial distance within a particle (m)

\[ R \]

gas law constant \( (\text{kgm}^2\text{s}^{-2}\text{°K}^{-1}) \)

\[ R(t) \]

dimensionless position of reaction front (Section 4.4 only)

\[ R(x,t) = R^*/a \]

dimensionless position of reaction front

\[ R^*(t^*) \]

position of reaction front (m) (Section 4.4 only)

\[ R^*(x^*,t^*) \]

position of the moving reaction front within the particle (m)

\[ R^k_j = R(jAx,kAt) \]

discretised value of the position of the reaction front within a particle of the dump at time \( k \) and mesh node point \( j \)

\[ S_x \]

the bounding surface of a block in the neighbourhood of \( x \)
$S(x,t)$ function describing the exchange of liquid flowing between the fissures and the porous blocks

t = $t^*/t^*_4$ dimensionless time

t = $D_2t^*/a$ dimensionless time (only in Section 4.4)

t* time (s)

tc dimensionless time to react the particle at the surface of the dump

td dimensionless time to fully oxidise the dump from the upper bound solution

t"d dimensionless time to fully oxidise a semi-infinite dump to depth 18m, given by equation (5.2.28)

t""d dimensionless time to fully oxidise a dump corresponding to the lower bound solution

T temperature (°K)

$T_n(t)$ time dependent coefficient in series solution (5.3.1)

$u(x,t) = u^*/u_0$ dimensionless oxygen concentration

$u^*(x^*,t^*)$ oxygen concentration within the pore space of the dump (kgm$^{-3}$)

$\bar{u}(x,t)$ dimensionless oxygen concentration corresponding to $\bar{w}(x,t)$

$\underline{u}(x,t)$ dimensionless oxygen concentration corresponding to $\underline{w}(x,t)$

$u_0$ concentration of oxygen at the surface of the dump (concentration of oxygen in air)(kgm$^{-3}$)

$u^*_j = u(j\Delta x,k\Delta t)$ discretised value of the oxygen concentration at time k and mesh node point j

$v(r,t) = v^*/v^0$ dimensionless oxygen concentration within a single particle (Section 4.4 only)

$v(r,x,t) = v^*/\gamma u_0$ dimensionless oxygen concentration within the particles of the dump

$v^*(r^*,t^*)$ oxygen concentration within a single particle (kgm$^{-3}$) (Section 4.4 only)

$v^*(r^*,x^*,t^*)$ concentration of oxygen within a particle within the dump (kgm$^{-3}$)
$v^o$ maximum oxygen concentration outside the particle (kgm$^{-3}$)

$v_o$ solubility of oxygen in water (kgm$^{-3}$)

$v_1$ density of water

$V$ volume occupied by a block in the neighbourhood of $x$

$w(x,t)$ defined by equation (5.1.3)

$\bar{w}(x,t)$ upper bound solution for $w(x,t)$

$w_1(x,t)$ upper bound solution for $t \leq t_c$

$w_2(x,t)$ upper bound solution for $t > t_c$ and $0 \leq x \leq X(t)$

$w_3(x,t)$ upper bound solution for $t > t_c$ and $X(t) \leq x \leq 1$

$\underline{w}(x,t)$ lower bound solution for $w(x,t)$

$x = x*/L$ dimensionless spatial coordinate

$x = (r-1)/(R(t)-1)$ transformation variable (Section 4.4 only)

$x*$ vertical spatial coordinate (m)

$x$ coordinates associated with the fissure system

$x_o$ mole fraction of oxygen in water (dimensionless)

$X(t)$ dimensionless position of the planar moving front

$X*(t*)$ position of the planar moving front within the dump (m)

$X_n(x)$ coefficient in the series solution (5.3.1)

$y = R(t)$ transformation variable

$Y$ coordinates associated with the porous blocks only

$z$ dummy integration variable
GREEK SYMBOLS

\( \alpha \) 
constant found from the transcendental equation (A.6) 
(only in Section 4.4)

\( \alpha = \varepsilon \rho_s / (1 - p_1) v_0 \)

\( \beta = 6k \)

\( \beta' = \beta / \delta_1 \)

\( \gamma \) 
a proportionality constant encompassing both 
Henry's law and the gas law

\( \gamma \) 
root of the transcendental equation (4.4.15) 
(Section 4.4 only)

\( \delta \) 
heat produced from the oxidation reaction per 
mass of sulphur oxidised (Jkg\(^{-1}\))

\( \delta_1 = \tau_1 / \tau_4 \)

\( \delta_2 = \tau_2 / \tau_4 \)

\( \delta_s \) 
mass of SO\(_4\) produced per mass of sulphur consumed 
by the chemical reaction

\( \Delta H \) 
heat output of reaction (4.3.1) 
(= 1440kJ mol\(^{-1}\))

\( \Delta t \) 
time increment

\( \Delta x \) 
spatial mesh interval

\( \epsilon \) 
mass of oxygen used per mass of sulphur in the 
oxidation reaction

\( \theta = \tanh \sqrt{\beta} \)

dummy integration variable

\( \lambda \)

\( \lambda_n = \frac{(2n-1)\pi}{2} \)

\( \mu = RT/M_0 \)

\( \nu \) 
number of particles per unit volume of the dump (m\(^{-3}\))

\( \nu(a)da \) 
number of particles per unit volume of the dump 
whose radius lies in the range \( a \) to \( a+da \) (m\(^{-3}\))

\( \xi, \tau \) 
new independent variables (Appendix A only)

\( \rho \) 
density of the particulate mass of the dump (kgm\(^{-3}\))
\( \rho_s \)  
\( \rho_T \)  
\( \sigma \)  
\( \tau \)  
\( \tau_1 = \rho_1 L^2 / D_1 \)  
\( \tau_2 = a^2 / D_2 \)  
\( \tau_3 = \varepsilon \rho_s a^2 / [\gamma u_0 D_2 (1-p_1)] \)  
\( \tau_4 = L^2 \varepsilon \rho_s / (D_1 u_0) \)  
\( \phi(\xi) \)  
\( \phi(x,y) \)  
\( \nabla^2 \)  
\( \text{dot} \)  
\( \text{dash} \)  

Density of sulphur within the dump (kgm\(^{-3}\))

Overall density of the dump (kgm\(^{-3}\))

Constant given by equation (4.4.19)

Dummy integration variable

\( \rho_s \)

\( \rho_T \)

\( \sigma \)

\( \tau \)

\( \tau_1 = \rho_1 L^2 / D_1 \)

\( \tau_2 = a^2 / D_2 \)

\( \tau_3 = \varepsilon \rho_s a^2 / [\gamma u_0 D_2 (1-p_1)] \)

\( \tau_4 = L^2 \varepsilon \rho_s / (D_1 u_0) \)

\( \phi(\xi) \)

\( \phi(x,y) \)

Function defined by equation (A.10)

Function defined by equation (4.4.9)

Laplacian operator

Differentiation with respect to time

Differentiation with respect to the spatial coordinate.
CHAPTER 1

INTRODUCTION

1.1 General Introduction

Mining ventures throughout the world are, more recently, being assessed for their potentially detrimental environmental impact. A pollution problem common to many mining operations is high acidity and heavy metal pollution in runoff and seepage water from waste rock dumps and tailings dams containing pyritic material (Raicevic, 1979; Hore-Lacey, 1979; Olson et al., 1979). As long ago as the mid 16th century the German scholar Georgius Agricola (1556), in his classical Latin work De Re Metallica, not only pointed out the value of "waste" material: "There are some people who wash over the dumps, from exhausted and abandoned mines, and those dumps which are derived from the drains of tunnels; and others who smelt the old slags; from all of which they make an ample return." but also drew attention to the environmental hazards wrought by mining ventures: "...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.". Iron pyrites poses such a widespread pollution problem for the mining industry today, because it is frequently associated with minerals of economic importance such as copper, nickel, zinc, coal and uranium and because, upon exposure to air and water it oxidizes, leading to the production of polluted groundwater.

In the Appalachian coalfields of the United States of America, for example, acid mine drainage has affected thousands of kilometres
of rivers and streams (Kinney, 1964). Also in the United States the mining of silver, lead, zinc and antimony has led to the pollution of some 150 kms of the Coeur d’Alene River in northern Idaho by trace metal contamination and acid mine drainage during approximately eighty years of operation (Norbeck et al., 1974; Trexler et al., 1974). Hore-Lacey (1976) comments that "In the UK this is said to be possibly the main environmental problem faced by the mining industry.". There are also numerous examples of such pollution problems in Australia, most notably in central western and north eastern regions of Tasmania, Captain’s Flat and the Hunter Valley of New South Wales, and Rum Jungle in the Northern Territory. Environmentally deleterious pollution levels of copper, cadmium, lead and zinc in the King, Queen and South Esk Rivers of Tasmania has arisen from the mining of sulphide orebodies (Lake et al., 1977; Roberts and Watson, 1980; Tyler and Buckney, 1973; Norris et al., 1980, 1981) while the Molonglo River, which flows into Lake Burley Griffin (on the banks of which stands the Federal Parliament House) in the Australian Capital Territory, has been affected adversely by zinc mining operations at Captain’s Flat in New South Wales (Weatherley et al., 1967; Fitzgerald and Haldane, 1977; Craze, 1980). Water quality of the Molongolo has recently been improved by rehabilitation works costing some $2.5 million including reducing slope steepness of mine wastes and covering them with layers of rocks, clay, topsoil and vegetation. Acid mine drainage is also a problem in the lower Hunter Valley since pyrites is present in the Greta coal seam (Greenhalgh, 1980; Hannan, 1978) and the oxidation of pyritic mine waste at the abandoned uranium mine at Rum Jungle
in the Northern Territory of Australia has led to pollution of the East Branch of the Finniss River system with such trace metals as copper, manganese and zinc (Davy, 1975).

These examples show the widespread occurrence of pyrites, associated with many different minerals. The impact of polluted waters from such mining operations on the environs of mine sites is therefore of increasing concern. This is especially so since, if other metal sulphides are associated with the pyrites, heavy metal contamination results and the presence of a few parts per million of dissolved salts of heavy metals such as copper, manganese and zinc leads to the depletion of plant life on waste mine material itself and both plant and aquatic life in nearby waterways. During the operation of a mine the quality of water may well be controlled by collecting and reprocessing polluted water. However the natural oxidation of pyritic material continues long after the cessation of mining operations and therefore long-term, cost-effective measures need to be formulated which will limit the deleterious effects of such acid leaching on the environs of disused mine sites. There is therefore a need to understand the processes involved in pyritic oxidation and to quantify the rate-limiting mechanisms in these processes.

Optimum conditions for pyrite oxidation are hard to define, however, much is known concerning the chemical reactions governing the oxidation of pyrites and subsequent heavy metal solubilisation (Dugan, 1972; Lowson, 1975) as well as the role of bacteria, such
as Thiobacillus Ferrooxidans, in catalysing the oxidation processes (Brierley, 1978). Much has been done in fact (Bhappu et al., 1969; Auck and Wadsworth, 1973; Roach, 1975; Murr et al., 1977; Liddel, 1980; Murr, 1980) in assessing the critical physical, chemical and biological factors affecting the leaching of low-grade ore in order to maximise the heavy metal solubilisation for commercial leaching applications. Commercial heap leaching of copper, for example, has been practised extensively (Taylor and Whelan, 1942) for many years and a current review of the leaching and recovery of copper has been sponsored by the Solution Mining Committee of the Society of Mining Engineers of A.I.M.E. (Schlitt, 1980). Here, however, we are more interested in minimising the pollution load to the environment under natural weathering conditions. Little work has been done in this area to actually quantify the mechanisms that control the rate of oxidation of pyrite contained in such mine waste. Since both water and oxygen are necessary for oxidation to occur it would seem obvious to suggest that the reduction of supply of either water or oxygen to reaction sites would slow the oxidation rate. Such a strategy for the reclamation of a disused mine site has been implemented (Schubert, 1979; Greenhalgh, 1980; Wilkey and Zellmer, 1977) by the establishment of vegetation on top of waste material. However, what is not clear in such a scheme is how much water and/or oxygen has to be excluded to achieve a given improvement in the water quality in the mine environs.

A useful tool for identifying, quantifying and understanding
the mechanisms involved in the oxidation of pyritic mine waste is a mathematical model. A mathematical model, although in many aspects an idealisation of the real problem, can be valuable in a number of ways. It enables the prediction of future events based on certain rules and/or previous data or, it may indicate which parameters in a real world system are most important in a sensitivity sense or, through altering the state of the model problem it may indicate what could happen for a parallel change in the real problem (see Aris, 1978 or Andrews and McLone, 1976 for a more complete discussion of mathematical modelling). We require that our mathematical model of pyritic oxidation include each of the above points. For example, we may wish to know the interval of time until a waste rock dump is completely oxidised so that land may be reclaimed for use. Also a sensitivity analysis may indicate to the experimenter which parameters are important for measurement studies while negating others. It may also be, that, in rehabilitating a disused mine site we attempt to either speed up the oxidation process so that the pyritic mine waste is fully reacted sooner or, in fact, slow down the process so that the pollution problem is kept below acceptable levels. It may therefore be possible to gauge the effect of such a change in the real problem, from the mathematical model, before affecting that change in the real situation.

The widespread occurrence of pollution from pyritic oxidation and the subsequent need to quantify the complex transport and reaction processes involved, therefore necessitates the development of a
mathematical model adequately describing such mechanisms in waste rock dumps.

1.2 Scope of the Thesis

In developing the model equations presented in this thesis and in assessment of model predictions, reference is often made to experimental measurements collected at the abandoned uranium mine site at Rum Jungle in the Northern Territory of Australia. Accordingly in Chapter 2 a description of the mine site and environs, and an indication of the extent of pollution at that site, is given. In particular we describe in detail the waste rock pile known as White's overburden dump since data obtained from White's dump are used for comparison with model predictions. Also in Chapter 2 an earlier attempt at modelling the pyritic oxidation process within the waste material comprising White's dump is described.

In Chapter 3 we survey previous models of processes involved in the leaching of low-grade ore, whether it be with commercial application in mind (in which case prepared piles of ore are acid leached and the resultant pregnant liquor is processed to regain valuable minerals) or through concern for the environmental impact of pollutants emanating from oxidising waste dumps. We also discuss in this chapter "dual region" models developed in fields of interest outside that of the mining industry such as biology, metallurgy, soil science and chromatography. We investigate the essential features of such models for possible inclusion in a more comprehensive model of a waste rock dump undergoing pyritic oxidation.
In Chapter 4, mathematical equations modelling transport and reaction mechanisms within a waste rock dump are proposed. Input to the model includes the physicochemical characteristics of the ore and of the waste dump itself. Thus a predictive model is developed not a curve fitting one. A new solution procedure is developed in this chapter to investigate a non-steady state moving boundary formulation describing transport and reaction mechanisms within a single particle of the dump. Such an analysis gives insight into the importance of individual processes within particles of the dump relative to the oxidation processes throughout the dump. Analysis of the moving boundary formulation for a single particle of the dump, and consideration of parameter values appropriate to White's dump at Rum Jungle, then leads to a simplifying approximation valid for the complete model equations. Chapter 4 also includes equations appropriate to output parameters such as the heat source distribution and the sulphate production rate, which are indicators of regions of high oxidation within the waste material and of pollutant production levels, respectively. Finally in Chapter 4 the model equations are modified to incorporate a particle size distribution to take account of the wide variability of particle sizes within a waste dump.

Approximate upper and lower bound solutions of the model equations are given in Chapter 5. The upper bound solution is found by solving a planar moving boundary formulation involving two linear, diffusion type partial differential equations. The approximate solutions are not only accurate for average properties of the dump and easily
evaluated, but also expose the underlying structure of the more general solution.

A numerical method is developed in Chapter 6 to solve the general model equations of Chapter 4. The technique couples the Crank-Nicolson and Backward Euler discretisations which are then solved using the Cholesky $LDL^T$ decomposition at each time step and a simple Newton’s method. The numerical method is employed to assess the usefulness and accuracy of the approximate upper bound result of Chapter 5. Comparison is also undertaken with the simple homogeneous model of Ritchie (1977). Physical parameters such as oxygen concentration profiles, heat source distributions and total sulphate production rates are used for comparison of the simple model solution and the approximate solution with the numerical result. A sensitivity analysis of the model equations is also presented, in this chapter, which indicates how changes in the physicochemical input data for the model affect model predictions. The importance of the inclusion of a particle size distribution within the model equations is assessed in the final section of Chapter 6. Both the upper and lower particle radius size assumed for the distribution, are varied in order to show their effect on the results of the model. Comparison is made between single particle size results and results obtained for a range of particle sizes.

Model predictions are compared with experimental findings in Chapter 7. Data available for comparison includes oxygen concentration profiles, sulphate production levels and heat source distribution
estimates. Included in Chapter 7 is an assessment of a rehabilitation strategy, when used to limit the production of pollutant within an oxidising waste rock dump, by alteration of the model equations and then numerical solution.

Clearly it is of interest to know under what circumstances the present model is preferable to the simple model, and under what circumstances a calculation including a particle size distribution is preferable to a single particle size calculation. The accuracy of the approximate and simple model results in prediction of various parameters within the model is also of interest. A summary of such conclusions is given in Chapter 8.
CHAPTER 2

PHYSICAL LAYOUT OF RUM JUNGLE AND SIMPLE MODEL

2.1 Introduction

In this thesis we are particularly interested in the pollution aspects of the abandoned uranium mine site at Rum Jungle in the Northern Territory of Australia. As previously indicated heavy metal and high acidity pollution not only pose a threat to the ecology of the immediate mine site area but also to nearby waterways, which are fed from the Rum Jungle region. In modelling such a system the topographical and historical aspects of the mining operation are therefore of practical interest, since they become a basis for further investigation.

Accordingly the next section contains a résumé of the mining history of Rum Jungle, geographical details of the area and an indication of the severity of the pollution problem, with reference to the effect of pollutant levels on native fauna and flora. Section 2.3 describes in more detail the mining operation as carried out for White's orebody and some of the geographical detail. The physical characteristics of White's overburden dump are also described. In the final section of this chapter an initial attempt, developed by Ritchie (1977), to model White's waste rock dump is outlined.

2.2 The Rum Jungle Mine

Rum Jungle is located 64km south of Darwin (over 100km by road) and 80km east of Joseph Bonaparte Gulf (part of the Timor Sea) in
the Northern Territory of Australia (Map 2.1). The region derives its name from a brawl between drivers of two bullock teams over a cargo of rum. The actual mine site is approximately 8km north of the township of Batchelor. Rum Jungle has a monsoonal climate with distinct wet (Oct-April) and dry seasons; the average annual rainfall being approximately 1.5m. Temperatures in the region range from 15°C to 30°C in the "winter", while in the "summer" season the range is 24°C to 33°C. Geographically the area surrounding Rum Jungle is an expanse of gently sloping land bordered by vast plains. The vegetation consists mainly of scrub with the only "jungle" appearing, if anywhere, along the banks of creeks and streams.

The main river in the region is the Finniss River, whose length is approximately 140km. The East Branch of the Finniss River has its source in the Rum Jungle area; and flows in a north-westerly direction to its junction with the main stream of the Finniss River, which then continues westward where it enters the Timor Sea at Fog Bay, after traversing wide flat marshland (primarily mangrove swamps). The East Branch is a seasonal tributary with almost no flow from July to December and an average annual flow past the mine site of approximately $4 \times 10^7 \text{ m}^3$, while the Finniss River itself has permanent flow.

The extensive mineralisation of the Rum Jungle area was first noted by a surveyor named Wood in 1869 and copper was recovered for a short time in the early 1900's. The first find of uranium was reported by Mr J.M. White, a local farmer and amateur prospector. In
1953, Territory Enterprises Pty Ltd, a wholly owned subsidiary company of Consolidated Zinc Pty Ltd (later to amalgamate with Rio Tinto Pty Ltd as Conzinc Riotinto of Australia Pty Ltd) was formed to mine and treat the uranium orebodies on behalf of the Australian Commonwealth Government (Berkman, 1968). The production of uranium oxide commenced in 1954. White's orebody was the first to be recovered and since it lay directly beneath the bed of the East Branch a diversion channel was cut on the southern side of White's deposit to allow mining by opencut techniques. As a result the Rum Jungle mine site straddles the East Branch and is located about 8.5km above the Finniss River junction with the East Branch (Map 2.2). The opencut method was also used to recover ore from Dyson's, Rum Jungle Creek South and Intermediate orebodies. Processing of the ore continued until Rum Jungle Creek South ore had been treated in 1971, when the treatment plant was closed down. Mining operations had been completed in 1963. Today the abandoned mine site consists primarily of: water-filled opencuts and overburden dumps associated with White's, Dyson's and Intermediate orebodies; a tailings dispersal area; a low-grade copper sulphide and copper oxide heap leaching experiment (Harris, 1969); White's North low-grade ore pile; and some abandoned mine buildings (Map 2.2). A detailed history of the Rum Jungle region (not only mining operations) can be found in the newly published work by Barrie(1982).

At the start of operations in 1954, tailings were discharged into a disposal area north of the treatment plant known as Old
Tailings Dam, which overflowed spasmodically into Old Tailings Creek and thence into the East Branch. Indeed from the outset nearly all run-off water from the mine site and all plant effluent made its way into the East Branch of the Finniss. Hence, rivers in the area became polluted from the commencement of mining operations (Lowson, 1975). Two other interrelated sources of contamination became apparent in later years. These sources consisted of heavy metal pollution from the leaching of stockpiles and pyrite laden overburden dumps, by natural weathering. The natural leaching of the waste rock dumps, came to the fore when acidic run-off waters containing significant quantities of heavy metals were observed. Also springs with temperatures up to 36.5°C developed at the base of heaps. This can be compared with the river temperature of around 28°C.

The advent of high pollutant levels in streams near the Rum Jungle mine site produced an adverse effect on both wildlife and vegetation in the region and continues to do so. The seasonal flow of the East Branch of the Finniss River contributes much to the accumulation of pollutants making it barren of wildlife and often giving it an unnatural bluey green colouring (due to high copper concentrations). Indeed the high concentration of heavy metals and the low pH of the East Branch allow few aquatic species of animals to survive downstream of the mine site in the East Branch (Jeffree and Williams, 1975). The seasonal flow also causes problems for the Finniss River proper since at the first rain of the wet season a
"slug" of pollutant concentrate is washed downstream from such feeder tributaries, killing fish and damaging vegetation. The damage to vegetation is, however, most obvious along the banks of the East Branch and around the waste rock piles themselves (see Photograph 2.1). Along the East Branch erosion of stream banks, absence of rooted aquatic plants and the destruction of closely hanging Pandanus palms has been marked (Jeffree and Williams, 1975). It is interesting to note also that in some low lying areas of the Finniss River grasses contain high concentrations of copper and also manganese and zinc. In Table 2.1 (Davy and Jones, 1975) sulphate, copper, manganese and zinc levels are estimated for the East Branch downstream of the mine site in the wet seasons 1969-70 through to 1973-74. Three of the five seasons had approximately average rainfalls while one of the others was well above average and the other was well below.

A comparison of pollution loads of copper, zinc and manganese from various sources at Rum Jungle are also given in Table 2.2 (Conway et al., 1975). These levels of pollution were recorded during the 1973-74 wet season which had a higher than average rainfall of 2.0m and therefore the pollution loads measured are generally higher than those expected for a wet season of average rainfall (1.5m). The relative size of the pollution loads, however should not vary greatly from wet season to wet season. Table 2.2 shows clearly that the main source of copper and zinc pollution are the waste rock dumps and the heap leach pile. Information regarding chemical composition and physical sizes of the waste rock dumps can be found in Harries.
Photograph 2.1  Looking south along the east wall of White's dump, June 1982
(Courtesy of Dr. A.I.M. Ritchie, A.A.E.C.). Note the lack of
vegetation close to the heap. White patches are heavy
concentrations of metal salts (mainly manganese).
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Rainfall (mm)</td>
<td>896</td>
<td>1611</td>
<td>1542</td>
<td>1545</td>
<td>2000</td>
</tr>
<tr>
<td>Period of flow in East Branch</td>
<td>Dec-May</td>
<td>Nov-Aug</td>
<td>Nov-July</td>
<td>Dec-July</td>
<td>Nov-Sept</td>
</tr>
<tr>
<td>Flow ($m^3 \times 10^{-6}$)</td>
<td>7.0</td>
<td>33.2</td>
<td>30.9</td>
<td>26</td>
<td>n.a.</td>
</tr>
<tr>
<td>Pollution load (tonne)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>44</td>
<td>77</td>
<td>51</td>
<td>45</td>
<td>130</td>
</tr>
<tr>
<td>Mn</td>
<td>46</td>
<td>110</td>
<td>64</td>
<td>49</td>
<td>100</td>
</tr>
<tr>
<td>Zn</td>
<td>n.a.</td>
<td>24</td>
<td>19</td>
<td>16</td>
<td>40</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>3300</td>
<td>12000</td>
<td>6600</td>
<td>5500</td>
<td>13000</td>
</tr>
</tbody>
</table>

Table 2.1 Pollution load carried by the East Branch of the Finniss River (Davy and Jones, 1975).
<table>
<thead>
<tr>
<th>Source</th>
<th>Annual release (tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Dyson's opencut</td>
<td>1</td>
</tr>
<tr>
<td>Dyson's waste rock</td>
<td>0.2</td>
</tr>
<tr>
<td>White's opencut</td>
<td>8</td>
</tr>
<tr>
<td>White's waste rock</td>
<td>29-53</td>
</tr>
<tr>
<td>Intermediate opencut</td>
<td>3</td>
</tr>
<tr>
<td>Intermediate waste rock</td>
<td>16-30</td>
</tr>
<tr>
<td>Heap leach pile</td>
<td>32-42</td>
</tr>
<tr>
<td>Tailings area</td>
<td>5</td>
</tr>
<tr>
<td>Old Acid Dam</td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>95-142</td>
</tr>
</tbody>
</table>

Table 2.2 Annual release of heavy metals (in tonnes) from each source in the Rum Jungle area (1973-74) (Conway et al. 1975).
and Ritchie (1983) as well as a general summary of the experimental work carried out at the Rum Jungle mine site.

In the next section we describe in more detail the mining operation as carried out for the White's orebody and subsequently describe the particular waste rock dump considered for modelling in this thesis, namely, White's overburden dump at Rum Jungle.

2.3 White's Overburden Dump

As previously mentioned the Rum Jungle mine produced three overburden dumps in close proximity to each other; White's, Dyson's and Intermediate. The first orebody to be recovered was that of White's, then Dyson's and finally Intermediate, extending over some ten years. Here we consider only White's orebody and overburden dump in detail.

Both the shortage of experienced underground miners in the early 1950's and the irregular shape of the orebody contributed to the decision to recover White's deposit by opencut operation, even though initially underground mining was intended. Upon excavation White's orebody was found to extend some 160m below the original ground surface, of which approximately the first 120m was recovered. The ore was observed to occur in several distinct layers, the details of which can be found in Lowson (1975), and interestingly all layers were mixed with pyrites. Contractors excavated the overburden material from White's opencut and built White's heap (known locally as Mt. Wimpey) south of the diversion channel on a reasonably level, well
drained portion of land. The central core of the heap consisted of a ramp of hematite-quartzite breccia. Slates and shales which form the major portion of the overburden dump were back dumped from this ramp. A smaller proportion (10-15%) of dolomite also occurs. Chemical analyses of crushed and bulked samples from an auger drill survey showed that the heap contained approximately 3% sulphur (Lowson, 1975) which can be assumed to be in the form of heavy metal sulphides, principally pyrites. For a more complete discussion of the geology and geography of the Rum Jungle mine site the reader is referred to Lowson (1975).

White's waste pile is heart shaped (Map 2.3) with the ramp approaches sloping downhill northwards, while the southern end of the dump rises to 18m above the original ground surface. The walls of the heap slope outwards at an approximate angle of 30 degrees to the horizontal (Photograph 2.1) while a typical diameter of the dump is of the order of 500m (Photograph 2.2). Photograph 2.2 also shows the flat pancake shape of White's dump. The dump contains approximately $4 \times 10^6 \text{ m}^3$ of material with an estimated density of $1.67 \times 10^3 \text{ kg m}^{-3}$ and therefore the total mass of material can be estimated at 6.68M tonnes. The dark grey colour of the dump (Photograph 2.1 and 2.2) is due to the high percentage of dump material made up of carbonaceous slates and graphitic schists.

Some areas of the dump such as the northwest and western regions support flourishing grasses and shrubs and there are even some sturdy trees present, however over much of the dump surface there is scant
Photograph 2.2  Aerial view looking south west towards White's dump, March 1983 (Courtesy of Dr. J.R. Harries, A.A.E.C.). Note the flat pancake shape of the dump.
Photograph 2.2  Aerial view looking south west towards White's dump, March 1983 (Courtesy of Dr. J.R. Harries, A.A.E.C.). Note the flat pancake shape of the dump.
Map 2.3  Whites Overburden Dump
vegetation especially where pyrites abounds. The radial dumping of material during construction formed a number of rainfall catchment areas. The drainage pattern therefore on White's dump is fairly well defined with the main run-off channel being down the central ramp region of the dump. A weir has been built at the base of the run-off channel to monitor discharge events and the level of pollutants dissolved in run-off water. A water balance model for White's dump developed by Daniel et al. (1982) indicates that only 16% of rainwater incident on White's dump runs off. Of the other 84%, approximately 25-35% evaporates, 5% is discharged as springwater and the bulk, 50%, percolates through the dump to the groundwater.

The seepage of springwater from the base of the dump, laden with metal salts, often produces salt encrustations such as the one shown in Photograph 2.1. By about the middle of the wet season springs such as these develop along the complete length of the eastern wall and they continue to flow into Fitch creek until the early part of the dry season. Springs also develop around the base of the northwest area but flow ceases 5-7 days after an intense storm.

For a more general discussion of the effect of mining on the environment at Rum Jungle see Davy (1975).

2.4 Simple Model of White's Heap (Ritchie, 1977)

Motivated by the need to understand the rate-limiting mechanisms of pyritic oxidation in such waste rock dumps and to quantify various parameters concerning the transportation of reactants and reaction
products to and from reaction sites within the heap, a mathematical model was developed by Ritchie (1977). The model considers the flat pancake shape of White's dump to be a homogeneous permeable semi-infinite slab with one face open to the atmosphere, and investigates the consequences of assuming the oxidation rate is governed by the rate at which oxygen can be transported from the surface of the dump to reaction sites within the dump by diffusion.

All reactants, besides oxygen, required for the oxidation process were assumed available including bacteria which catalyse heavy metal solubilisation. Catalysing bacteria are present in White's dump and serve to accelerate the chemical reaction rate. However, enhancement of the reaction rate is of little consequence to the model, since the rate of reaction is already assumed faster than the bulk diffusion of molecular oxygen to oxidation sites within the dump.

A planar moving boundary formulation was therefore adopted where, between the surface of the dump and the moving reaction interface lay a region which was fully reacted, while ahead of the interface the dump was totally unreacted. Because bulk diffusion of oxygen through the pore spaces of the dump was assumed to be the rate-controlling step, this necessarily implied the instantaneous reaction of oxygen arriving at the reaction interface and therefore a zero concentration of oxygen at that point. Also the mass flux of oxygen through the moving boundary (that is, oxygen removed by the oxidation of pyrites) was taken to be directly proportional to the velocity of the front and depended explicitly on the density of the pyrites in White's
dump, the ratio of the mass of oxygen to the mass of pyrites consumed in the oxidation reaction and the diffusion coefficient of oxygen within the pore spaces of White's dump.

Ritchie (1977) outlines the analytic solution for the oxygen profile and motion of the moving reaction front within the dump as well as calculating temperature profiles for the heap with this simple model. The equations governing the model and solutions to these equations for, say, the spatial oxygen concentration profile and the motion of the planar moving front are given in Appendix A together with a summary of an alternate (more general) solution procedure developed by Davis and Hill (1982a) (see also Appendix P).

The model as proposed by Ritchie (1977) estimates an annual oxygen consumption of the same order as that indicated by measurement of pollution levels emanating from the heap, indicating that diffusion is a feasible transport mechanism of oxygen within the dump. However, the model necessarily predicted the heat source density to be a δ-function centered on the moving reaction front itself whereas experimentally a spatial distribution is observed. In subsequent chapters comparison will be made between this relatively simple (and useful) model and the more detailed model considered in this thesis.
CHAPTER 3

LITERATURE SURVEY

3.1 Introduction

As indicated in Chapter 1 using heap leaching, as a commercially viable process, to recover valuable minerals has been proceeding for many years. Investigations, studying mechanisms that control the rate of extraction of minerals from heap leaching have been extensive, especially in the areas of chemistry, physics and biology. Such studies have produced a firm empirical and, to a degree, theoretical base upon which models may be developed, describing in a predictive sense the behaviour of leaching ore piles.

In Section 3.2 various commercial heap leaching models are surveyed with a view to assessing the merit of such models under natural weathering conditions. Also two models which use concepts similar to those discussed in Section 3.2 (with particular reference to mining engineering), will be considered in Section 3.3 but with reference to other branches of science, namely metallurgy, soil science, petroleum engineering, chemical engineering, chromatography, biology and others. Consideration of such alternate models and phenomena can only aid in our understanding of our own modelling attempts and also enable more precise models to be developed. Therefore before proceeding to model the oxidation of pyritic mine waste, under natural weathering conditions, we consider previous heap leaching models and models from other areas of interest.
3.2 Heap Leaching Models

Over the last twenty years or so models have been proposed which govern leaching processes in low-grade heap leach piles mainly with a view to commercial production of copper, but also nickel and uranium. Industrial leaching of low-grade ore as dumps, has been proceeding for many years, most noticeably at Rio Tinto Spain. Qualitative observations at such leaching operations (Taylor and Whelan, 1943) indicate that one of the major limiting mechanisms involved is transportation (or availability) of oxidising agent to reaction sites within waste heaps. Accordingly, techniques to maximise the rate of recovery of minerals from heap leaching have been developed, ranging from alternate wetting and drying of the heap to "rubblization" (sic) of ore by nuclear detonation (Lewis, 1970, Lewis et al., 1973). Models therefore have been proposed to quantify the effectiveness of such techniques in optimising parameters to maintain high production levels.

Harris (1969) was one of the first to propose a model for the leaching of low-grade ores. He investigated the heap leaching of copper sulphide and copper oxide ores at the Rum Jungle mine site in the Northern Territory (in operation during the 1960's). The model of Harris considered the kinetics of a representative particle of the waste heap relative to the leaching kinetics of the dump itself, however, the controlling parameters were based on the leaching response of the entire heap and therefore can only predict heap leaching behaviour on past response. Moreover, he introduced
a characteristic length scale $L$ which may be the size of a particle or the height of the heap and therefore presents difficulties when utilizing the model. Townsend (1969), in investigating the same leaching system, developed convective dispersal side capacitance equations to describe the movement of solute within waste heaps. The model was drawn from the chemical reaction engineering literature and was found to be validated by experimental results.

In the mid 1970's a number of models of the extraction of minerals (especially copper) by heap and in-situ leaching were published. Three main models 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 models 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 3.1 highlights the details of the models by showing a segment of a particle and graphically illustrating the change in concentration of copper and reactant with location in the particle. All three models assume spherical geometry for the particles and describe the kinetics in terms of the inward radial diffusion of reactant and chemical reaction within the particles.

The model of Bartlett (1973) (Figure 3.1-a) predicted the rate of oxidative leaching of copper from an in-situ fragmented low-grade sulphide ore. It consisted of the non-steady state diffusion of oxidant in the particle coupled with an empirically determined loss mechanism describing the oxidation reaction within grains of sulphide
disseminated throughout the particle. The model assumed a relatively slow chemical reaction rate and therefore a large reaction zone resulted containing mineral grains at various stages of oxidation. The net average extraction for the ore was determined by a weighted sum over all particle sizes.

The model of Braun et al. (1974) (Figure 3.1-b) is applicable to in-situ solution mining where ore is converted into rubble and then inundated by a leach solution containing oxidants. A "computerised geometric model" was proposed which introduced the concept of a narrow moving reaction zone, within the particles of the ore, of a specific experimentally determined thickness. Within the postulated reaction zone, sulphide grains were assumed to be in all stages of reaction. Steady state diffusion of reactant through the previously reacted portion of the ore particle was assumed, followed by chemical reaction within the reaction zone. The physical properties of the ore included in the model were size, shape and mineral content of the ore. This model corresponds to a faster chemical reaction rate than the model of Bartlett (1973). Madsen et al. (1975) applied the model of Braun et al. (1974) to experimental results obtained from pilot scale (7 tonnes), long term (500 days) leaching studies. They concluded that excellent agreement was found between the theoretical mixed model and the laboratory leaching results. A valuable discussion of the relative importance of surface reaction control compared to diffusion control for a single reacting particle is also included in this paper.

Roman et al. (1974) (Figure 3.1-c) proposed a model describing
the leaching of copper oxide ore in heaps. The model considered the
reaction zone within the particle to be a distinct moving reaction
front brought about by an instantaneous chemical reaction rate. They
too considered the pseudo-steady state case which is equivalent to
assuming the equilibrium concentration profile behind the reaction
front is established rapidly since the reaction front is moving
slowly. The model assumed that the rate of leaching was controlled
by a deficiency of reactant in the bulk solution and by the diffusion
of reactant through particles to the moving reaction interface. To
account for the loss of reactant in the bulk solution, the model
heap was divided into unit heaps and an approximation was made to the
depletion of acid in the leaching liquor as it was transported down
through each unit heap. By contrast, the models of Bartlett (1973)
and Braun et al. (1974) both assumed constant oxidant concentration
around each particle within the ore mass being leached. This
assumption may well be valid in commercial applications where the
bulk transport of reactant is not deemed rate controlling, that is,
the chemical reaction rate is slow compared to transport processes.

Models describing heap leaching behaviour have also been proposed
and Averill (1976). In a series of papers Roach and Prosser (1975,
1977, 1978) developed constitutive equations describing the rates of
chemical processes for leaching reactions in terms of the various
chemical and physical parameters of the ore, the values of which are
available in the literature. Their aim ultimately is to develop model
equations appropriate to more than one ore type. The model equations developed thus far assume steady state conditions and are similar to previous recovery models. The ultimate recovery and rate of recovery of an ore are fundamental objectives in modelling processes involved in a commercial heap leaching venture, so Roach and Prosser (1975) attempted to relate these important output parameters to a few, potentially measurable, mineralogical features. Quantifying the accessibility of the valuable mineral to the external reagent is also important in leaching low grade concentrates and they have been at least partially successful in this area.

Cathles and Apps (1975) propose a model which includes temperature dependence, oxygen balance and air convection effects. The individual particle kinetics are described in terms of the quasi-steady state reaction zone formulation of Braun et al. (1974). The oxidant concentration outside the particle is non-constant and oxidant is assumed driven through the dump by a pressure difference over the dump brought about by the loss of oxygen and production of heat in the chemical reaction within the particles. The model was used to simulate a small test dump and results showed good agreement. Cathles et al. (1977) and Cathles (1979) extended the model to include the effects of bacterial catalysis and, after calibration of the model on test dumps built and operated by the Kennecott corporation, it was compared with results from large scale leaching experiments conducted at the New Mexico Institute of Mining and Technology in Socorro, New Mexico. The large scale tests tended to confirm the general
validity of the model, however, detailed predictions were well off in some circumstances. Subsequently, a two dimensional model has been proposed by Cathles and Schlitt (1980) in an attempt to account for the lateral transport of heat and oxidant within leaching dumps.

Averill (1976) considered the leaching behaviour of two types of copper ore; sulphide and oxide ores. The model of Braun et al. (1974) was utilized for the sulphide ore with a non-constant bulk oxidant concentration, the aim being to allow scale-up of experimental data to full scale dump leaching. When investigating the kinetics of the copper oxide ore, the bulk transport of reactant to the particle surface was accounted for by considering the major transport mechanism within the pore space of the dump to be forced mass transport of lixiviant governed by a constant velocity profile. The predictive capabilities of these models were shown to be reasonably accurate when compared with experimental results.

In general the models reviewed in this section describe the leaching response of the entire heap by focusing on transport and reaction mechanisms within particles of the heap. Often in these models, the bulk transport mechanism, delivering oxidant from outside the heap to reaction sites within the heap, is neglected as unimportant. The usual assumption, therefore, is that the oxygen concentration surrounding each particle of the dump is constant, which greatly simplifies the mathematics involved. In some cases a bulk advective transport mechanism is included in the model. The assumption of a constant oxygen concentration through the heap may
well be valid in a commercial heap leaching operation, however, for naturally weathering waste rock dumps, bulk transport processes are of prime importance since oxidant in a naturally reacting system is not artificially replenished by pumping of oxidant through heap piles, which is the case for commercial recovery of minerals by hydrometallurgical techniques. On the other hand, the model of Ritchie (1977) (see Section 2.4) considers White's dump (undergoing natural pyritic oxidation) to be a homogeneous slab where transport of oxygen from the atmosphere, exterior to the dump is diffusional, thus taking no account of heterogeneities in the system introduced by the particles of the dump. So the simple model of Ritchie (1977) considers important rate-limiting mechanisms in a naturally oxidising system, to be associated with the bulk transport properties of the dump rather than microstructural phenomena within the particles of the dump.

In this thesis we attempt to marry the two concepts of a bulk transport mechanism and the particulate microstructure of a waste dump when modelling naturally oxidising pyritic material. Both concepts are seen as integral parts of a comprehensive model of a waste rock dump where the interaction between oxidising particles and pore space oxygen concentration plays an important role. The union of the two important concepts yields a dual region formulation in which transport processes within the pore space of the dump and transport and reaction mechanisms within particles of the dump are both accounted for.
In the next section we review literature pertaining to two models, which take differing points of view when modelling dual region formulations. The difference in the two models lies in their identification of the microstructure of the system, in our case, particles making up a waste rock dump.

### 3.3 Dual Region Models

Two models that may be of value to us in our own modelling attempts, we will refer to as the two path model and the two stage model. Both models appear in a wide range of literature and attempt to describe mass transport processes in porous media. One formulation is based on the concept of a dual system of connected pathways at each point within a medium, whereas the other model identifies specific macroscopic and microscopic pathways, where the microscopic system is a geometrically well defined, physically separate region of the medium. Both approaches take the point of view that the microscopic configuration is important to the macroscopic description. However, the two models differ in their identification of the microstructure. Since both of these models are used extensively in other areas we review the literature with a view to considering the appropriateness of either model when modelling the oxidation of pyritic mine waste.

#### Two Path Model

When studying seepage in fissured rocks (for application to petroleum engineering) Barenblatt et al. (1960) introduced the concept of a "doubly porous" media. They considered that a fissured (or fractured) rock contained within it an interconnected network of
two types of pathways, fissures and pores, where the "porous blocks" are completely surrounded by fissures. Two average pressures were identified within the media; one associated with the fissure system, and the other with the porous matrix blocks. The rock was considered macroscopically rigid while being compressible on a microscopic scale. Also the liquid was considered compressible and the velocity of the liquid in the pores and fissures was assumed given by Darcy's law. The coupled system of partial differential equations governing pressure changes in a "doubly porous" medium were then written as

\[
\begin{align*}
\frac{\partial p_1}{\partial t} &= D_1 \nabla^2 p_1 - k_1'' p_1 + k_2'' p_2, \\
\frac{\partial p_2}{\partial t} &= D_2 \nabla^2 p_2 + k_1'' p_1 - k_2'' p_2,
\end{align*}
\] (3.3.1)

with appropriate boundary and initial conditions, and where the constants \(D_i, k_i'' (i=1,2)\) are measures of the porosity, permeability, compressibility and size of the rock, and the viscosity and compressibility of the liquid. Barenblatt et al. (1960) assumed the transfer of the liquid from one path to the other to be proportional to the pressure difference between the pathways and therefore took \(k_i'' = k_i'\) and \(k_i'' = k_i''\). The region of fissures was thought to have low porosity and a high permeability, whereas the region of porous blocks was thought to have a high porosity and a low permeability. This enabled a simplification to be made to (3.3.1), by neglecting appropriately small terms, written as
\[
D_1 \nabla^2 P_1 + k_1' (P_2 - P_1) = 0, \\
\frac{3P_2}{\partial t} + k_1'' (P_2 - P_1) = 0.
\] (3.3.2)

Equations (3.3.2) were solved in Barenblatt et al. (1960), Barenblatt and Zheltov (1960) and Barenblatt (1963) for various boundary conditions. In later work Barenblatt (1964) extended the equations to consider the flow of two immiscible fluids (a liquid and a gas) in a fissured-porous media. Criticism of this model (Boulton and Streltsova-Adams, 1978; Streltsova-Adams, 1979) centres on the assumption that in any infinitesimally small volume there are a large number of fissures and matrix blocks. Therefore, in practice, it is impossible to know whether a particular point lies in a porous block or fissure.

In a number of papers Aifantis (1979, 1980) rederived equations (3.3.1) using the continuum theory of mixtures, and introduced in Aifantis (1977), the concept of a "multiporous media" showing Barenblatt's equations to be a simplifying case. These equations have also been derived in Hill (1980) and, Hara and Fujita (1978) from a probabilistic viewpoint by extension of the classical random walk model of diffusion. These authors consider that, per time step, a particle jumps one spatial unit to the right or left, or stays stationary as in the classical random walk model but also included was the possibility of the particle changing pathways. Both authors extended their models in subsequent papers (Hill, 1979; Hara, 1979). Other areas of application of this model are noted briefly below.
When considering heat conduction in a two component heterogeneous medium, where an average temperature is identified with each component of the medium and Fourier's law for heat conduction is assumed to be obeyed in each component, equations similar to (3.3.1) can be obtained (Rubinstein, 1948). A metallurgical application in Hill (1979), Aifantis and Hill (1980), and Aifantis (1979) considered not only lattice diffusion of atoms in metal but also the possibility of diffusion along grain boundaries, dislocations, free surfaces or microcracks. This model was described in terms of two possible diffusion paths and has been termed by the authors as "double diffusivity". Another interesting application, proposed by Molz (1976, 1981) and Aifantis (1977) is in the area of water transport in plants. Molz (1976, 1981) gave a rigorous and detailed derivation of water flow through plant tissue where two fairly distinct flow pathways were assumed present, the symplasm pathway which is interior to the plasmalemma and the apoplasm pathway which is exterior. The theoretical development and evaluation of physical constants were compared with experimental findings. Aifantis (1977) derived a more general set of equations but no experimental verification was attempted. Solutions to (3.3.1) have been obtained by Hill and Aifantis (1980), who have written down solutions to specific boundary value problems in terms of known solutions of the classical diffusion equation. Solutions have also been found by Zhongxiang and Lishang (1980) by construction of a new class of special functions.

Before moving on to the two stage model it should be emphasised
that equations (3.3.1) assume that at every point of a particular medium the possibility exists for a change of paths, and that the medium is separated into two overlapping continuums, each filling the entire space. This implies that variables and coefficients appearing in these equations have the meaning of macroscopically averaged values at a point. It is interesting to note also that equations (3.3.1) appear extensively in the chemical engineering literature, from as early as 1908 (Eucken, 1908), describing the diffusion of two species within a medium with a first order reversible chemical reaction occurring (see also Sherwood and Pigford, 1952, page 328). However, here we are interested in two region porous media models not two species ones.

**Two Stage Model**

We refer to the second approach as the two stage model for two reasons; firstly because the model equations are formulated in two stages by considering transport mechanisms in the macrostructure of the media (which includes a loss mechanism to the microsystem) linked to transport and reaction processes in a geometrically well defined separate microstructure. Secondly the technique for solving such a formulation occurs in two stages; solving for the equations governing the microstructure (which are linked to the macrosystem only via boundary conditions on the microsystem), which then enables solution of the equations governing the macrostructure. We will now proceed to describe the two stage model via fluid flow in a fissured porous media thus enabling comparison with the "doubly porous" media model
of Barenblatt (1960). Other areas of application will also be discussed.

McNabb (1978) reconsidered the problem of propagation of pressure in a fractured porous medium, where the fissures partitioned the rock into blocks, by identifying with the porous blocks a specific geometry. McNabb, like Barenblatt (although unaware of Barenblatt's work) introduced the concept of two pressures in the medium, however, in contrast to Barenblatt one pressure is assumed to be contained specifically within the blocks of the medium and the other within the fissures, neither being averaged over a large number of porous blocks.

The fluid pressure in the fissure at position \( x \) and time \( t \) we denote by \( P_1(x, t) \) whereas the pressure in the block at time \( t \), at the point \( y \) and in the neighbourhood of \( x \), we denote by \( P_2(x, y, t) \). It can be seen from this formulation that we are locating a particular porous block within the medium via \( x \) and then describing the pressure changes within the block using \( y \) and \( t \). The equation governing pressure transmission in a block can be written as

\[
\frac{\partial P_2}{\partial t} = D_2 \frac{\partial^2 P_2}{\partial y^2} \quad \text{for} \quad y \in V_x, \tag{3.3.3}
\]

where a necessary boundary condition is that the pressure is continuous across the block-fissure interface given by

\[
P_2(x, y, t) = P_1(x, t) \quad \text{for} \quad y \in S_x, \tag{3.3.4}
\]

where \( V_x \) is the volume occupied and \( S_x \) the bounding surface of a block in the neighbourhood of \( x \) and \( D_2 \) is a constant depending on
properties of the rock and liquid. The equation for flow in the fissure system can be written

\[ \frac{\partial P_1}{\partial t} = D_1 \nabla^2 P_1 + S(x, t), \tag{3.3.5} \]

where \( S(x, t) \) describes the exchange of fluid flowing into the fissures from the blocks (or vice versa) expressed in general form as

\[ S(x, t) = \frac{D_2}{V_x} \int \int_{S_x} \text{grad} P_2(x, y, t) \cdot dS \quad \text{for} \quad y \in S_x. \tag{3.3.6} \]

The constant \( D_1 \) again depends on properties of the liquid and porous media. In petroleum engineering, well drawdown dynamics have been investigated using similar models to the one outlined above, however included also is a two species formulation usually involving the interaction between oil and water or gas. Such papers (de Swaan, 1978; Streltsova-Adams, 1979; and Davis and Hill, 1982b, Appendix P) develop integrodifferential equations which account for the delayed yield from storage of oil when water is used as a displacing medium. These models are not pursued further here.

It is apparent from the formulation of equations (3.3.3) to (3.3.6) that the method of solution becomes a two stage one. We can solve for \( P_2 \) from (3.3.3) and (3.3.4) after assuming a specific geometry relating to \( y \) and then substitute \( P_2 \) into (3.3.6) to give \( S(x, t) \) which in turn can be substituted into (3.3.5) to give \( P_1 \). An illustration of the method of solution for this approach can be found in Skopp and Warrick (1974) where the transport of a reactive solute in soil was described in terms of the model outlined above except that an advection term was included instead of the diffusion term in
the macrosystem. In Skopp and Warrick the "porous blocks" (particles of soil) were considered to be a stationary immobile phase where only lateral diffusion occurs, thus acting as a trapping region and the "fissures" (pore space) were considered to be a parallel mobile phase whose loss term consisted of the flux through the boundary into the immobile phase. One of the first to consider such a trapping region was Turner (1958) who, when modelling flow in packed beds, assumed that connected with each flow channel was a certain distribution of dead-water pockets in which diffusion but no flow took place. This model was further generalised in Aris (1959). Variations of the same model have also appeared in the chromatography literature (Kubin, 1965; Kucera, 1965). In Kucera (1965), for example, two concentrations were identified, one in the free volume of the mobile phase and the other in the porous grains of the packing material. Consideration was given to longitudinal diffusion and convection and radial diffusion into grains of varying shapes. In Babcock et al. (1966) the longitudinal dispersal mechanism of heat during flow of a fluid through unconsolidated spherical beads was studied. Convection and diffusion were assumed important vertically whilst the microstructure was assumed to be spherical particles. McNabb (1975) used the two stage approach, in a three stage model to describe the reduction of agglomerates of ferrous oxide granules. Three regions were postulated where transport process (primarily diffusional) controlled the reduction process. Another metallurgical application of these equations occurs in Ma and Lee (1976) where diffusion in porous pellets formed from zeolite crystals was seen to
involve two main mechanisms, diffusion through the micropore structure within the crystals (intracrystalline diffusion) and diffusion through the macropore structure between crystals (intercrystalline diffusion). The geometry considered was one of spheres embedded within spheres. A further interesting application of this model is in the area of medical research (Mor et al., 1980) where under investigation was the possibility of replacing the transfusion of blood of jaundiced infants by the process of removal of bilirubin from blood by packed bed absorption (hemoperfusion). The authors obtained reasonable agreement between their theoretical and experimental results. The model equations are usually written in terms of the Laplace transform and then either numerically inverted (Ma and Lee, 1976), or the first few moments are obtained (Kubin, 1965; Kucera, 1965) or a simplified solution is found (McNabb, 1978). Analytic inversion is also possible in some instances (Skopp and Warrick, 1974; Babcock, et al. 1966).

3.4 Summary

The models proposed by McNabb (1978) and Barenblatt et al. (1960), outlined in the previous section, are clearly different, although both approaches claim to model the same phenomenon and both involve a two region analysis. In examining the appropriateness of either model in a given physical situation we need to consider the known basic information concerning the microstructure. In references cited in the last section consideration of the microstructure has lead to solving initially the diffusion equation in a semi-infinite
plane (Skopp and Warrick, 1976; Kucera, 1965), cylinders (Kucera, 1965) or spheres (see, for example Turner, 1958, and Mor et al. 1980). It is necessary in each of these cases to identify the microstructure with a characteristic length scale which may or may not be an obvious parameter of the system or indeed constant in value (as in the case of particles of soil). The two path model however, assumes a microstructure that is random in nature and dispersed throughout the medium, seemingly dictating that no characteristic length scale need be associated with the model. In Barenblatt’s application as outlined, however, identification of the parameters k', and k'' is a non-trivial problem since these constants involve a characteristic length scale for the system which becomes difficult to quantify for such an assumed "blurred" media. The two path model does also present other difficulties, since it forces an assumption about the form of the transfer function between the two phases, which is generally taken to be a linear function of the two dependent parameters but in general it need not be. Indeed, it is clear from the derivation presented by Barenblatt et al. (1960) that the system of equations proposed are a highly linearised version of a more complex non-linear system.

In summary the applicability of either model to a given situation depends somewhat on the degree of randomness of the microstructure and also the accessibility of experimental data pertaining to the microsystem. In a well ordered system, with reasonably well defined static geometrical microstructure, the two stage model could be used
to best advantage, however, if the microstructure of the medium is
disordered and random in nature then the dual path approach would
be more appropriate given the necessary data. It may be of interest
therefore to attempt a description of the model for water flow in
plants as in Molz (1976) via the two stage model, because of the
specific microstructural geometry involved. Conversely it may also
be feasible to consider the problem of Skopp and Warrick (1974) using
the two path model.

Here we pursue a model using the two stage model because of
the discrete particulate nature of waste rock material. Even though
there are a wide range of particle sizes and shapes, it is
reasonable to assume spherically shaped particles embedded within a
planar geometry. The two stage model then allows us to describe the
processes of oxidation within particles of a dump containing pyrites
without an ad-hoc decision about the transfer function between the
two regions. The experimental data available also allows us to
proceed in this direction.
CHAPTER 4

THE MATHEMATICAL MODEL

4.1 Introduction

In previous chapters the geographical framework, in which to study the pollution problem at Rum Jungle, has been established and previous models of both heap leaching and related phenomena have been discussed. In Chapter 3, in particular, we outlined various mining engineering models of leaching systems, which focus attention on rate-limiting processes within reacting particles of the ore heap. Also, in Chapter 3, dual region models concerned with the interaction between microstructural phenomena, such as reacting particles of a leaching heap, and macrosystem bulk transport mechanisms, were reviewed. In this chapter we adopt the two stage model, as given in Section 3.3, and use it to develop mathematical equations, modelling the oxidation of waste mine material containing pyrite, with particular reference to White's overburden dump at Rum Jungle. Our goal is to develop a predictive model (not a curve fitting model) whereby the unknown physicochemical parameters and constants appearing in the model are obtained directly from measurement of the various physical and chemical aspects of the waste dump itself and the reacting ore, or obtained directly from tables of such data.

Harries and Ritchie (1981) investigated the pyritic oxidation rate in White's dump at Rum Jungle using temperature profiles measured down probe holes drilled through from the surface to the base of the dump. They produced oxidation rate profiles for the dump, in the
form of spatial heat source distributions, showing that oxidation of pyrite proceeds at an appreciable rate, in at least one region of the dump, to a depth of 15m. This implies that oxygen not only needs to be supplied to a depth of 15m but supplied at a rate commensurate with that of the oxidation rate, estimated by Harries and Ritchie (1981) to be $8 \times 10^{-8} \text{kg s}^{-1}\text{m}^{-2}$. Suppose, for the moment, that oxygen is supplied from the atmosphere at the surface of the dump and that the oxygen concentration distribution from the surface to 15m in depth is linear and where at 15m the oxygen concentration is set to zero. That is, oxygen is reacted as fast as it is transported to the reaction site at 15m. The diffusional supply of oxygen, then, can be found, from these assumptions, to be $7 \times 10^{-8} \text{kg s}^{-1}\text{m}^{-2}$ which is comparable to the rate estimated from the measurement studies of Harries and Ritchie (1981).

In this thesis, therefore, we examine the consequences of modelling oxidising pyritic waste material assuming that diffusion is the bulk transport mechanism for the supply of oxygen from the atmosphere exterior to the dump to reaction sites within the dump. Also, we consider the model to be diffusion rate-limited where other possible limiting processes, such as the chemical reaction rate, are faster than the rate of supply of oxygen by diffusion.

The two stage model proposed, for the oxidising waste rock dump, is given in Section 4.2 where the first stage consists of the diffusional transport of oxygen through the pore spaces from the surface of the dump to particles embedded within the dump; and
the second stage accounts for the transport of oxygen to oxidation sites within the particles of the dump. The various constants in the model are assigned values or a range of values in Section 4.3. A new semi-analytic solution procedure is outlined in Section 4.4, to solve equations governing reaction and transport processes within a single oxidising particle of the dump. By researching transport and reaction mechanisms within a single particle of the dump, using the new solution technique, we gain information regarding parameters of interest, and insight into parameters of importance, within the oxidising dump. This analysis becomes particularly useful when tackling the interaction between the particles of the dump and the bulk transport mechanism within the pore space of the dump. Approximate dimensionless model equations are derived and justified in Section 4.5 while in Section 4.6 formulae are developed for the heat source distribution and sulphate production rate. In the final section the model equations are modified to include a particle size distribution appropriate to White's overburden dump.

4.2 The Model Equations

In this section equations are proposed which describe the natural leaching behaviour of White's overburden waste rock dump at Rum Jungle. Since White's heap is small in height (~18m) compared with its extent (~500m in diameter) we model the dump as a porous slab with the surface open to the atmosphere while the base of the dump is assumed impermeable to oxygen. Figure 4.1 shows the basic geometrical structure as assumed here compared to that of Ritchie (1977). As
Figure 4.1  Schematic diagrams of models describing pyritic oxidation within White's dump
(b) The present proposed model.
illustrated the basic conceptual difference lies in identifying where in the dump the chemical reaction occurs. In Ritchie (1977) the dump is assumed homogeneous and therefore a macroscopic moving boundary formulation is adopted, whereas here we take account of some of the heterogeneity of the dump by assuming a particulate microstructure within which the oxidation of pyrites occurs. Hence the oxidising waste dump is conceptually a two stage model (see Chapter 3) and is considered geometrically to be a planar finite dimensional slab with spherical pyrite-containing particles embedded within it. We also propose that pyrite is evenly distributed throughout the particles of the dump and that the oxidation process proceeds within each particle. Further, since one of the reactants required in the pyritic oxidation reaction is water, then we associate with the particles of the dump an aqueous phase through which oxygen is transported to reach reaction sites within particles.

In the preceeding section we concluded that diffusion is a feasible transport mechanism for the supply of oxygen from the surface of the dump to reaction sites within the dump. Therefore we assume (as does Ritchie, 1977) that all reactants required for the oxidation process are freely available except for oxygen which is supplied via diffusion from the atmosphere exterior to the dump. Also, even though bacteria are known to catalyse the oxidation process (Brierley, 1978), we ignore their effect since for a diffusion rate-limited model any chemical reaction rates are assumed much faster than the rate of supply of oxygen by diffusion to the reaction sites, and
bacterial catalysis will only enhance this effect by accelerating the reaction rate. Therefore a diffusion transport model is adopted for the mass balance of oxygen within the pore space of the dump. Since oxidation proceeds at reaction sites within particles, the model must also include an exchange or volume loss mechanism whereby oxygen is transferred from the pore space of the dump across the gas-liquid interface into the reacting particles. If oxygen transport within reacting particles is assumed driven by a concentration gradient then the exchange rate is simply the diffusional mass flux of oxygen through the gas-liquid interface.

The assumption that diffusion of oxygen is the "slow" process and that pyrites is evenly disseminated throughout particles of the dump, leads to a shrinking-core or moving reaction front formulation within each of the particles of the dump. This is because oxygen transported to the reaction front is instantly reacted by the oxidation of pyrites (see, for example, Levenspiel, 1972, page 364 or Szekely et al., 1976, page 65). This formulation divides each particle into two regions (Figure 4.2) - an outer reacted region and a shrinking unreacted core separated by a clearly defined moving reaction front, with the velocity of the interface being related directly to the mass flux of oxygen through the moving front. There is a large amount of literature dealing with such moving boundary problems, some of which will be discussed in Section 4.4.

Therefore the model governing oxygen transport in a dump undergoing pyritic oxidation is a two stage one - diffusion of
Figure 4.2 Schematic diagram of an oxidising particle of the dump.
gaseous oxygen from the surface of the dump through the pore space, followed by diffusion into reaction sites within particles comprising the dump.

The model equations given below are outlined for a dump comprised of single sized particles, however a particle size range will be considered in a subsequent section and is omitted here for simplicity.

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

\[
\frac{\partial u^*}{\partial t^*} (x^*, t^*) = D_1 \frac{\partial^2 u^*}{\partial x^2} (x^*, t^*) - q^* (x^*, t^*), \quad 0 < x^* < L, \quad (4.2.1)
\]

where \( u^* (x^*, t^*) \) is the concentration of oxygen within the pore space of the dump, \( q^* (x^*, t^*) \) is the rate of volume loss of oxygen from the pore space to the particles of the dump, \( p_1 \) is the porosity of the dump, \( D_1 \) is the diffusion coefficient of oxygen in the pore space of the dump, \( L \) is the height of the dump, \( x^* \) is the vertical coordinate (depth in the dump) and \( t^* \) is time. We assume that the concentration of oxygen at the top surface of the dump is just the concentration of oxygen in air,

\[
u^* (0, t^*) = u_0, \quad (4.2.2)
\]

while at the base of the dump a "no flow" condition is applied

\[
\frac{\partial u^*}{\partial x^*} (L, t^*) = 0. \quad (4.2.3)
\]

We further assume that initially there is no oxygen within the dump,

\[
u^* (x^*, 0) = 0. \quad (4.2.4)
\]
Consider now the loss term $q^*(x^*, t^*)$ in (4.2.1). As previously indicated, since water is necessary for both the oxidation of pyrite and the bacteria that catalyse the reaction, the oxidation sites within the particles are assumed in an aqueous phase. Also since the particles of the dump are assumed spherical and to all have the same size radius, for the moment, then the loss term takes the form

$$q^*(x^*, t^*) = v D_2 a \frac{\partial v^*}{\partial r^*}(a, x^*, t^*), \quad (4.2.5)$$

where $v^*(r^*, x^*, t^*)$ is the concentration of oxygen within a particle of the dump, $r^*$ is the radial distance within a particle, $a$ is the radius of the particle, $D_2$ is the diffusion coefficient of oxygen in water and $v$ is the number of particles per unit volume of the dump. A dimensionless factor could also be introduced into equation (4.2.5) to take account of the fact that the effective surface area of a spherical particle is different to an actual particle of the dump due to non-sphericity or convolution of the particle surface. For perfectly spherical particles the constant $v$ can be given as

$$v = \frac{3(1 - \pi_1)}{4\pi a^3}, \quad (4.2.6)$$

and therefore (4.2.5) can be rewritten as

$$q^*(x^*, t^*) = \frac{3(1 - \pi_1)D_2}{a} \frac{\partial v^*}{\partial r^*}(a, x^*, t^*). \quad (4.2.7)$$

Having accounted for the bulk gaseous transport of oxygen within the pore space of the dump we now develop equations governing mass transport and chemical reaction processes within the particles. The
diffusional transport of oxygen from the surface of the particle to the moving reaction front can be written in radially symmetric spherical coordinates as

\[
\frac{\partial v^*}{\partial t^*}(r^*,x^*,t^*) = D_2 \frac{\partial^2 v^*}{\partial r^*2}(r^*,x^*,t^*) + \frac{2}{r^*} \frac{\partial v^*}{\partial r^*}(r^*,x^*,t^*), \quad (4.2.8)
\]

for \( R^*(x^*,t^*) < r^* < a \), where \( R^*(x^*,t^*) \) is the position of the reaction front within particles of the dump varying both with time and depth in the dump. Since the reaction rate proceeds as fast as oxygen can diffuse from the surface of the dump, then the concentration of oxygen at the front will be zero,

\[
v^*(R^*(x^*,t^*), x^*, t^*) = 0. \quad (4.2.9)
\]

Also a mass balance for oxygen transport and reaction across the moving reaction front (Crank, 1975, page 301) gives

\[
\frac{\partial R^*}{\partial t^*} = \frac{(1 - p_1)}{\varepsilon \rho_S} \left( D_2 \frac{\partial v^*}{\partial r^*}(R^*,x^*,t^*) + v^*(R^*,x^*,t^*) \frac{\partial R^*}{\partial t^*} \right), \quad (4.2.10)
\]

however, upon substitution of (4.2.9), equation (4.2.10) simplifies to

\[
D_2 \frac{\partial v^*}{\partial r^*}(R^*,x^*,t^*) = - \frac{\varepsilon \rho_S}{(1 - p_1)} \frac{\partial R^*}{\partial t^*}, \quad (4.2.11)
\]

where \( \varepsilon \) is the mass of oxygen used per mass of sulphur in the oxidation reaction and \( \rho_S \) is the density of sulphur in the dump. Initially the moving interface is at the surface of the particle, written as

\[
R^*(x^*,0) = a. \quad (4.2.12)
\]

Note that (4.2.9) and (4.2.12) imply a zero initial condition for the oxygen concentration in the particle.
The model now lacks only a boundary condition at the outside of the particle linking oxygen concentrations in the pore spaces of the dump with those in the particle. Since oxidation occurs in the aqueous phase we are led to consider a gas-liquid interface, on both sides of which the transportation of oxygen is diffusional. We therefore equate the concentration of oxygen (within the water) within the particle at the outer boundary of the particle with the maximum solubility of oxygen in water at the partial pressure of oxygen in the pore space. Then using Henry's law and the gas law (see Section 4.3) we can relate the partial pressure of oxygen in the pore space to \( u^* \) and \( v^*(a, x^*, t^*) \) to yield the outer boundary condition for the particles of the dump,

\[
v^*(a, x^*, t^*) = \gamma u^*(x^*, t^*),
\]

(4.2.13)

where \( \gamma \) is a constant. It should be emphasised that the boundary condition (4.2.13) 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 at the outside of each particle, including a mass transfer coefficient measuring the mass flow through the gas-liquid interface (see, for example, Bird et al., 1960).

From physical considerations when \( R^*(x^*, 0) = 0 \) for any \( x^* \) and \( t^* \) we impose the extra condition

\[
\frac{\partial v^*}{\partial r}(0, x^*, t^*) = 0,
\]

(4.2.14)
that is, when a particle is fully reacted no oxygen is transported through the centre of the particle, and the oxygen concentration in the particle then increases with time to complete saturation (or maximum concentration) which from (4.2.13) is $\gamma u(x^*, t^*)$.

Equations (4.2.1) to (4.2.14) now define a physically reasonable model of the dump and can be rewritten together as

$$\frac{\partial u^*}{\partial t^*} = \frac{D_1}{p_1} \frac{\partial^2 u^*}{\partial x^2} - \frac{3(1 - p_1)}{a} \frac{\partial^2 v^*}{\partial r^2}(a, x^*, t^*), 0 < x^* < L, \quad (4.2.15)$$

$$\frac{\partial v^*}{\partial t^*} = D_2 \left( \frac{\partial^2 v^*}{\partial r^2} + \frac{2}{r} \frac{\partial v^*}{\partial r} \right), \quad R^* < r^* < a, \quad (4.2.16)$$

where the boundary conditions on $u^*$, $v^*$ and $R^*$ are given by

$$u^*(0, t^*) = u_0, \quad -\frac{\partial u^*}{\partial x^*}(L, t^*) = 0. \quad (4.2.17)$$

$$v^*(a, x^*, t^*) = \gamma u^*(x^*, t^*), \quad v^*(R^*, x^*, t^*) = 0. \quad (4.2.18)$$

$$D_2 \frac{\partial v^*}{\partial r^*}(R^*, x^*, t^*) = -\frac{E_D}{1 - p_1} \frac{\partial R^*}{\partial t^*}, \quad (4.2.19)$$

and the initial conditions are

$$u^*(x^*, 0) = 0, \quad R^*(x^*, 0) = a. \quad (4.2.20)$$

We observe that the model equations (4.2.15) to (4.2.20) require us to solve a coupled system of three partial differential equations for the triplet $u^*(x^*, t^*), v^*(r^*, x^*, t^*)$ and $R^*(x^*, t^*)$. Values of various parameters appearing in the model are given in Section 4.3.
4.3 Parameters in the Model

Estimates of parameters in the model equations are tabulated in Table 4.1 with references to the sources of the data. Parameters \( u_0, \varepsilon, \gamma, L, D_2 \) and \( \rho_S \) have fairly well defined values, however the diffusion coefficient \( D_1 \) (which depends on the porosity \( p_l \)) and the radius of the particles of the dump \( (a) \) are not so well defined.

The concentration of oxygen in air \( u_0 \) is easily found from tables, and presents no difficulty.

The ratio of the mass of oxygen to sulphur consumed during the oxidation of pyrites \((\varepsilon)\) can be determined by the chemical equation

\[
\text{FeS}_2 + \text{H}_2\text{O} + \frac{7}{2}\text{O}_2 \rightarrow \text{FeSO}_4 + \text{H}_2\text{SO}_4, \tag{4.3.1}
\]

which describes the oxidation of iron pyrites to ferrous sulphate and is considered the major oxidation process (Lowson, 1975). The oxidation of other metal sulphides may be important, however their concentration in White's dump is low compared to ferrous sulphide hence \( \varepsilon \) is defined by (4.3.1).

All sulphur present in the dump is assumed to be in the form of pyrites. The sulphur concentration for each particle of the dump, assuming a uniform distribution of sulphur, is equal to the overall dump concentration of sulphur \((\rho_S)\) divided by the volume fraction of particle space. Chemical analysis of bulked, crushed auger drill samples from White's dump (Lowson, 1975) yielded a best estimate of the sulphur content as 3.27% of the total dump density.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value or Range of Values</th>
<th>Source of Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_1$</td>
<td>$6.72 \times 10^{-6} \text{m}^2\text{s}^{-1}$</td>
<td>AAEC/E429</td>
</tr>
<tr>
<td>$D_2$</td>
<td>$2.6 \times 10^{-9} \text{m}^2\text{s}^{-1}$</td>
<td>Perry (1950)</td>
</tr>
<tr>
<td>$P_1$</td>
<td>0.4</td>
<td>AAEC/E429</td>
</tr>
<tr>
<td>$u_0$</td>
<td>0.265 $\text{kgm}^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$L$</td>
<td>18 m</td>
<td>AAEC/E365</td>
</tr>
<tr>
<td>$a$</td>
<td>1 mm - 20 cm</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>1.746</td>
<td>Eqn (4.3.1)</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>16.7 - 167.0 $\text{kgm}^{-3}$</td>
<td>AAEC/E365</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1 Values or range of values for parameters that appear in the model.
This estimate of the sulphur density will be used extensively in evaluating the model equations, however, in order to accommodate other estimates a range of values for $\rho_s$, from 1 to 10% of the total dump density, are considered.

The proportionality constant $\gamma$ relating the oxygen concentration in the pore space around the particle and the oxygen concentration (within the water) within the particle but at the outer boundary of the particle is defined by equation (4.2.13). Below we briefly derive and justify the value of $\gamma$ given in Table 4.1. Through Henry's law (see, for example, Levenspiel, 1972, page 413) we can relate the partial pressure of oxygen in air ($p_0$) to the mole fraction of oxygen in water $x_0$ thus

$$p_0 = H x_0,$$

where $H$ is Henry's law constant for oxygen in water. Now using the gas law we may also write an expression relating oxygen concentration in air with its partial pressure, as

$$p_0 = \mu u,$$

where $\mu$ is a known constant given by

$$\mu = \frac{RT}{M_o},$$

and $R$ is the gas law constant, $T$ is temperature in degrees Kelvin ($^0K$) and $M_o$ is the molecular weight of oxygen. We now require an expression relating the mole fraction of oxygen ($x_0$) to the solubility of oxygen ($v_0$). We may write $x_0$ as

$$x_0 = \frac{n_0}{\sum_i n_i},$$
where \( n_i \) are the number of moles of species \( i \) per volume, and particularly \( n_o(n_1) \) is the number of moles of oxygen (water) in a volume \( V \). Equation (4.3.5) may be rewritten to give

\[
x_o = \frac{M_1}{M_o} \left( \frac{V_o}{v_1 + \frac{M_1}{M_o} v_o + \ldots} \right),
\]

(4.3.6)

where \( M_1(v_1) \) is the molecular weight (density) of water. Obviously for dilute solutions, which we assume prevail in White's dump, \( v_1 \gg v_1 \) and therefore we can approximate (4.3.6) with

\[
x_o = \frac{M_1 v_0}{M_0 v_1},
\]

(4.3.7)

however, it should be recognised that \( S O_4 \) concentration levels in the water may become appreciable. Using (4.3.2), (4.3.3) and (4.3.7) we can write an expression relating \( u^* \) and \( v_o \) as

\[
v_o = \frac{M_0 v_1}{M_1 H} u^*,
\]

(4.3.8)

and therefore the constant \( \gamma \) in (4.2.13) is given by

\[
\gamma = \frac{M_0 v_1}{M_1 H}. \quad (4.3.9)
\]

A value for \( H \) can be obtained from solubility tables found in Perry (1950, page 675) for various temperatures (here we have taken \( T = 303^\circ K \)). A check on the value of \( \gamma \) given in Table 4.1 can be obtained by considering that when both \( u^* \) and \( v_o \) are at a maximum we have \( u^* \approx 0.265 kg m^{-3} \) and \( v_o \approx 8 \times 10^{-3} kg m^{-3} \) and using (4.2.13) we find \( \gamma \approx 3.02 \times 10^{-2} \).

The height of White's overburden above the original ground surface (\( L \)) varies from 13m to 18m; here we take it to be 18m.
The diffusion coefficient of oxygen, in the particles of the dump through water ($D_2$), is taken directly from tables (Perry, 1950, page 540) and adjusted to the required temperature.

The diffusivity governing oxygen transport through the pore space of White's dump ($D_1$), has been considered previously (Ritchie, 1977), where ($D_1$) is taken from Papendick and Runkles (1965) who measured the dependence of the diffusion coefficient for oxygen in soil on the soil porosity. Estimates of the porosity of White's dump range from 11% to 40% (Lowson, 1975). The most reliable estimate is 37% calculated from the ratio of the average density of the heap to the density of the overburden from the opencut.

The overburden material making up White's dump ranges in size from fine grains to large rocks (even boulders), so we do not choose a single particle size $a$. Results will be presented for various particle sizes and in Section 4.7 the model equations will be modified to include a particle size distribution.

4.4 A Moving Boundary Problem for a Particle of the Dump

It is instructive at this point to consider equations (4.2.8) to (4.2.12) in isolation since by independent investigation of the equations governing the moving boundary problem in the particles of the dump we gain insight into the underlying structure of the more complex system. We include in the model equations (in this section) a time invariant boundary condition at the surface of the particle and also neglect the vertical spatial dependence of $v^*$.
and \( R^* \). Equations (4.2.8) to (4.2.12), and the new outer boundary condition, can therefore be rewritten as

\[
\frac{\partial v^*}{\partial t^*}(r^*, t^*) = D_2 \left( \frac{\partial^2 v^*}{\partial r^*^2}(r^*, t^*) + \frac{2}{r^*} \frac{\partial v^*}{\partial r^*}(r^*, t^*) \right), \quad R(t^*) < r^* < a,
\]

\[v^*(a, t^*) = v^0, \quad v^*(R^*(t^*), t^*) = 0,
\]

and

\[
D_2 \frac{\partial v^*}{\partial r^*}(r^*, t^*) = -\frac{\epsilon \rho_s}{(1 - P_1)} \frac{dR^*}{dt^*}(t^*), \quad R(0) = a,
\]

where \( v^0 \) is the maximum concentration outside the particle. If we take dimensionless coordinates given by

\[v = \frac{v^*}{v^0}, \quad r = \frac{r^*}{a}, \quad R = \frac{R^*}{a}, \quad t = \frac{D_2 t^*}{a^2},
\]

we can write equations (4.4.1) to (4.4.3) as

\[
\frac{\partial v}{\partial t} + \frac{2}{r} \frac{\partial v}{\partial r}, \quad R(t) < r < 1,
\]

\[v(1, t) = 1, \quad v(R(t), t) = 0,
\]

and

\[
\frac{\partial v}{\partial r}(R(t), t) = -\alpha \frac{dR(t)}{dt}, \quad R(0) = 1,
\]

where \( \alpha = \epsilon \rho_s / (1 - P_1) v^0 \).

Moving boundary problems, such as (4.4.5) to (4.4.7), are not only important in chemical reaction engineering applications but also in many other industrial processes such as the freezing or thawing of food and ice, and the solidification or melting of metals. Reviews of such models are given in Bankoff (1964) and Evans.
Indeed moving boundary problems in general have received much attention recently (Ockendon and Hodgkins, 1975; Wilson et al., 1978; and Elliott and Ockendon, 1981) because of the widespread applicability of such models to industry. Analytic pseudo-steady state solutions to moving boundary problems have been known for some time but analytic solutions to the fully time dependent problems have not been found except in some planar geometry situations. The underlying difficulty in moving boundary problems is the intrinsic non-linearity introduced into the model by the presence of the moving front. Success therefore in solving moving boundary problems often lies in finding an appropriate change of variable which transforms the problem into a more tractable form.

Even though a closed form solution has not been found for equations (4.4.5) to (4.4.7) approximate analytic solutions have been developed (see Davis and Hill, 1982c and the references therein). A new technique is employed here to solve the equations governing such a moving boundary problem for a spherical reacting particle, in which a transformation is given, which considerably simplifies the non-linearities associated with the moving boundary and enables an iterative analytic series solution to be found. Below we briefly outline the technique and give some of the main results. For more detail the reader is referred to Appendix P, Davis and Hill (1982c).

We introduce the transformed variables

\[ x = \frac{r - 1}{R(t) - 1}, \quad y = R(t), \]

(4.4.8)
and let

\[ \phi(x, y) = rv(r, t), \quad (4.4.9) \]

which when substituted into equations (4.4.5) through to (4.4.7) yields

\[ \frac{\partial^2 \phi}{\partial x^2} = \frac{\partial \phi}{\partial x} (1, y) \left( \frac{\partial \phi}{\partial x} - (y - 1) \frac{\partial \phi}{\partial y} \right), \quad (4.4.10) \]

\[ \phi(0, y) = 1, \quad \phi(1, y) = 0, \quad (4.4.11) \]

and

\[ \frac{\partial \phi}{\partial x} (1, y) = -\alpha y (y - 1) \dot{y}, \quad y(0) = 1. \quad (4.4.12) \]

Thus the moving boundary problem reduces to the non-linear boundary value problem (4.4.10) to (4.4.12) which has fixed boundaries. A formal solution of this problem can be found by assuming a series solution for \( \phi(x, y) \), such that

\[ \phi(x, y) = \sum_{n=0}^{\infty} A_n(x)(y - 1)^n, \quad (4.4.13) \]

which upon substitution into (4.4.10) gives a recurrence relation for the coefficients \( A_n(x) \). In principle the functions \( A_n(x) \) for \( n = 0, 1, 2, \ldots \) can all be found recursively, however in practice the calculations become lengthy and we consider only the first three terms of the series, \( A_0, A_1, \) and \( A_2 \), which can be written in terms of the confluent hypergeometric function. It is interesting to note that \( A_0(x) \) can be written simply as

\[ A_0(x) = \frac{\int_0^1 e^{\frac{-\lambda^2}{2}} \frac{d\lambda}{x}}{\int_0^1 e^{\frac{-\lambda^2}{2}} d\lambda}, \quad (4.4.14) \]
where the constant $\gamma$ is determined as a root of the transcendental equation

$$\alpha \gamma \int_0^1 e^{-\frac{\gamma \lambda}{2}} d\lambda = e^{\frac{\gamma}{2}} \quad (4.4.15)$$

which is precisely the solution for the classical planar moving boundary problem as outlined in Section 2.4. Note that equation (4.4.15) is well known and a graphical representation is given in Crank (1975, see page 293). Details of coefficients $A_1(x)$ and $A_2(x)$ can be found in Davis and Hill (1982c).

The motion of the moving front within the spherical particle is also of interest, especially the time it takes to reach the centre of the sphere. For the pseudo-steady state situation, that is neglecting the time derivative in equation (4.4.5), we can solve for $v(r,t)$ to give

$$v(r,t) = \frac{1 - R(t)/r}{1 - R(t)} \quad (4.4.16)$$

On substitution of (4.4.16) into (4.4.7) and integrating once with respect to time we obtain an equation for the motion of the moving boundary in the quasi-steady case

$$2R^3(t) - 3R^2(t) + 1 = \frac{6t}{\alpha} \quad (4.4.17)$$

For the non-steady case, using equations (4.4.12), (4.4.13) and the results for $A_0(x), A_1(x)$ and $A_2(x)$ we obtain a series expansion describing the motion of the moving front given by

$$t = \frac{1}{\gamma} \left( \frac{(y-1)^2}{2} + \frac{(y-1)^3}{(3+\gamma)} - \frac{\sigma(y-1)^4}{2(3+\gamma)^2} + \ldots \right) \quad (4.4.18)$$
where the constant \( \sigma \) is defined as

\[
\sigma = \frac{\alpha \gamma (\gamma^2 + 2\gamma - 3) + (\gamma^3 + 3\gamma^2 - 3\gamma + 3)}{\alpha \gamma (\gamma + 5) + (\gamma^2 + 6\gamma + 3)}.
\]  

(4.4.19)

Therefore we can write the time \( t_c \) to complete reaction of the sphere \((y(t)=0)\) as

\[
t_c = \frac{1}{2} \gamma \left( \frac{1}{2} - \frac{1}{(3 + \gamma)} - \frac{\sigma}{2(3 + \gamma)^2} + \ldots \right).
\]  

(4.4.20)

Notice that when \( \alpha \to \infty \) we have from (4.4.15) that

\[
\gamma \to \frac{1}{\alpha},
\]  

(4.4.21)

and therefore from (4.4.19) and (4.4.20) we have

\[
t_c = \frac{\alpha}{6} + o(1),
\]  

(4.4.22)

which is the same result as for the pseudo-steady state obtained by letting \( R(t) = 0 \) in equation (4.4.17).

Physically the quasi-steady state assumption represents a slowly moving reaction front allowing rapid establishment of the equilibrium concentration distribution between the surface of the particle and the moving front itself. The validity of the pseudo-steady state approximation is discussed by Bischoff (1963, 1965) and Bowen (1965) for both infinite and finite reaction rates. Bischoff (1963) concluded, in fact, that the pseudo-steady assumption is reasonable if \( \alpha \sim 10^3 \) but that errors could become large if \( \alpha \sim 1 \). Table 4.2 (after Davis and Hill, 1982c) is reproduced here to show the comparison of this new technique (outlined above) with that of Selim and Seagrave (1973a,b) and also to highlight the accuracy of the pseudo-steady
<table>
<thead>
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<th>( \alpha )</th>
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<th>Pseudo-Steady State</th>
<th>This Work</th>
</tr>
</thead>
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<td>0.833</td>
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<td>1.67</td>
<td>1.83</td>
</tr>
<tr>
<td>50.0</td>
<td>8.49</td>
<td>8.33</td>
<td>8.50</td>
</tr>
<tr>
<td>100.0</td>
<td>16.7</td>
<td>16.7</td>
<td>16.8</td>
</tr>
</tbody>
</table>

Table 4.2  Dimensionless times for the moving reaction front to reach the centre of the spherical particle (\( t_c \)) for various \( \alpha \).
state result in at least the parameter \( t_c \) for values of \( \alpha \) as low as \( 10^2 \).

Figure 4.3 gives the position of the moving boundary with time for a variety of \( \alpha \), showing the tendency for the velocity of the reaction front to decrease with increasing \( \alpha \). The constant \( \alpha \) is the ratio of the density of non-diffusing reactive material (pyrite) to the diffusing reactant concentration at the outside of the particle. A large \( \alpha \), therefore, indicates that a large amount of the spherical particle has potential for reaction and consequently a greater amount of the diffusing reactant is required to advance the reaction interface than is the case for a smaller \( \alpha \). In Figure 4.4 the concentration of the diffusing reactant is given at radial distances within the spherical particles for \( R(t) = 0, 0.2 \) and \( 0.4 \) and with \( \alpha = 0.5 \) and 50. Figure 4.4 not only illustrates the shape of the concentration profiles behind the reaction front but also the dependence of the shape on the velocity of the interface. For \( \alpha = 50 \) the reaction front is moving more slowly than for \( \alpha = 0.5 \), therefore allowing more time for a build-up of concentration behind the moving front. This phenomenon is particularly enhanced when the reaction front has reached the centre of the particle \( (R(t) = 0) \), a consequence being that the interval of time between complete saturation of the particle by the diffusing reactant is shorter for larger \( \alpha \). The results presented in Table 4.2 and Figures 4.3 and 4.4 are obtained by considering only the first three terms of the analytic-series expansion for the concentration of the diffusing reactant, given
Figure 4.3  The position of the moving reaction front within the particle as a function of time for various values of $\alpha$. 

\begin{figure}[h!]
\centering
\includegraphics[width=\textwidth]{figure43.png}
\caption{The position of the moving reaction front within the particle as a function of time for various values of $\alpha$.}
\end{figure}
Figure 4.4 The radial oxygen distribution within the particle for $\alpha = 0.5$ (—) and 50 (---) with the position of the reaction front being $R = 0, 0.2$ and 0.4.
by equation (4.4.13), and the motion of the moving front, given by (4.4.18). Three terms in the expansion are shown in Davis and Hill (1982c) to be sufficient to give good agreement with previous results.

The solution technique outlined above therefore allows an accurate description of the motion of the moving boundary and concentration profiles within a particle where the outer boundary condition is constant for a range of \( \alpha \), agreement with numerical results of previous authors being obtained by taking only the first three terms of the assumed series solution given by equation (4.4.13).

A necessary restriction on the technique employed is that the boundary condition at the outside boundary of the particle is time independent. This is unrealistic in the overall model of the waste rock dump since the oxygen concentration in the pore spaces surrounding particles of the dump increases with time. Now even though the rate of increase of oxygen concentration may well be small, over the life time of the dump it can become a significant factor and so at this stage the time dependence of oxygen concentration in the pore spaces of the dump and therefore the time dependence of the outer boundary condition of the oxidising particles of the dump cannot be neglected. Therefore, while the technique outlined in this section is useful in identifying and quantifying parameters of importance within the oxidising particles of the dump, and in considering the particle at the surface of the dump, since it has a constant concentration at its outer boundary (due to boundary condition (4.2.2)), in studying the
overall diffusional mass transport and chemical reaction equations proposed in Section 4.2, we must research a different approach.

4.5 Approximate Dimensionless Model

In this section we make equations (4.2.15) to (4.2.20) dimensionless and then proceed to an approximate system of equations governing the pyritic oxidation process. Using the dimensionless quantities

\[ u = \frac{u}{u_0}, \quad v = \frac{v}{\gamma u_0}, \quad R = \frac{R}{a}, \quad x = \frac{x}{L}, \quad r = \frac{r}{a}, \]

equations (4.2.15) to (4.2.20) become

\[ \tau_1 \frac{\partial u}{\partial t^*} = \frac{\partial^2 u}{\partial x^2} - k_1 \frac{\partial v}{\partial x}(1, x, t^*), \quad 0 < x < 1, \]  
\[ \tau_2 \frac{\partial v}{\partial t^*} = \frac{\partial^2 v}{\partial r^2} + \frac{2}{r} \frac{\partial v}{\partial r}, \quad R(x, t^*) < r < 1, \]

where the boundary conditions become

\[ u(0, t^*) = 1, \quad \frac{\partial u}{\partial x}(1, t^*) = 0, \]
\[ v(1, x, t^*) = u(x, t^*), \quad v(R(x, t^*), x, t^*) = 0, \]
\[ \frac{\partial v}{\partial r}(R(x, t^*), x, t^*) = -\tau_3 \frac{\partial R}{\partial t^*}(x, t^*), \]

and the initial conditions become

\[ u(x, 0) = 0, \quad R(x, 0) = 1, \]

where the constants \( \tau_1, \tau_2, \tau_3 \) and \( k_1 \) are given by

\[ \tau_1 = \frac{p_1 L^2}{D_1}, \quad \tau_2 = \frac{a^2}{D_2}, \]
The constants \( \tau_1, \tau_2 \) and \( \tau_3 \) represent three of the four possible characteristic times of the system. The four characteristic times associated with the problem can be stated as follows:

i. \( \tau_1 \) is the characteristic time for the diffusional transfer of oxygen within the pore space of a dump of height \( L \), with no chemical reaction;

ii. \( \tau_2 \) describes the characteristic time for oxygen diffusing within a chemically inert particle of radius \( a \);

iii. \( \tau_3 \) describes the characteristic time for oxygen diffusing within a particle of radius \( a \), with a competing chemical reaction within the particle; and

iv. \( \tau_4 (\frac{L^2 \varepsilon a}{D_1 u_0}) \) is the characteristic time for transport of oxygen diffusing through the pore spaces of the dump when there is a competing chemical reaction.

The selection of an appropriate time scale from those mentioned above depends primarily on which parameters in the model we are most interested in. Viewing equations (4.2.8) to (4.2.12) in isolation
(as in the previous section) would dictate scaling time with respect to $\tau_2$ or $\tau_3$. However in the full problem $\tau_2$ and $\tau_3$ are time scales associated with the particles of the dump and therefore may be too small to enable observation of macroscopic phenomena. Whilst we are interested in the microstructure, we are more interested in the effect of the presence of the microstructural configuration, within the model, on macrostructural output parameters such as the spatial oxygen concentration distribution in the pore spaces of the dump. The aim therefore is to scale the time with respect to the largest time scale possible such that

$$0 < t \sim 1, \quad (4.5.9)$$

where $t$ is the scaled (dimensionless) time. The largest time scale, for reasonably small sized particles in the dump, is $\tau_4$. It is apparent also that this is the appropriate scale for the simpler model proposed by Ritchie (1977) (see Appendix A) in considering a homogeneous dump and so should be a reasonable choice here.

Therefore scaling time in equations (4.5.2) to (4.5.6) with respect to $\tau_4$ gives

$$\delta \frac{\partial^2 u}{\partial t^2} = \frac{\partial^2 u}{\partial x^2} - k_1 \frac{\partial v}{\partial r}(1, x, t), \quad 0 < x < 1, \quad (4.5.10)$$

$$\delta \frac{\partial^2 v}{\partial t^2} = \frac{\partial^2 v}{\partial r^2} + \frac{2 \partial v}{r \partial r}, \quad R(x, t) < r < 1, \quad (4.5.11)$$

where the boundary conditions become

$$u(0, t) = 1, \quad \frac{\partial u}{\partial x}(1, t) = 0, \quad (4.5.12)$$
\(v(1, x, t) = u(x, t), \quad v(R(x, t), x, t) = 0, \quad (4.5.13)\)

\(\frac{\partial v}{\partial t}(R(x, t), x, t) = -k_2 \frac{\partial R}{\partial t}(x, t), \quad (4.5.14)\)

and the initial conditions (4.5.7) remain the same, and the constants \(\delta_1, \delta_2\) and \(k_2\) are defined as

\[
\delta_1 = \frac{\tau_1}{\tau_4} = \frac{p_1 u_0}{\varepsilon \rho_s},
\]

\[
\delta_2 = \frac{\tau_2}{\tau_4} = \frac{u_0 D_1}{\varepsilon \rho_s D_2} \left( \frac{a}{L} \right)^2,
\]

\[
k_2 = \frac{\tau_3}{\tau_4} = \frac{1}{\gamma(1 - p_1)} \frac{D_1}{D_2} \left( \frac{a}{L} \right)^2.
\]

We now proceed to neglect the time derivative in equation (4.5.11) because the ratio of the two time scales \(\tau_2\) and \(\tau_4\) given by \(\delta_2\) is small (from Table 4.1 for moderate values of \(a\), \(\delta_2 \sim 10^{-6}\)). A pseudo-steady state approximation for the particles of the dump is supported also by the analysis and discussion in Section 4.4. Solving the steady state equivalent of (4.5.11) using the boundary conditions (4.5.13), then yields an explicit expression for the pseudo-steady state case where \(v(r, x, t)\) can be written in terms of \(u(x, t)\) and \(R(x, t)\) as

\[
v(r, x, t) = \frac{u(x, t)}{1 - R(x, t)} \left( 1 - \frac{R(x, t)}{r} \right), \quad R < r < 1. \quad (4.5.16)
\]

Note that

\[
\frac{\partial v}{\partial r}(1, x, t) = \frac{u(x, t) R(x, t)}{1 - R(x, t)}, \quad (4.5.17)
\]

and

\[
\frac{\partial v}{\partial r}(R(x, t), x, t) = \frac{u(x, t)}{R(x, t)[1 - R(x, t)]}, \quad (4.5.18)
\]

and therefore substitution of (4.5.17) and (4.5.18) into equations (4.5.10) through to (4.5.14) enables elimination of \(v(r, x, t)\) from
the system of equations, which now reads

\[ \frac{3u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - 3k \frac{ur}{1 - R}, \quad 0 < x < 1, \]  
\[ \frac{3R}{\partial t} = -\frac{ku}{R(1 - R)}, \quad 0 < R < 1, \]  

with the boundary and initial conditions given simply as

\[ u(0, t) = 1, \quad \frac{\partial u}{\partial x}(1, t) = 0, \]  
\[ u(x, 0) = 0, \quad R(x, 0) = 1, \]  

and the constant \( k \) given as

\[ k = \frac{1}{k_2} = \frac{k_1}{3} = \gamma(1 - p_1) \frac{D_2}{D_1} \left( \frac{L}{a} \right)^2. \]  

4.6 Heat Source Distribution and Sulphate Production Rate

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 (Harries and Ritchie, 1981). 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.

Heat Source Distribution

The heat output for a single particle in the dump may be written in terms of the flux of oxygen across the moving reaction front in
each particle as

\[-\frac{\delta \rho_s}{(1 - p_1)} 4 \pi R^2 (x, t) \frac{\partial R^*}{\partial t} (x, t), \tag{4.6.1}\]

where \(\delta\) is the heat produced from the pyritic oxidation reaction per unit mass of sulphur oxidised. If we now denote the heat output, in watts per cubic metre of the dump, as \(H(x^*, t^*)\) we can write

\[H(x^*, t^*) = -\frac{\nu \delta \rho_s}{(1 - p_1)} 4 \pi R^2 \frac{\partial R^*}{\partial t}. \tag{4.6.2}\]

Substituting equation (4.2.6) for \(\nu\) in equation (4.6.2) and making the system dimensionless with respect to equation (4.5.1)_3, (4.5.1)_4 and \(\tau_4\) we have

\[H(x, t) = \frac{\delta \rho_s 3 (R^3)}{\tau_4} \frac{\partial R^*}{\partial t}, \tag{4.6.3}\]

which describes the heat output as the rate of volume change of the unreacted-core region of the particles of the dump. Note that using (4.5.20) we can rewrite (4.6.3) as

\[H(x, t) = \frac{k_3 u(x, t) R(x, t)}{1 - R(x, t)}, \tag{4.6.4}\]

where \(k_3\) is given by

\[k_3 = \frac{36 \rho_s k}{\tau_4} = \frac{3(1 - p_1) \delta \gamma u_0 D_2}{\varepsilon a^2}. \tag{4.6.5}\]

The total heat production of the dump at any time \(t\) denoted \(H_t(t)\) can be obtained by integrating equation (4.6.2) over the height of the dump \(L\) such that

\[H_t(t) = L \int_0^1 H(x, t) dx. \tag{4.6.6}\]
The cumulative heat output of the dump $H_c(t)$ can also be found by integrating equation (4.6.6) with respect to time from zero to $t$, after using (4.6.3), to give

$$H_c(t) = \frac{\delta \rho_s L}{T_4} \left( 1 - \int_0^1 R^3(x, t) \, dx \right). \quad (4.6.7)$$

The constant $\delta$ appearing in equation (4.6.1) is as yet unspecified in value. During a discussion on the heat production of various chemical reactions which proceed in a pyrite-laden oxidising waste dump, Harries and Ritchie (1981) single out equation (4.3.1) as the reaction producing most of the heat ($\Delta H = 1440 \text{kJ mol}^{-1}$). The value of $\delta$ appropriate to White's dump can then be calculated, from (4.3.1) and the value for $\Delta H$, to be

$$\delta = 2.246 \times 10^4 \text{kJ kg}^{-1}. \quad (4.6.8)$$

This value of $\delta$ is used throughout calculations presented in this thesis.

**Sulphate Production Rate**

The sulphate production rate in mass of $\text{SO}_4$ produced per unit time per unit volume of the dump is a similar expression to that of the heat source distribution with the constant $\delta$ replaced by $\delta_s$ where $\delta_s$ is the mass of $\text{SO}_4$ produced per mass of sulphur consumed by the chemical reaction, equation (4.3.1). The production rate of $\text{SO}_4$ can be written as

$$\frac{\delta_s}{\delta} H(x, t). \quad (4.6.9)$$

The $\text{SO}_4$ production rate integrated over the whole dump is, as noted earlier, particularly useful since it yields an estimate of the
total pollution load of the dump, at any time $t$, presented to the environment by the dump. It is written simply as

$$\frac{\delta}{\delta t} S H_T(t).$$  \hfill (4.6.10)

4.7 The Particle Size Distribution

The mathematical model to this point has included the simplifying assumption of a single particle size throughout the dump. We concede, however, that particles making up a waste rock dump are not uniform in size and we therefore attempt to account for this variation by including in the model a particle size distribution.

It is assumed that in any elemental volume of the dump we have a specified distribution of particle sizes (instead of single sized particles) and that in such a volume $u(x,t)$ is constant. That is, throughout an elemental volume we assume a constant oxygen concentration in the pore space of the dump surrounding each of the different sized particles.

Using this assumption, the mathematical formulation remains in terms of equations (4.2.1) through to (4.2.4), however, the volume absorption term $q^*$ given in (4.2.1) must be rederived. Since $q^*(x^*, t^*)$ is the rate of volume loss of oxygen from the pore space to the particles of the dump then, for a continuous particle size range, $q^*$ can be rewritten as

$$q^*(x^*, t^*) = \int_{a \rightarrow a_0}^{a_n} 4\pi a^2 D_2 \frac{\partial v^*}{\partial r^*}(a, x^*, t^*) v(a) \, da,$$  \hfill (4.7.1)
where \( v(a) \, da \) is the number of particles per unit volume of the dump whose radius lies in the range \( a \) to \( a + da \), and \( a_0 (a_n) \) is the minimum (maximum) particle size radius considered in the integration. Now if \( N(a) \, da \) is the number of particles of radius between \( a \) and \( a + da \) in a sample of mass \( M \) we have

\[
\frac{N(a) \, da}{M} = \frac{v(a) \, da}{\rho_T}, \tag{4.7.2}
\]

which in turn yields

\[
v(a) = \frac{\rho_T \, N(a)}{M} = \frac{3(1 - p_1) N(a)}{\int_a^{a_n} \frac{3}{a} N(a) \, da}, \tag{4.7.3}
\]

where \( \rho_T \) is the overall density of the dump.

Equation (4.7.1) can now be made dimensionless in accord with the approximate dimensionless model of Section 4.5 to give

\[
\frac{k^- u}{a_0 \, R(a)} \int_a^{a_n} \frac{N(a) \, da}{[1 - R(a)]}, \tag{4.7.4}
\]

where we have substituted equation (4.7.3) into equation (4.7.1), and where \( k^- = 3a^2 k \). So written explicitly the equation to be solved governing bulk oxygen transport within the pore space of the dump is simply

\[
\frac{\partial^2 u}{\partial x^2} - q(x, t), \tag{4.7.5}
\]

where \( q(x,t) \) is given by equation (4.7.4).

The equations governing diffusion and reaction within the particles of the dump, (4.2.8) through to (4.2.13), remain the
same since theoretically we may solve for a general particle radius size \( a \) and then integrate over the particle size in (4.7.4) to obtain \( q(x,t) \). In practice we numerically solve for discrete particle sizes from equation (4.5.20) and then sum over the range of particle sizes using the discretised form of equation (4.7.4).

In order to perform the integrations in equation (4.7.4) we require an expression for the function \( N(a) \), as well as values of the constants \( a_0 \) and \( a_n \). The values of \( a_0 \) and \( a_n \) will be assigned in Section 6.5 where results for various minimum and maximum cut-off radii of the particle size distribution are compared to results for single sized particles. Typically \( a_n \) is of the order of 10cm while \( a_0 \) ranges from a minimum of approximately 1mm upwards.

We now obtain an expression for \( N(a) \). If \( N(a) \, da \) is the number of particles in a sample, with radius between \( a \) and \( a + da \), then we can write the mass, for the same radial interval, as

\[
\frac{4}{3} \pi a^3 \rho N(a) \, da, \quad (4.7.6)
\]

where \( \rho \) is the density of the particulate mass of the dump. From measurement of particle radii sizes, and associated masses, in a sample taken from White's overburden dump at Rum Jungle, at a depth of about 3m, we can derive a reasonable expression for \( N(a) \) (Davis and Ritchie, 1983) given by

\[
N(a) = 5.02 \times 10^6 \frac{a^{2.61}}{a_0^{3.61}}. \quad (4.7.7)
\]

Figure 4.5 shows a comparison between the experimental information and the fitted distribution using equation (4.7.7). Not only does
Figure 4.5 The mass of material per unit particle size interval \( \frac{4}{3} \pi a^3 N(a) \rho \) for a sample from White's waste rock dump.
Figure 4.5 show the close agreement between the two curves but it also highlights the heavy weighting of the particle size distribution towards particles of small radius.

We can now substitute (4.7.7) into (4.7.4), which after analytic integration of the denominator, yields

$$q(x, t) = k_a u \int_{a_0}^{a_n} \frac{R(a)}{[1 - R(a)]} a^{-2.61} da, \quad (4.7.8)$$

where

$$k_a = \frac{0.39k'}{0.39 - \frac{0.39}{a_n} - a_o} \quad (4.7.9)$$

We observe here that since $R(a)$ is zero for any a "small enough" (and provided $u(x, t) > 0$) we may then set $a_0$, in the integration procedure (equation (4.7.8)) to the maximum value of a that makes $R$ vanish at each time step. Indeed from integrating equation (4.5.20) with respect to time we have

$$3R^2(x, t) - 2R^3(x, t) - 1 + 6kw(x, t) = 0, \quad (4.7.10)$$

where $w(x, t)$ is given as

$$w(x, t) = \int_0^t u(x, \tau) d\tau, \quad (4.7.11)$$

and when $R(x, t) = 0$ we have

$$w(x, t) = (6k)^{-1}. \quad (4.7.12)$$

Now since $k' = 3a^2k$ we may obtain an expression for $a_0$ given by

$$a_0 = (2k')^{-\frac{1}{2}}, \quad (4.7.13)$$
and therefore, for a given value of $w(x,t)$, we are required to do the integration only for $a_0$ given by (4.7.13), which indicates that, since $w(x,t)$ is increasing with time, the integration will be over a shorter interval at each successive time step for a fixed depth in the dump.
5.1 Introduction

In Chapter 4 the dimensionless model equations were developed, and a pseudo-steady state approach for the particles of the dump justified. In this chapter we present approximate solutions to these equations by noting the underlying features of the model and making an approximation to the position of the reaction interface within the particles. Results are presented which illustrate various aspects of the model's behaviour.

Before proceeding to the approximate solutions we note that equations (4.5.19) to (4.5.22) can be simplified further. Observe that (4.5.20) can be written as

\[
\frac{\partial (R^3)}{\partial t} = -3k \frac{uR}{1-R}, \quad (5.1.1)
\]

and therefore (4.5.19) can be rewritten as

\[
\delta \frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} + \frac{\partial (R^3)}{\partial t}. \quad (5.1.2)
\]

Now if we let

\[
w(x, t) = \int_0^t u(x, \tau) \, d\tau, \quad (5.1.3)
\]

we can integrate equations (5.1.2) and (4.5.22) once with respect to time, using initial conditions (4.5.22), to give

\[
\delta \frac{\partial w}{\partial t}(x, t) = \frac{\partial^2 w}{\partial x^2}(x, t) - [1 - R^3(x, t)], \quad (5.1.4)
\]
whilst the boundary and initial conditions on $w(x, t)$ become

$$w(0, t) = t, \quad (5.1.6)_1$$

$$\frac{\partial w}{\partial x}(1, t) = 0, \quad (5.1.6)_2$$

$$\frac{\partial w}{\partial t}(x, 0) = 0. \quad (5.1.6)_3$$

The three coupled partial differential equations have now simplified to one non-linear diffusion equation coupled to a cubic equation and can be, clearly, further reduced by substituting (5.1.5) into (5.1.4) to obtain a single one dimensional non-linear diffusion type equation in the parameter $R(x, t)$. If the resulting equation were soluble for $R(x, t)$ then it would be a simple matter to find the corresponding $w(x, t)$ and $u(x, t)$ solutions, however, the resulting equation is highly non-linear and not amenable to analytic solution, nor is numerical solution of such a formulation a simple task. Hence in this chapter approximate results will be developed from the form of the equations given in (5.1.4) and (5.1.5). We note further that if the concentration surrounding the particles of the dump were held constant then equation (5.1.5) is recognisable as the pseudo-steady state result for a diffusion-controlled shrinking-core model of a reacting particle (Szekely, 1976), since $w(x, t)$ would then simplify to $w(x, t) = t$ which, when substituted into (5.1.5), gives an equivalent result to equation (4.4.17).

From physical considerations we impose condition (4.2.13) upon
the solution, once the moving boundary has reached the centre of the particle \((R(x, t) = 0)\), and therefore equation (5.1.4) and (5.1.5) are strictly valid only for \(0 < R(x, t) < 1\). However, once \(R(x, t) = 0\) at any point down the dump the equation to be solved becomes

\[
\frac{\partial w}{\partial t} = \frac{\partial^2 w}{\partial x^2} (x, t) - 1. \tag{5.1.7}
\]

Equation (5.1.5) allows us to quantify when this changeover occurs, since if we set \(R(x, t) = 0\) we obtain

\[
w(X, t) = \frac{1}{6k}, \tag{5.1.8}
\]

where we define \(X = X(t)\) 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 (5.1.8) indicates that whenever \(w(x, t)\) (a measure of the cumulative oxygen concentration), at any point \(x\) and time \(t\) reaches \((6k)^{-1}\) then the particle at that point \(x = X(t)\), has fully reacted. Also, a consequence of the pseudo-steady state simplification is that the oxygen concentration within the particle is constant with \(X\) once the particle has finished reacting, since if \(R(x, t) = 0\) in equation (4.5.16) then \(v(r, x, t)\) attains its maximum instantaneously, but 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. However, it can be shown that, for the range of parameter values relevant to White's overburden dump at Rum Jungle, the pseudo-steady approach is quite accurate, since the
oxygen volume difference and time delay between complete reaction and saturation become miniscule (as indicated in Section 4.4 for large \( \alpha \)). Note that the time to fully react the particle at the surface of the dump can be written simply (since \( w(0, t) = t \)) as

\[
t_c = \frac{1}{6k}.
\]  
(5.1.9)

Figure 5.1 shows a schematic diagram of regions of reaction in a mass of pyritic material such as White's dump for \( t > t_c \). For \( t < t_c \) equations (5.1.4) and (5.1.5) are valid throughout the reacting dump, however, for \( t > t_c \) we are led to consider two regions within the dump separated by a planar moving interface \( X(t) \). For \( t > t_c \), in the region where \( R(x, t) = 0 \) (\( w(x, t) > t_c \)), we are required to solve (5.1.7) subject to (5.1.6). In the region of the dump where \( R(x, t) \neq 0 \) (\( w(x, t) < t_c \)), however, we must solve (5.1.4) and (5.1.5) subject to (5.1.6)\_2. The matching condition for the two region solution is given by equation (5.1.8).

5.2 Approximate Upper Bound Solution

Approximation and Solution Procedure

We proceed in this section to obtain an upper bound solution for \( w(x, t) \) and to find the corresponding expressions for \( u(x, t) \) and \( R(x, t) \). It should be noted from the outset that even though we can find an upper bound for \( w(x, t) \), this gives no guarantee that \( u(x, t) = \frac{\partial w}{\partial t}(x, t) \) is an upper or lower bound on the dimensionless oxygen concentration.

For \( 0 < R(x, t) < 1 \), and starting with the inequality \( R^2(x, t) > R^3(x, t) \),
Figure 5.1 Schematic diagram of the model dump where $t > t_c$. 
it is easily shown that
\[ 2R^3 - 3R^2 + 1 < 1 - R^3. \] (5.2.1)

Using equation (5.1.5) we can write (5.2.1) as
\[ 6kw < 1 - R^3, \] (5.2.2)
for all \( R \) and \( w \) such that \( 0 < R < 1 \) and \( 0 < w < t_C \). Therefore, by replacing the loss term \( (1 - R^3) \), in equation (5.1.4), by \( 6kw \), we are now required to solve the equation
\[ \frac{\delta}{\delta t} \frac{\partial w}{\partial x} = \frac{\partial^2 w}{\partial x^2} - \beta w(x, t), \] (5.2.3)
subject to (5.1.6), where \( \beta \) is given by
\[ \beta = 6k, \] (5.2.4)
to find the upper bound solution for \( w(x, t) \) in the region of the dump where \( w(x, t) < t_C \).

Once \( R \) becomes zero at some point \( x \) in the dump (that is \( w(x, t) > t_C \)) we must solve equation (5.1.7) instead of (5.2.3). As indicated in Section 5.1 there is a planar moving boundary within the dump, since particles near the surface of the dump finish reacting first (equation (5.1.7) then holds) whereas lower in the dump particles are continuing to react (where equation (5.2.3) still holds). Therefore we write the upper bound solution \( \bar{w}(x, t) \) as
\[ \bar{w}(x, t) = w_1(x, t) \text{ for } t < t_C, \] (5.2.5)_1
while for \( t > t_C \)
\[ \bar{w}(x, t) = w_2(x, t), \text{ } 0 < x < X(t), \] (5.2.5)_2
and

\[ \bar{w}(x, t) = w_3(x, t), \quad X(t) < x < 1, \quad (5.2.5) \]

where \( w_1(x, t) \) is the solution of (5.2.3) subject to (5.1.6), \( w_2(x, t) \) is the solution of (5.1.7) subject to (5.1.6) \(_1\) and (5.1.8), and \( w_3(x, t) \) is the solution of (5.2.3) subject to (5.1.6) \(_2\) and (5.1.8), while the initial conditions on \( w_2(x, t) \) and \( w_3(x, t) \) are given by

\[ w_2(x, t_c) = w_3(x, t_c) = w^*(x, t_c). \quad (5.2.6) \]

In solving for \( w_1(x, t) \) we consider equations (5.2.3), (5.1.6) \(_1\), and (5.1.6) \(_3\), however, we take the extra condition

\[ w(x, t) \text{ is finite as } x \to \infty, \quad (5.2.7) \]

instead of (5.1.6) \(_2\). Equation (5.2.7) now describes the dump as a semi-infinite slab, which facilitates 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 (5.1.6) \(_2\) to (5.2.7) is a reasonable one since for moderately sized particles (< 10mm) \( t_c \) 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 \( w_1(x, t) \) is therefore given, after using (5.2.7), as

\[ w_1(x, t) = \int_0^t \left[ 1 + \beta^*(t - \tau) \right] e^{-\beta^* \tau} \text{erfc} \left( \frac{\sqrt{\delta_1 x}}{2\tau^2} \right) d\tau, \quad (5.2.8) \]

where \( \beta^* = \beta / \delta_1 \). Equation (5.2.8) may also be considered reasonable for larger particles (> 10mm) if \( t_c \) is short compared to the reactive
lifetime of the dump. However, it is clearly not applicable for, say, 100mm particles where $t_c$ is of the order of hundreds of years since this is of the same order as the time to oxidise the whole dump as predicted by the simple homogeneous semi-infinite slab model of Ritchie (1977). In solving for a dump comprised of 100mm sized particles (an unlikely occurrence) the more complicated infinite series result, using boundary condition (5.1.6)$_2$, would therefore be required. Also, of course, since $\delta_1$ is small the pseudo-steady state result for $w_1(x,t)$ could have been given instead of (5.2.8), however, it does not depict the transient stages of the model solution at all well. Indeed, since $w_1(x,t)$ for the pseudo-steady state is only a linear function of time (from solving the steady state equation (5.2.3) subject to (5.1.6)$_1$, and (5.1.6)$_2$) the oxygen profile from equation (5.1.3) becomes constant in time and therefore could not possibly describe the small time behaviour of the oxidising dump.

We go on now to construct solutions 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 $w_3(x,t)$ because $\delta_1$ is small ($\sim 10^{-3}$), time is now greater than $t_c$, and the quasi-steady consideration expedites an analytic result. Also, our experience with diffusion-controlled moving boundary problems (see Section 4.4) indicates to us that the pseudo or quasi-steady state result, whether it be for a 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 (see Szekely, 1976). The non-trivial and useful
nature of the solution obtained via the quasi-steady technique, which
dictates that the equilibrium concentration profile behind the moving
front is established rapidly, can be tied to the time dependence
associated with the moving interface. We should keep in mind,
however, that for certain parameter values (α small in Section 4.4)
the quasi-steady state solution does yield inaccurate results.

For $0 < x < X(t)$, in the region of the dump where $R(x, t) = 0$,
equation (5.1.7) holds. In solving the steady state equivalent
of (5.1.7) we only require the two appropriate boundary conditions
(5.1.6) and (5.1.8). Equation (5.1.6), a consequence of the time
integration of the surface boundary condition for the dimensionless
oxygen concentration, reintroduces time dependence into the problem,
while (5.1.8) simply states that $w(x, t)$ is constant on the planar
moving front $X(t)$. The second condition (5.1.8) is a matching
condition between the two regions either side of $X(t)$, and the
constant $t_c$ is known explicitly from equation (5.1.5). The result
for $w_2(x, t)$ can therefore be written as

$$w_2(x, t) = \frac{x^2}{2} - \frac{x}{X(t)} \left( \frac{X(t)^2}{2} + t - t_c \right) + t.$$  \hspace{1cm} (5.2.9)

We observe that 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 $w(x, t)$, we have, from
(5.2.9), that the oxygen profile is linear in $x$ for the quasi-steady
approximation which is as expected for planar moving boundary problems
(see, for example, Crank, 1975).
For \( X(t) < x < 1 \), in the region of the dump where \( R(x, t) \neq 0 \), the approximate equation (5.2.3) holds. At the upper boundary of the region \( x = X(t) \) equation (5.1.8) again holds while at the lower boundary, the base of the dump, the no flux condition, equation (5.1.6) holds. Upon neglecting the time derivative of equation (5.2.3) and solving the resultant ordinary differential equation using boundary conditions (5.1.8) and (5.1.6) we can then write \( w_3(x, t) \) as

\[
w_3(x, t) = \frac{t_c \cosh \sqrt{\beta} (1 - x)}{\cosh \sqrt{\beta} (1 - X(t))},
\]

where \( w_3(x, t) \) depends on time only through its functional dependence on \( X(t) \).

We note that the solutions \( w_2(x, t) \) and \( w_3(x, t) \), given by equations (5.2.8) and (5.2.10) respectively, depend explicitly on the position of the planar moving boundary \( X(t) \), which at this stage is still unknown. We require, therefore, an extra boundary condition at the moving front \( X(t) \). Unlike the boundary condition at the moving front in the classical planar moving boundary problem (given by equation (A 3) in Appendix A) we have no chemical reaction proceeding at the planar moving front \( X(t) \), since the reaction is continuing in particles dispersed throughout the dump. Therefore, we state 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 continuous). The extra boundary condition on \( w(x, t) \) follows as

\[
\frac{\partial w_2}{\partial x}(X(t), t) = \frac{\partial w_3}{\partial x}(X(t), t).
\]

Substituting (5.2.9) and (5.2.10) into (5.2.11) gives a transcendental
equation for $X(t)$, viz

$$t = t_c + \frac{X^2}{2} + t_c \sqrt{\beta} X \tanh \sqrt{\beta} (1 - X). \quad (5.2.12)$$

Therefore the pseudo-steady state upper bound solution $\bar{w}(x, t)$ is given by equation (5.2.8) for $t < t_c$, while for $t > t_c$ the upper bound solution is given by equation (5.2.9) between the surface of the dump and the planar moving front and by equation (5.2.10) ahead of the planar moving front to the base of the dump, where the position of the moving boundary $X(t)$ is given by equation (5.2.12).

We are, however, more interested in finding the approximate solution to $u(x, t)$, the oxygen concentration in the pore spaces of the dump, and since

$$u(x, t) = \frac{\partial w}{\partial t}(x, t), \quad (5.2.14)$$

we obtain from (5.2.8) that for $t < t_c$

$$\bar{u}(x, t) = e^{-\beta t} \text{erfc}(\frac{\sqrt{\beta} X}{2\sqrt{t}}) + \sqrt{\beta} \int_0^t e^{-\beta \tau} \text{erfc}(\frac{\sqrt{\beta} X}{2\sqrt{\tau}}) \, d\tau, \quad (5.2.15)_1$$

and for $t > t_c$ we have

$$\bar{u}(x, t) = 1 - \frac{x}{X^2} \left( -\frac{x^2}{2} - (t - t_c)X + X \right), \quad (5.2.15)_2$$

for $0 < x < X(t)$ and

$$\bar{u}(x, t) = t_c \sqrt{\beta} X \tanh \sqrt{\beta} (1 - X) \frac{\cosh \sqrt{\beta} (1 - x)}{\cosh \sqrt{\beta} (1 - X)}, \quad (5.2.15)_3$$

for $X(t) < x < 1$ where $\dot{X}(t) = dX(t)/dt$. An expression for $\dot{X}(t)$ can be obtained by differentiating equation (5.2.12) with respect to time, and noting that $t_c \beta = 1$, to give

$$\dot{X}(t) = [X \tanh \sqrt{\beta} (1 - X) + t_c \sqrt{\beta} \tanh \sqrt{\beta} (1 - X)]^{-1}. \quad (5.2.16)$$
We may rewrite equation (5.2.16) by using (5.2.12), again, to give
\[ X(t) = \frac{t_c X}{(t - t_c - \frac{X^2}{2})(t - \frac{X^2}{2})} \]  
(5.2.17)
Substitution of (5.2.17) and (5.2.12) into (5.2.15) \textsuperscript{2} finally gives, for \( t > t_c \),
\[ x^2_{t - t_c - \frac{X^2}{2}} \sqrt{\beta} \frac{X(t)}{X(t)} = 1 - \frac{t - t_c - \frac{X^2}{2}}{t - \frac{X^2}{2}}, \quad 0 < x < X(t), \]  
(5.2.18) \textsuperscript{1}
and
\[ u(x, t) = \frac{t_c \cosh \sqrt{\beta} (1 - x)}{(t - \frac{X^2}{2}) \cosh \sqrt{\beta} (1 - X)}, \quad X(t) < x < 1, \]  
(5.2.18) \textsuperscript{2}
while the solution for \( t \leq t_c \) remains unchanged as given in equation (5.2.15) \textsuperscript{1}.

Motion of the Planar Moving Front

A number of observations can be made concerning the motion of the moving interface \( X(t) \). The moving front separates the dump into two regions. Behind the front, between the surface of the dump and the moving boundary itself, is a region which is fully reacted whilst ahead of the front is a region which is partially reacted. In the simple homogeneous semi-infinite dump formulation (Ritchie, 1977) it is assumed that a distinct boundary exists, separating totally reacted and unreacted portions of the dump. Here, from the mathematical analysis, we obtain a partially reacted region immediately in front of the moving interface, primarily because we consider as part of the model, the microstructure of the dump (that is, we include reacting particles). Characteristics of the moving front \( X(t) \) are considered below.
Firstly if we set \( X(t) = 1 \), in equation (5.2.12), that is allowing the moving front to reach the bottom of the dump (indicating that the dump has fully reacted), we obtain an expression for the reactive lifetime of the waste rock dump, given by

\[
t_d = \frac{1}{2} + t_c. \quad (5.2.19)
\]

The time \( t_d \) consists precisely of the time to completely oxidise the particle at the surface of the dump \( (t_c) \) (that is the delay until the moving front \( X(t) \) appeared) and the time for the moving front \( X(t) \) to travel the full depth of the dump. The simple homogeneous dump model of Ritchie (1977) gives rise to the classical moving boundary solution,

\[
t_d = \frac{1}{2}, \quad (5.2.20)
\]

after allowing for scaling factors. Hence the approximate upper bound solution indicates that the more complex model equations have introduced a delay in the oxidation process down the dump consisting of the time for the surface particle to fully react. We note also that, from equations (4.5.23) and (5.1.9), as \( \alpha \to 0 \) then \( t_c \to 0 \), and (5.2.19) collapses on the classical result (5.2.20).

For \( X(t) \approx 0 \) we can obtain an explicit expression for \( X(t) \) from equation (5.2.12) given by

\[
X(t) = \frac{\left( t_c \theta^2 + 2(2 \theta^2 - 1)(t - t_c) \right)^{\frac{1}{2}} - \theta t_c^{\frac{1}{2}}}{(2 \theta^2 - 1)}, \quad (5.2.21)
\]

where \( \theta = \tanh \sqrt{\beta} \). The velocity of the moving front near \( X(t) = 0 \) can therefore be expressed as

\[
\dot{X}(t) = \left( t_c \theta^2 + 2(2 \theta^2 - 1)(1 - t_c) \right)^{-\frac{1}{2}}, \quad (5.2.22)
\]
and since $X(t) \sim 0$ implies $t \sim t_c$, we have

$$X(t_c) = \frac{1}{\theta t_c^2}. \quad (5.2.23)$$

Therefore, for $X(t) \sim 0$, equation (5.2.23) gives a finite velocity for the moving front ($a \neq 0$), unlike the classical solution which has an infinite velocity initially. However, in the limit as $a \to 0$, equation (5.2.23) gives an infinite velocity as well. Also for $X(t) \sim 1$, using (5.2.12), we can observe that

$$X(t) = 1 - \left[1 - 2(t - t_c)\right]^2, \quad (5.2.24)$$

which gives a velocity of the planar moving front $X(t)$ as

$$\frac{d}{dt} X(t) = \left[1 - 2(t - t_c)\right]^{-\frac{1}{2}}, \quad (5.2.25)$$

and as $t \sim t_d$ (which is true for $X(t) \to 1$), from equations (5.2.19) and (5.2.25), the velocity $X(t)$ becomes infinite. The occurrence of an infinite velocity at $X(t) = 1$ ($t = t_d$) is shown below to be solely a property of the finite depth of the dump.

Consider for the moment the situation where the model dump is semi-infinite in depth while retaining all other characteristics of the finite depth model described in Chapter 4. In the semi-infinite system we will place an artificial cut-off point at $x = 1$ which we will consider to be the base of the dump. So we acknowledge then that the time for the planar moving front $X(t)$ to reach $x = 1$ is the time for the dump to finish reacting even though the region below $x = 1$ has properties identical to the dump above the "base". For a semi-infinite dump the "bottom" boundary condition on $w(x, t)$ can be
written as

\[ w(x, t) \text{ is finite as } x \to \infty, \quad (5.2.26) \]

instead of (5.1.6). Solving for \( w_3(x, t) \) again, using (5.2.26), and
then employing the matching condition (5.2.11), allows the position
of the moving front to be expressed as

\[ X(t) = -t_{c}^{\frac{1}{2}} + \left[ t_{c} + 2(t - t_{c}) \right]^\frac{1}{2}. \quad (5.2.27) \]

The time for the planar moving front to reach \( X(t) = 1 \) can be obtained
directly from (5.2.27) as

\[ t_{d'} = t_{c}(1 + \sqrt{8}) + \frac{1}{2}. \quad (5.2.28) \]

The velocity of the planar moving front can be obtained from (5.2.27) as

\[ \dot{X}(t) = \left[ t_{c} + 2(t - t_{c}) \right]^{-\frac{1}{2}}, \quad (5.2.29) \]

which for \( t = t_{c} \) gives

\[ \dot{X}(t_{c}) = \frac{1}{\sqrt{t_{c}}}. \quad (5.2.30) \]

Also for \( X(t) = 1 \) or \( t = t_{d'} \) we have from (5.2.29) that

\[ \dot{X}(t_{d'}) = \left( t_{c} + 1 \right)^{-\frac{1}{2}}. \quad (5.2.31) \]

Hence both equations (5.2.30) and (5.2.31) indicate that for \( a \neq 0 \),
the moving boundary \( X(t) \) in a semi-infinite model of the dump has
a finite velocity both when the front first appears in the dump
\( (t = t_{c}) \) and when the front reaches the "base" of the dump \( (X(t) = 1) \).
Note that the time to fully react the dump \( (t_{d'}) \) given by equation
(5.2.28) for the semi-infinite model, is greater than the time to
fully react the finite depth dump given by equation (5.2.19). This follows from condition (5.2.26) which allows oxygen to be transported through the point \( x = 1 \) for the semi-infinite dump whereas for the finite dump model, condition (5.1.6) implies that no transfer of oxygen will occur through the point \( x = 1 \) leading to the accumulation of oxygen in the region \( 0 < x < 1 \).

Finally, we note the functional dependence on \( X(t) \) of the oxygen concentration at \( X(t) \), given by

\[
\bar{u}(X(t), t) = \left( 1 + \sqrt{\beta} X(t) \tanh \sqrt{\beta} \left[ 1 - X(t) \right] \right)^{-1}, \tag{5.2.32}
\]

where we have used equations (5.2.18) and (5.2.12). We can see from (5.2.32) that at \( X = 1 \), \( \bar{u} = 1 \) indicating that the instant the planar moving front reaches the base of the dump the pore spaces attain their maximal oxygen concentration. This is a trait common to steady state solutions of many different moving boundary problems and has been discussed briefly in Section 5.1.

### 5.3 Approximate Lower Bound Solution

In subsequent sections we will primarily be interested in the approximate results of the previous section. However, for completeness, a further approximate solution is outlined describing a lower bound solution for the function \( w(x, t) \). The corresponding approximation to the oxygen concentration is found to be an upper bound on the actual concentration \( u(x, t) \). The lower bound result also gives extra information regarding the motion of the planar moving front within the dump.
Since $0 < R(x, t) < 1$ we have that $R^3$ is reasonably small compared to one, and therefore on reconsideration of equation (5.1.4) we can obtain an approximate lower bound solution $w(x, t)$ by solving equation (5.1.7) for all time $t > 0$ subject to the boundary conditions (5.1.6). However we should recognise that the solution will give unreal results, especially for short times where $w(x, t)$ will be negative.

Consider the non-steady state equation (5.1.7) which is defined for all time and is amenable to solution. Assume a solution of the form

$$w(x, t) = t + f(x) + \sum_{n=1}^{\infty} C_n X_n(x) T_n(t). \tag{5.3.1}$$

The initial and boundary conditions (5.1.6) are satisfied if

$$\sum_{n=1}^{\infty} C_n X_n(x) T_n(0) = -1,$$

$$f(0) = 0, X_n(0) = 0, \tag{5.3.2}$$

$$f'(1) = 0, X'_n(1)=0$$

Substitution of (5.3.1) into equation (5.1.7) and then solving for $f(x)$ gives

$$f(x) = \frac{(1 + \delta_1)}{2} x^2 + Ax + B, \tag{5.3.3}$$

where using (5.3.2)$_2$ and (5.3.2)$_4$ we have

$$f(x) = \frac{(1 + \delta_1)}{2} (x^2 - 2x). \tag{5.3.4}$$

The solutions for $X_n(x)$ and $T_n(t)$ become

$$X_n(x) = A_n \cos \lambda_n x + B_n \sin \lambda_n x,$$

$$T_n(t) = C_n e^{-\lambda_n^2 t/6_1}. \tag{5.3.5}$$
Using (5.3.2) for (5.3.5) we obtain for \( X_n(x) \) and \( T_n(t) \)
\[
X_n(x) = \sin\left[ \frac{(2n-1)\pi x}{2} \right],
\]
\[
T_n(t) = \exp\left[-\frac{(2n-1)^2\pi^2 t}{4\delta_1} \right],
\]
and therefore \( w(x,t) \) can be written as
\[
w(x,t) = t + \frac{(1+\delta_1)}{2} (x^2 - 2x) + \frac{16}{\pi^3} \sum_{n=1}^{\infty} \frac{e^{-\frac{(2n-1)^2\pi^2 t}{4\delta_1}}}{(2n-1)^3} \sin\left[ \frac{(2n-1)\pi x}{2} \right].
\]

We note from (5.3.7) that \( w(x,t) \) is non-positive when \( t=0 \) given by
\[
w(x, 0) = \frac{1}{2} (x^2 - 2x),
\]

since
\[
\frac{16}{\pi^3} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^3} \sin\left[ \frac{(2n-1)\pi x}{2} \right] = -\frac{\delta_1}{2} (x^2 - 2x).
\]

Expression (5.3.9) can be found using identity 546 on page 102 of Jolley (1961). In particular if \( a+1 \) in identity 546 of Jolley (1961) and we formally integrate the resultant equation twice with respect to \( x \) we obtain equation (5.3.9). The left hand side of equation (5.3.9) can also be recognised as the Fourier series expansion of the quadratic polynomial on the right hand side of (5.3.9).

The fact that \( w(x,t) \) is negative for some times, and spatial coordinates, as indicated in equation (5.3.8), is a consequence of the contradiction between the form of the differential equation (5.1.7) and the original definition of \( w(x, t) \) given by equation (5.1.3). However, even though \( w(x, t) < 0 \), for some times, the approximate oxygen concentration, \( u(x,t) = \frac{3}{\delta t} w(x, t) \), takes the form
\[
u(x,t) = 1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{e^{-\frac{(2n-1)^2\pi^2 t}{4\delta_1}}}{(2n-1)^3} \sin\left[ \frac{(2n-1)\pi x}{2} \right],
\]
which is always positive or zero and less than or equal to one. Therefore \( u(x, t) \) has the correct behaviour in order to be a reasonable approximation to \( u(x, t) \). We observe, in fact, that solution (5.3.10) is precisely the solution obtained if \( R(x, t) = 0 \) in equation (4.5.19).

Of interest, at this point, is to impose the identity (5.1.8) upon the solution (5.3.7). This yields a transcendental equation to solve for \( X(t) \) in terms of time, given by

\[
t = t_c - \frac{(1+\delta_1)}{2} X(X - 2) - \frac{16\delta_1}{\pi^3} \sum_{n=1}^{\infty} e^{-(2n-1)^2 \pi^2 t / 4\delta_1} \sin[\frac{(2n-1)\pi X}{2}].
\]

(5.3.11)

For \( X(t) \sim 1 \) (that is \( t \sim t_d^- \)) equation (5.3.11) can be simplified and rearranged to give

\[
X(t) = 1 - \left(1 - \frac{2(t - t_c)}{(1+\delta_1)}\right)^{\frac{1}{2}}.
\]

(5.3.12)

The time to complete reaction of the dump \( (t_d^-) \) predicted by this approximate solution can then be obtained by setting \( X(t) = 1 \) in equation (5.3.12) to give

\[
t_d^- = t_c + \frac{(1+\delta_1)}{2} = t_d + \frac{\delta_1}{2}.
\]

(5.3.13)

We note that the lower bound solution and the upper bound solution give nearly identical times to complete reaction of the waste heap model, differing only by the factor \( \delta_1/2 \) and since \( \delta_1 \sim 10^{-3} \) then the difference is very small. Therefore the actual time to complete reaction of the model dump for the more precise equations (5.1.4) to (5.1.7) may be postulated as lying close to \( t_d \) given by equation (5.2.19).
6.1 Introduction

Thus far model equations for White's dump at Rum Jungle have been developed, simplified and approximate solutions obtained. So as to assess the model's full potential as a predictive tool for a naturally leaching waste rock dump, and to investigate the accuracy and validity of the approximate solutions a numerical solution procedure is required.

In the next section the numerical technique adopted is outlined with the various advantages of the scheme underscored. In summary the numerical method is a combination of two stable schemes each dealing with different aspects of the model equations. Under these schemes the coupled system of partial differential equations, (4.5.19) and (4.5.20), become an implicit system of difference equations which is solved iteratively using standard techniques. Mention is also made of an initial attempt to numerically integrate the model equations and of the difficulties encountered. The limitations of the scheme used in this initial attempt are stated and an explanation is forwarded as to why the technique and the model equations seem incompatible.

In Section 6.3 general characteristics of the model solution are outlined while a comparison is made between the approximate, numerical and simple model solutions. The approximate solution (approximate upper bound solution of Chapter 5) is shown to be a reasonably
accurate, easily evaluated analytic result especially useful for parametric sensitivity investigations. The simple model solution is also shown to be a limiting case of the numerical and approximate results. Results are presented in graphical form, illustrating oxygen profiles, heat source distributions, total sulphate production levels, the position of the reaction front R(x,t) within particles of the dump, and the distance of the planar moving front X(t) from the top surface of the dump.

In Section 6.3 we outline results for the model which describe in more detail the physical characteristics of the dump model and we vary some of the parameters in order to investigate the sensitivity of the model results to such changes. In Section 6.5 the implication of the particle size distribution (discussed in Section 4.7) on output parameters of the model is investigated.

6.2 The Numerical Method

The aim in this section is to derive a numerical method which will adequately integrate equations (4.5.19) through to (4.5.22) for the range of parameter values suggested in Table 4.1.

A simple-minded approach and the scheme initially attempted by the author (Davis and Ritchie, 1982) is to discretise the spatial diffusion portion of equation (4.5.19) using central differences resulting in two coupled ordinary differential equations in time at each spatial point down the dump. A procedure able to integrate such systems of equations is the DIFSUB routine, a computer code written
by Gear (1971) designed to integrate a set of ordinary differential first order equations over one time step at each call. To facilitate the use of the package the initial condition for $R(x,t)$, equation (4.5.22), needs to be changed to read

$$R(x, 0) = 0.9999, \quad (6.2.1)$$

because singularities are apparent in both equations (4.5.19) and (4.5.20) initially a particle starts to react. The DIFSUB routine is found to produce acceptable answers to the model equations, with a smooth progression of the planar moving front down the waste dump and a smooth diffusion solution in its wake. So output parameters such as oxygen concentration and heat source density are adequately found using the DIFSUB package.

The time steps used by DIFSUB, however, are limiting in that they remain extremely small throughout the entire calculation. This occurs because DIFSUB controls the step size to achieve a desired accuracy (user supplied) and at any time in the calculation both the case $R = 0$ and $R = 1$ may be present in the system at some depth within the dump. DIFSUB, therefore, while retaining the accuracy of the end result, necessarily restricts the time step size to be unreasonably small, so much so, that for reasonably accuracy, to run the model from the creation of the dump to the present day (~ 26 years) becomes a large job (of the order of hours) let alone predicting the dump's behaviour until it finishes reacting (~ 250 years, from equation (5.2.19) and Table 4.1). Hence the DIFSUB routine limits the extent to which information can be extracted from the model readily and in
particular limits the predictive and parameter testing capabilities of the model.

In assessing why DIFSUB is inappropriate to solve the model equations we note that the time stepping algorithm in DIFSUB is an explicit one and therefore not only requires a small time step for accuracy but also for stability reasons. So in researching a numerical technique, particular to the problem at hand, the experience with DIFSUB suggests that implicit time stepping may well be useful as part of such a scheme. Below we design a simple integration scheme, specific to such features of the problem, which is used in obtaining the numerical results presented in this thesis.

For diffusion (parabolic) type equations the Crank-Nicolson (Crank and Nicolson, 1947) discretisation has become a somewhat standard integration scheme, a particular advantage being that the scheme is numerically stable. The technique uses central differences on the spatial diffusion portion of the partial differential equation while numerical stability is achieved by applying a trapezoidal rule in the time domain. To avoid the singularity at \( R(x, t) = 1 \) in the remaining loss term of equation (4.5.19) we employ a Backward Euler formulation which is also numerically stable. Equation (4.5.19) can therefore be written in finite difference form as

\[
\delta_1 (u_{j}^{k+1} - u_{j}^{k}) = \frac{\Delta t}{2A} (u_{j+1}^{k+1} + u_{j-1}^{k+1} - 2u_{j}^{k+1} - 2u_{j}^{k} + u_{j-1}^{k} + u_{j+1}^{k}) \\
- \frac{3k^2u_{j}^{k+1}R_{j}^{k+1}}{(1 - R_{j}^{k+1})}, \tag{6.2.2}
\]

for \( j = 1, 2, \ldots, N \), where \( u_{j}^{k+1} \) is the discretised value of the oxygen
concentration at mesh space \( j \) and discrete time \( k + 1 \), \( \Delta t \) is the time interval step and \( \Delta x \) is the vertical mesh spacing. Collecting terms in \( t + \Delta t \) on the left hand side and terms in \( t \) on the right hand side of equation (6.2.2) we have a tridiagonal system of implicit equations written as

\[
\frac{\Delta t}{2\Delta x^2} (u_{j+1} + u_{j-1}) + u_j \left( \delta_1 + \frac{\Delta t}{\Delta x^2} + \frac{3k\Delta t R_j^{k+1}}{1 - R_j^{k+1}} \right) = \frac{\Delta t}{2\Delta x^2} (u_{j+1} + u_{j-1}) + u_j \left( \delta_1 - \frac{\Delta t}{\Delta x^2} \right),
\]

for \( j = 1, 2, \ldots, N \). Equations (6.2.3) can now be written in matrix form, solvable using the Cholesky LDL^T decomposition and then forward and backward substitution until the final result is achieved. The Cholesky decomposition is particularly appropriate since the system of equations is not only tridiagonal but also symmetric.

Before the numerical scheme can be implemented, however, we are required to find each of the \( R_j^{k+1} \) in equation (6.2.3) at each time step. Equation (4.5.20) describes the relationship between \( R(x,t) \) and \( u(x,t) \) and therefore upon integration with respect to time, using the trapezoidal rule to integrate \( u(x,t) \) and Backward Euler again to integrate the time derivative of \( R(x,t) \), we obtain

\[
\left( \frac{1}{2} R_j^{k+1} - \frac{1}{3} R_j^{k+1} \right) - \left( \frac{1}{2} R_j^k - \frac{1}{3} R_j^k \right) = -\frac{k\Delta t}{2} (u_j^{k+1} + u_j^k).
\]

The cubic polynomial gives \( R_j^{k+1} \) in terms of \( u_j^{k+1} \) and can be readily solved using a simple Newton's method given that we know each of the \( u_j^{k+1} \).
The coupled equations (6.2.3) and (6.2.4) still require a starting guess for the position of the reaction interface at node point \( j \) in the dump \( R_j \) at the next time interval in order to solve for the next time step. Therefore \( R_j^{k+1} \) is approximated by

\[
R_j^{k+1} = 2R_j^k - R_j^{k-1}.
\]  

(6.2.5)

The solution algorithm can therefore be written as:-

i. Guess a value for each \( R_j^{k+1} \) using equation (6.2.5);

ii. Solve for \( u(x,t) \) at each node point using the tridiagonal system given by equation (6.2.3);

iii. Solve for \( R(x,t) \) at each node point by substituting the result for \( u(x,t) \) from (ii) into (6.2.4) and employing Newton's method to solve the cubic polynomial;

iv. Iterate between steps (ii) and (iii) until convergence, within prescribed error bounds, to the required solution doublet \( u(x,t) \) and \( R(x,t) \).

The boundary conditions (4.5.21) can be readily accommodated in the scheme. Equation (4.5.21) simply implies substituting

\[
u_0 = 1,
\]  

(6.2.6)
for all time in equation (6.2.3). The bottom boundary condition (4.5.21) requires a little more consideration. We conceive of an imaginary \( (N+1) \)th point below the base of the dump and discretise the boundary condition thus

\[
\frac{\partial u}{\partial x}(1, t) = \frac{u_{N+1}^k - u_{N-1}^k}{2\Delta x} = 0, \quad (6.2.7)
\]

and therefore we have immediately

\[
u_{N+1}^k = u_{N-1}^k. \quad (6.2.8)
\]

We now replace (6.2.8) into equation (6.2.3) with \( j = N \) and divide the resulting equation by two in order to retain the symmetric form of the required system of equations.

An advantage that becomes immediately apparent is that, for similar accuracy criteria and mesh interval size, the combined Crank-Nicolson and Backward Euler scheme, outlined above, is of the order of 600 times faster than the DIFSUB routine. The time step for the combined scheme had a range given by

\[
10^{-7} < \Delta t < 10^{-5}, \quad (6.2.9)
\]

depending primarily on the radius size of particles comprising the dump. The mesh spacing bears directly on the size of vectors required in the solution procedure. For the results presented here, the mesh spacing varied from 1/16 of a metre \((N = 288)\) to 1/2 a metre \((N = 36)\) to gain acceptable accuracy. The variation in mesh size depends also, in the main, on the size of particles considered in the model equations. For small sized particles a small spatial mesh interval
is required whereas for large sized particles a course grid proves sufficient. The reasons for this requirement will become clear in results and discussions of subsequent sections.

The results presented here were all obtained on the central IBM computer at the Australian Atomic Energy Commission, Lucas Heights N.S.W. while the initial development of the programme was undertaken on the UNIVAC machine at the University of Wollongong, Wollongong, N.S.W.

6.3 Approximate, Numerical and Simple Model Solutions

Values used in the calculations, to obtain the results presented in this section, for parameters such as pyrite content (3%), diffusion coefficients \(D_1 = 6.72 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}\), porosity (40%) and dump height (18m) are those generally applicable to White's dump. Numerical results presented in this section are obtained using the combined Crank-Nicolson and Backward Euler numerical algorithm of Section 6.2. The approximate solution used for comparison purposes is the approximate upper bound solution developed in Chapter 5. Results for the lower bound case will not be presented.

Consider for comparison purposes the case where the dump is composed of single sized particles. Assumptions have led us to describe the pyritic oxidation reaction within the particles, in terms of a moving reaction front formulation where between the outer surface of the particle and the front itself is a fully reacted region and between the front and the centre of the particle is
a totally unreacted region. It follows that a macroscopic planar moving front is then in evidence within the dump proper which is somewhat analogous to the moving reaction front that appears in the simple homogeneous slab model of Ritchie (1977). Between the surface of the dump and the planar front lies a totally reacted portion of the dump whereas, unlike the model of Ritchie (1977), between the planar front and the base of the dump is a partially reacted region where particles are at all stages of oxidation.

Typically results show that below the planar front there are two regions, a high oxidation rate zone immediately below the front whilst deeper again there is a region where the oxidation rate is low and little oxidation of particles has occurred. The "width" of the high oxidation rate region depends on the size of particles in the dump (decreasing with decreasing particle size) but the region has no well defined lower limit, such as the planar front. This is because oxygen diffuses to the base of the dump through the pore spaces and therefore oxidation is occurring throughout the region below the planar front, even though in some areas (especially for small particles) the oxidation rate is miniscule. So the inclusion of spherical particles, describing the microstructure of the dump, within which the oxidation of pyrites is assumed to proceed, gives rise to a partially reacted region within the dump. Another difference between the simple model and the model presented here is that the planar moving front remains at the surface of the dump, for a time that increases with increasing particle size, before moving down
through the dump whereas for the simple model there is no time delay. Results given below serve to illustrate the points made above and also allow comparison of the approximate numerical and simple model solutions.

A direct measure of the pollutant load presented by the waste rock dump to the environment of the mine site, at any time during the reactive lifetime of the waste material, is the total sulphate production rate. The total sulphate production rate is a macroscopic (average) property of the dump since, within a constant of proportionality, it is the integral of the heat source distribution over the full height of the dump (see Section 4.6). Figure 6.1 shows the total $SO_4$ production rate as a function of time from close to the creation of the dump to the cessation of pyritic oxidation within the dump for two particle sizes, 1.0mm and 1.0cm and the simple model result. It is apparent that for much of the dump's lifetime (from about 20 years to 200 years for moderate to small sized particles) the numerical, approximate and simple model results are in excellent agreement. Similarly, over the same time span, the curves for different particle sizes show little deviation from one another. Separation of the curves is seen, however, close to the "birth" of the dump and also near the end of the dump's active life. We observe also that the numerical and approximate results, for the total $SO_4$ production rate, approach the simple model results for small particle size.

A pseudo-macroscopic property of the waste dump is the position
Figure 6.1 The integrated $SO_4$ production rate as a function of time after the creation of the waste rock dump.
of the planar moving front within the dump which is a good indicator of the proportion of dump material that has been oxidised at various stages of the dump's history. Figure 6.2 shows the distance of the planar interface from the top surface of the dump as it varies with time. We compare the results obtained from the approximate solution and those obtained using the more exact numerical solution for a number of different sized particles. The curve for the simple model is also included and it can be shown that in the limit as the particle size tends to zero the approximate result (5.2.12) gives the equivalent simple model result for the motion of the moving front. We observe that the time dependence of the planar front shown in Figure 6.2 is largely the same for different particle sizes with a constant time span between, when the moving front first appears, through to when the dump finishes oxidising. The approximate result is seen to diverge from the numerical result in the mid region of the dump, especially for larger particle sizes, however, the curves coincide both initially the moving front appears in the dump and when the moving front reaches the base of the dump. For moderate (10 mm) to small (10^-1 mm) sized particles the reactive lifetime of White's dump, from Figure 6.2, is predicted to be approximately 250 years assuming a maximum porosity of 40%.

The model as described in Chapter 4 assumes that the oxidation of pyrites within a waste rock dump, such as White's dump at Rum Jungle, is diffusion rate-limited. However, the model consists of two diffusion mechanisms; the diffusion of oxygen from the top
Figure 6.2  The distance of the planar moving front from the top surface of the dump as a function of time. Comparison of the exact numerical solution with the approximate solution for different size particles.
surface of the dump through the pore space to the outer surface of particles and then diffusion of oxygen in the aqueous phase, from the outer surface of the particle to the moving reaction front within individual particles of the dump. The rate-limiting process could therefore be either of these two diffusion mechanisms. From values of the diffusion coefficients of oxygen, $D_1$ and $D_2$ (see Table 4.1) it would seem that diffusion within particles of the dump is the appropriate limiting process, since $D_2 \ll D_1$, but it should be noted that the characteristic time for oxygen transport within the particles becomes extremely small for reasonably small particles (see equation (4.5.8)). This, coupled with the fact that particles within the dump are at all stages of oxidation, implies that the diffusional rate-limiting mechanism will be different in different regions down the dump and indeed be different at various stages of the dump's history. Microscopic parameters such as oxygen concentration within the pore space of the dump, the moving reaction interface position within reacting particles and the heat source distribution serve to illustrate the points made above, but particularly oxygen concentration profiles.

Accordingly, Figure 6.3 depicts the spatial distribution of the oxygen concentration in the pore space of the dump as predicted by the present model for the numerical and approximate solutions, as well as the oxygen concentration profile predicted by the simple model of Ritchie (1977). The oxygen profile of the simple model decreases from its maximum at the surface of the dump (atmospheric
Figure 6.3 The dimensionless oxygen concentration as a function of depth for various particle radii. Comparison of the numerical solution with the approximate and simple model solutions at time equal to 26 years.
oxygen concentration) in a near linear fashion to the planar reaction front. This is in contrast to the concentration predicted by the present model which for medium to small size particles (<10mm)) decreases linearly (pore space diffusion rate-limited) to the point where the whole volume of the particle is oxidised, then decreases in a curvilinear fashion to the base of the dump (aqueous diffusion rate-limited). For a particle radius of 50mm, none of the particles are fully oxidised in the time span considered (25 years) and so the oxygen concentration decreases curvilinearly over the whole depth of the dump. Oxygen concentration profiles are also presented corresponding to the numerical and approximate results for a dump comprised of 20mm particles. A large size particle radius is chosen to accentuate the differences between the two solution procedures in order to make the difference easily visible when the information is graphically presented. The approximate solution lies below both the numerical and simple model curves from the surface of the dump to a distance within the dump which varies with particle size. For the ore size illustrated (20mm) the curves cross over about 4m down the dump and from that point on the oxygen profile, obtained using the approximate technique, continues above that of the numerical technique. The discrepancy between the approximate and numerical solution for the oxygen profiles, however, becomes very small for particles of about 10mm radius or less. Figure 6.3 also shows, as indicated in previous figures for other parameters of interest, that for smaller particle radii the oxygen concentration profile of the present model approaches the oxygen profile of the simple model.
This points to consistency among results of the present model, a necessary feature of any simulation.

Of interest also is the position of the moving reaction interface within particles of the dump both as a function of time and as a function of the depth of the particle within the dump. Figure 6.4 shows the dimensionless distance of the moving reaction boundary from the centre of particles positioned at various depths within the dump and as a function of time. The numerical and approximate calculations are illustrated for a dump with 3% sulphur and a particle radius of 10mm only. It can be seen that, as was expected, the further the particle is from the surface of the dump the greater is the time it remains unreacted. It is clear also that once a particle starts to react and the further it is from the surface of the dump, the slower is the rate at which the reaction front moves towards the centre of the particle. It is interesting to note that even though it is not distinguishable in Figure 6.4, we have from equation (4.5.20), that the velocity of the reaction front \( R(x,t) \) becomes infinitely fast both initially the reaction front moves from the surface of the particle and when the reaction front approaches the centre of the particle. The infinite velocity when \( R(x, t) \sim 1 \) is solely a consequence of the instantaneous transfer of oxygen across the gas-liquid interface and, as discussed in Chapter 4, because the transport processes on both sides of the two-phase interface are assumed diffusional, boundary condition (4.2.13) is appropriate. Alternatively, adopting a flux (surface evaporation) type boundary
Figure 6.4 The position of the reaction front within the particle as a function of time. Comparison of the numerical solution with the approximate solution at various depths and for a dump comprised of particles of size 1cm.
condition would result in a finite velocity as the particle starts to oxidise, however, the associated mass transfer coefficient would have little meaning in the present context.

Included in Figure 6.4 are reaction front profiles calculated from the approximate solution of Section 5.2. Results are presented for a dump comprised of 10mm particles at 1m, 2m, 3m and 4m depths within the dump. We can observe from Figure 6.4 that the approximate result is a lower bound on the numerical solution with the closest agreement between the curves occurring near the end of the particle's reactive lifetime. This is also apparent from the fact that $\overline{w}(x,t)$ of Section 5.2 is an upper bound for $w(x,t)$ and therefore, from (5.15), the resultant value for $R(x,t)$ must, necessarily, be a lower bound on the actual position of the reaction front within particles of the dump. It is clear also that the approximate and numerical curves agree more closely the nearer to the surface of the dump the particle is situated, with agreement being exact at the surface. However, it cannot be said that agreement becomes worse with depth indefinitely, since from Figure 6.2, showing the position of the planar moving front within the dump, we have agreement between the approximate and numerical results initially, as stated but also when the dump is fully reacted. So the curves for the position of the reaction front within particles calculated using the approximate solution, deviate most from the numerical result when the mid-region of the dump is being oxidised. Times for particles at various depths to be totally reacted, can also be read off Figure 6.4. For example
it takes approximately 7.5 years for the 10mm particle at 1m depth to be totally oxidised bearing in mind that for a particle 1m down, from the surface of the dump, to be fully reacted, so also must be the total region from the surface to 1m depth.

Spatially dependent parameters, such as the oxygen concentration within the pore space of the dump or the position of moving reaction fronts within particles, are particularly useful when describing the microstructure of a dump undergoing pyritic oxidation. Another such parameter is the heat source distribution which gives insight into the spatial oxidation rate of pyrites within the dump. Also even though the total sulphate production rate (a macroscopic parameter) depicted in Figure 6.1, is useful for estimating the total pollution load presented to the environs of the mine site, the heat source distribution (the sulphate production rate distribution) is more useful for modelling and identifying such microscopic phenomena as regions of high and low oxidation within the waste dump.

From equation (4.6.5) we can see that the heat source distribution depends both on the oxygen concentration as well as the position of reaction fronts within particles. It is clear from the form of equation (4.6.5) that a small change in the position of the moving oxidation front \( R(x,t) \) will bring about a substantial change in the heat output predicted. So we expect from our discussion of the previous two figures, especially Figure 6.4, that the heat source distribution predicted by the approximate solution will deviate substantially from the numerical result. Figure 6.5, which shows
Figure 6.5 The spatial heat source for 1mm and 1cm particle sizes at 25 yrs. Comparison of numerical result with the approximate and simple model results.
the heat source distribution (the oxidation rate distribution) as it varies with depth down the dump, for the approximate, numerical and simple model solutions, illustrates this point for particle radii of 10mm and 1mm. Both the approximate and numerical solutions, calculated from equation (4.6.5) once \( u(x,t) \) and \( R(x,t) \) are known, show a spatial distribution down the dump whereas the simple model is depicted by a \( \delta \)-function whose position within the dump is close to the centre of the numerical distributions predicted by the present model. Observe that the smaller the particle the higher is the peak and the narrower is the "width" of the heat source distribution. Also in the limit as the particle size becomes vanishingly small the heat source distribution tends to the \( \delta \)-function predicted by the simple homogeneous slab model. It can be seen from Figure 6.5 that the approximate solution agrees qualitatively with the numerical solution, in that it has a spatial distribution unlike the simple model, however, quantitatively the peak heat production rate predicted by the approximate solution falls short of the numerical one while the approximate result also extends to a much greater depth down the dump.

So from the figures presented in this section we see that the approximate solution is generally in good qualitative agreement and reasonably good quantitative agreement with the numerical calculations. Clearly the approximate solution is adequate to calculate such quantities as the total \( \text{SO}_4 \) production rate and the lifetime of the dump as a pollution source as well as oxygen concentration
profiles for medium to small particles. The approximate solution also allows easy evaluation of such quantities, and therefore can be used to assess the impact of changing various parameters in the model with a view to the effect on the amount of pollutant emanating from waste rock dumps. In general, therefore, the approximate result is quite accurate in predicting macroscopic (average) properties of the dump as well as giving good qualitative information for microscopic parameters, however, in quantifying such parameters as the reaction front position and heat source distribution, clearly the numerical technique should be employed.

6.4 Sensitivity of the Model to Parameter Changes

Of importance in modelling physical phenomena is the variability of predictions of a model due to changing values of parameters within the model. Such variability is of interest in, say, modelling pyritic waste material from other mine sites or modelling mine material containing different densities of pyrites etc. Also, a parameter sensitivity study gives insight into which parameters control such quantities as pollution production rates within waste rock dumps.

In investigating the response of the model to variations in the parameter values we examine the sensitivity of the model to changes in the porosity of the dump (and corresponding changes in the diffusion coefficient of oxygen within the pore space of the dump) and the density of pyrites occurring in the waste ore comprising the dump. Porosity estimates considered, vary from 20% to 40% while the corresponding oxygen diffusivities are taken from a graphical
representation of oxygen diffusion coefficients in porous soil plotted against porosity, given in Papendick and Runkles (1965). Values of the density of pyrites considered for study here, range from 1% to 10% of the total dump density (the value appropriate for White's dump at Rum Jungle is thought to be 3.3%). Results are presented in this section for oxygen concentration, the motion of the planar moving front, the total sulphate production rate and the heat source distribution.

Figure 6.6 shows dimensionless oxygen concentration plotted against depth down the dump for two porosities 20% and 40% and two pyrite densities, 1% and 10%. It is clear that the pore space oxygen concentration is sensitive to changes in both the pyrite density and the oxygen diffusion coefficient and that both larger diffusivities and lower pyrite content bring about a higher oxygen concentration. This is to be expected since, for a larger porosity (40%) and corresponding larger diffusivity, oxygen will accumulate more quickly at depth within a waste rock pile. Also intuitively we expect that if the pyrite content of the ore is small then less oxygen will be required for oxidation and therefore the oxygen concentration within the pore space of the dump will be correspondingly larger. A substantial difference is, therefore, apparent in the oxygen profile for a dump of 40% porosity with a 1% pyrite content and that of a dump of 20% porosity with a 10% pyrite content.

Figure 6.7 depicts the motion of the planar moving front as it moves from the top surface to the base of the dump for 20% and 40%
Figure 6.6 The spatial oxygen concentration within the pore space of the dump for a particle size of 5mm and at 26 yrs after the creation of the dump.
Figure 6.7: The position of the planar moving interface as a function of time for a 5mm radius size and various values of the porosity and pyrite density.
porosity. The pyrite content is also varied from 1% to 10% with a result at 3% included. As expected the higher the pyrite content or the lower the porosity (and corresponding diffusivity) the longer is the time span between the initial movement of the front from the surface of the dump until it arrives at the bottom of the dump. In the time span considered (540yrs) both results, for the 20% and 40% porosity and 10% pyrite density, show that the planar moving front has not reached the base of the dump indicating that the dump has not finished reacting. This is in contrast to a 1% pyrite density which yields for 20% porosity a 230yr time span.

It is clear from Figure 6.7, that parameters such as the time to complete reaction of the dump and the velocity of the planar front are both sensitive to changes in the porosity or pyrite content of the waste dump. This is also evident from Section 5.2 which gives the dependence of such quantities explicitly in terms of the diffusivity, porosity and pyrite density. The approximate results of Section 5.2 have another advantage, in the present sensitivity analysis, since for long time results, associated with high pyrite density and low porosity, it is a simple and inexpensive task to numerically evaluate the approximate analytic result, in contrast to the full scale numerical technique of Section 6.2. Also, having already noted the accuracy of the approximate solution for small particle size (here \( a = 5\text{mm} \)), in Section 6.3, we can therefore use these readily obtainable results for large time analysis. For example, without proceeding with the full numerical method of Section 6.2, from \( t = 0 \)
to \( t = t_d \), we can use equation (5.2.19) to obtain the length of time until a dump is fully oxidised and, in particular, for 10% pyrite content and 20% porosity, equation (5.2.19) yields a time for the dump to finish reacting of 2295yrs approximately.

In Figures 6.6 and 6.7 we have shown, by raising the pyrite density of the dump or lowering the dump porosity, that the spatial oxygen concentration is lowered and the velocity of the planar interface slowed. Quantifying the effect of changes, in porosity and pyrite density, on the integrated sulphate production rate is also of interest, since we may wish to reduce the total sulphate production rate below a prescribed level in order to minimise the pollution load to the environs of a mine site. Alternately we may seek to accelerate the process of sulphate production and hence decrease the reactive lifetime of the dump to enable a shorter period of active monitoring of the site.

Accordingly, Figure 6.8 illustrates the total sulphate production rate for the same range of porosities and pyrite densities taken in the previous figures. It is clear that the lower the porosity (diffusivity) of the dump, the lower the production rate of sulphate until the dump with larger porosity finishes reacting. A dump with smaller porosity continues oxidising long after a more porous dump has ceased. A porosity of 20%, for example, produces sulphate less quickly, but for an extended period of time (230yrs), compared to a dump of 40% porosity which exhibits a higher production rate of sulphate throughout its reactive lifetime, but is totally oxidised
Figure 6.8  The total sulphate production rate as a function of time for a 5mm particle radius size. Comparison of calculations for 1% and 10% pyrite density and 20% and 40% porosity.
within 85yrs. We observe also from Figure 6.8 that a higher pyrite content produces a higher sulphate production rate for a longer period of time.

Figure 6.9 depicts the spatial heat source distribution as it varies with porosity and pyrite density of the overburden dump. As discussed for previous figures, especially Figure 6.6, for a lower porosity and higher density of pyrites we have a slowing of the movement of oxygen down the dump. This is borne out in Figure 6.9 in that the regions of high oxidation for 20% porosity and 10% density are closer to the surface of the dump than those for say 40% porosity and 1% density. The heat source distribution for a dump with 3% pyrite content and 40% porosity is also included in Figure 6.9 to show more of the gradation between 1% and 10% pyrite density. It is clear that the higher the pyrite density the higher the amplitude of the heat source distribution while the "width" of the high oxidation zone, within graphical accuracy, does not seem to vary. This appears to be true for both 20% and 40% porosity. We observe also from Figure 6.9 that for a lower porosity we attain a slightly higher peak and a narrowing of the distribution. Since a small porosity has associated with it a small diffusivity for oxygen, it follows that the penetration of oxygen through the reaction zone of the dump will not be as substantial as the penetration for a larger porosity and therefore the "width" of the reaction zone will be reduced (as observed).
Figure 6.9  The heat source distribution within the dump as a function of depth for a 5mm particle size at 26 yrs.
6.5 Import of the Particle Size Distribution

In Section 4.7 the model equations proposed in Section 4.2 were modified to include a particle size distribution appropriate to White's overburden dump. The particle size distribution depicted by Figure 4.5 is seen to be heavily weighted toward smaller size particles. In assessing the importance of the particle size distribution on model predictions we will graphically illustrate the heat source distribution for a calculation including the particle size distribution. Results are presented for four different calculations; two for different lower limit cut-off values, and two for different upper limit values, of the radii length in the particle size distribution. More specifically, the different calculations are performed for a 1mm to 10cm range, a 5mm to 10cm range, a 1mm to 20cm range and a 5mm to 20cm range. The heat source distribution is chosen as an appropriate parameter, in showing the import of the particle size distribution, since a small change in the position of the reaction front within particles of the dump, or a change in the oxygen concentration within the pore space of the dump, brings about a relatively large change in the amplitude and/or extent of the resultant heat source profile. The effect of including a particle size distribution in the model equations will therefore be readily apparent from the heat source distribution.

In general the numerical technique of Section 6.2 is easily extended to cope with the modified equations of Section 4.7. In detail, however, a decision must be made on a method to integrate over the particle size distribution in equation (4.7.8). A Gauss
quadrature technique is used which provides quadrature points (being the particle radii size) for the interval of integration. The kernel of the integral is solved for each of the particle sizes, produced by the Gauss routine, and then summed over the discrete particle sizes using the associated Gauss quadrature weightings.

When the Gauss quadrature technique is used directly on an interval appropriate to a particle size distribution (1mm to 10cm say), however, the particle sizes chosen by the Gauss routine tend toward the 10cm end of the range, and when used in the integration, produce inaccurate results, especially for such parameters as the heat source distribution. From the figures in Section 6.3, the smaller the particle size, for a single particle size calculation, the higher the peak of the heat source distribution and the narrower the "width", whilst the positioning of the peak was also further down the dump. These observations, together with the heavy weighting of the particle size distribution, equation (4.7.7), towards particles of a smaller size, suggest that, in order to obtain accurate information near the higher oxidation rate zone (especially), an integration scheme, accounting for the small particle size weighting of the integral kernel, should be adopted. The goal therefore was to obtain more particle size sample points near the 1mm end of the interval of integration.

To achieve this the "inverse interval" was taken, that is, Gauss quadrature points were obtained in the interval \( (a_n)^{-1} \) to \( (a_0)^{-1} \), while the weights appropriate to the quadrature points were
rewighted suitably, to account for the inversion procedure. The reworking of the Gauss procedure resulted in many more quadrature points being chosen near the small particle size end of the range, and consequently a more accurate integration. The integration scheme, as used, could be further improved upon, since it still required 16 Gauss quadrature points for reasonable accuracy and, even then, in the region of the dump where only large particles continue to react, greater accuracy could be achieved. In terms of computer time the CPU time used in a calculation is directly proportional to the number of Gauss quadrature points requested for the integration. So a calculation done including the particle size distribution can be lengthy (of the order of hours of CPU time) compared to a single particle size calculation (of the order of minutes of CPU time) depending on accuracy required and the amount of information required from the programme.

Figure 6.10 illustrates four calculations, each showing the spatial heat source distribution (oxidation rate) for a 1mm or 5mm lower limit cut-off value, and a 10cm or 20cm upper limit cut-off value. All results presented are for a pyrite density of 3.3%, a porosity of 40% and are given for time equal to 25yrs. It is clear from Figure 6.10 that the smaller the lower cut-off radius, the higher the peak and the narrower the "width" of the heat source distribution. The same is true of the single particle size calculation for smaller particle sizes (see Figure 6.5). The heat source distributions for a single size and a distributed particle size differ markedly,
Figure 6.10 The calculated heat source distribution within the dump as a function of depth for different lower and upper limit cut-off values of the particle size distribution, 25 yrs after the creation of the dump.
however, since for a single sized particle radius of 1mm, the model predicts a heat source distribution with a peak of about $14 \text{Wm}^{-3}$, centred around the 5.5m mark with a "width" of about 0.5m, whereas for the particle size distribution the peak of the heat distribution only attains a height of $1.1 \text{Wm}^{-3}$ positioned at a much greater depth of 7.5m, with a "width" that extends from the surface of the dump to a depth of over 8.5m. Clearly, the lowering in maximum amplitude and extension in "width" of the heat source distribution for a range of particle sizes is due to the presence of larger particles which react less rapidly than smaller particles, and therefore produce heat at a lower rate. This is borne out in Figure 6.5 of Section 6.3. It is clear from Figure 6.5 that, for a dump comprised of particles of size 1mm, say, there is no heat production in the region between the surface of the dump and approximately 5.4m in depth at some 25yrs after creation of the dump. This is because all particles in this region have fully oxidised in the time span considered and thus no longer produce heat. Contrarywise, the heat source distribution calculated for a range of particle sizes (Figure 6.10) exhibits heat production throughout the region between the high oxidation rate zone and the surface of the dump. The heat production in this shallower region is due to larger particles which have been left behind not totally reacted, and yet still producing heat from the oxidation of pyrites within them.

While it is reasonably easy to explain variations in the heat source distributions due to changes in the minimum particle size
assumed in the integration, it is more difficult to explain variations due to changes in the maximum particle size. We may well expect, for a larger upper limit particle size, from our experience thus far, that the maximum heat production would be reduced, which is observed from Figure 6.10, however, we find also that the positioning of the peak is further down the dump than is the case for a smaller upper limit radius cut-off value. This goes against our intuitive feel for the model which from Figure 6.5 is that larger particles imply a lower peak positioned further towards the surface of the dump. The positioning of the maximum heat output within the dump, therefore, requires explanation.

The inclusion of extra, large particles has the effect, within an elemental volume of the dump, of reducing the fractional volume weighting of particles of other sizes. In particular, the volume fraction of the smallest sized particles (1mm, say) is reduced, thus requiring less time for the most rapidly oxidising particles to be fully oxidised within an elemental volume. This in turn allows the peak of the heat distribution, for the larger upper limit on the particle size, to move further down the dump, while at the same time reducing the magnitude of the peak. This phenomenon is further suggested by comparison of heat source profiles when proceeding from a calculation for a single sized particle of 1mm (Figure 6.5), to a range of particle sizes, 1mm to 10cm, through to a range of 1mm to 20cm (Figure 6.10). It is clear, therefore, that the progressive inclusion of larger particles, via the particle size distribution,
pushes the peak of the heat source distribution further down the dump and reduces the peak output.

Figure 6.10 makes it clear that a calculation taking account of a range of particle sizes in the dump, with the particle size distribution given as in Figure 4.5, produces results substantially different from a calculation assuming just one particle size. Therefore a calculation of, say, the heat source distribution, assuming just one size of particle is inadequate for experimental comparison. The particle size distribution must be included in the calculation. We note, however, that for calculating the total sulphate production rate the single particle size model would be adequate since varying the particle size, in the single particle size calculation has little effect on this parameter (see Figure 6.1).

A value of about 1.0mm is thought reasonable for the value of the lower limit cut-off radius since a spherical particle of radius 0.5mm is fully oxidised in about a day after it is exposed to the atmosphere under the assumptions of the present model (see equation (4.4.20) or, equation (4.4.22) for a less accurate but adequate value). Now since the waste material forming the overburden is first excavated in the opencut and then transported to the waste rock dump site where it is back dumped on top of other waste rock, it is reasonable to suggest that all particles less than about 1.0mm in radius will be fully oxidised before being covered by other overburden material.

In this section we have only considered one particle size
distribution which is thought to be appropriate for White's overburden
dump at Rum Jungle. A different particle size distribution would
exhibit different results especially for such parameters as the
spatial heat source distribution. It is not investigated further
here, but assessing the model's results and predictions for various
particle size distributions would therefore be valuable in future
research, especially with a view to application of the model to
waste rock dumps other than White's dump at Rum Jungle. It is
instructive to note that Bartlett (1973), in developing a model for
the commercial in-situ leaching of copper ore, does in fact consider
differing particle size distributions and it is evident that the
extraction rate of copper varies quite markedly for the different
distributions suggested. Also Braun et al. (1974) consider different
ore particle size distributions when investigating the leaching of
a primary sulphide ore.
CHAPTER 7

EXPERIMENTAL COMPARISON AND EXTENSION OF THE MODEL

7.1 Introduction

In this chapter we seek to compare model predictions with experimental data as well as outline a strategy for rehabilitating a waste rock dump site. Section 7.2 contains a comparison of the present model with experimental data for oxygen concentrations, heat source distributions and the present estimated total sulphate production rate for the dump. Results of the model for various parameter estimates are also included. Explanations are forwarded for some of the discrepancies in the results, although it is clear that prediction of microscopic phenomena is difficult due to the heterogeneous nature of the dump. Section 7.3 contains a strategy for rehabilitation of a waste pile. The strategy is investigated, in detail, by alteration of the model equations which are then solved using the same numerical technique, as outlined in Section 6.2. Results are presented illustrating how such a rehabilitation proposal affects the subsequent pollution prospects for the environs of a waste rock dump undergoing pyritic oxidation.

7.2 Comparison of Model with Experimental Results

Monitoring and experimental measurement of parameters thought to be indicators of the rate of pollutant production has been proceeding at the abandoned uranium mine site at Rum Jungle for some years (see Davy, 1975 for a summary of results up to 1975). Since the initial work of Davy (1975), much of the field work has been concentrated,
in particular around the overburden dumps at Rum Jungle, primarily White's dump and more recently Intermediate dump. The interest in the waste rock dumps is due to the fact that they are the largest single source of heavy metal contamination feeding into the East Branch of the Finniss River and in order to quantify such parameters as rates of oxidation, amount of pollution emanating from the waste rock heaps and the lifetime of the heap as a pollution source etc. an intensive experimental programme has therefore been planned and implemented. Results have been obtained for heat source distributions calculated from experimentally determined temperature profiles within the dump (Harries and Ritchie, 1981), pore space oxygen concentration profiles measured down the dump (Harries and Ritchie, 1983) and estimates of the total sulphate production rate.

To monitor temperature profiles within White's dump six probe holes were drilled during September 1976 using a percussion drilling technique. The holes (see Map 2.3) each have a diameter of 90mm and penetrate from the top surface of the dump to the original ground surface. Each hole was fitted with a liner of black polyethylene pipe (~ 50mm diameter) sealed at the bottom to exclude water and the space between the liner and hole filled with dry sand. Temperature measurements, using a light weight probe and digital multimeter, were started in November-December 1978 (the beginning of the wet season) and have continued at intervals since then. The temperature distributions down the probe holes in June 1979 (see Harries and Ritchie, 1981) indicate a wide range of temperatures within the heap.
For example, in hole A, near the southern tip of the heap, the maximum temperature is \( \sim 56^\circ C \) at a depth of 14m which is approximately 26\(^\circ\)C above the near-surface temperature. This is in contrast to temperature profiles for other holes where there is little evidence of subsurface heating, the maximum being a 2.4\(^\circ\)C temperature peak above the near-surface temperature in hole C. For further discussion of temperature profiles, monitoring procedures and equipment the reader is referred to Harries and Ritchie (1981).

In Harries and Ritchie (1981) the temperature profiles obtained for each of the holes, were used to estimate the pyritic oxidation rate in White's waste rock dump by producing results describing the heat source distribution within the dump. A one dimensional heat conduction equation was assumed and values of the thermal diffusivity and heat capacity were found from experiment. Results pertaining to hole A are reproduced for comparison purposes in Figure 7.1, along with the theoretical model predictions. The theoretical curve is calculated for 3.3\% pyrite density, 40\% porosity and a range of particle sizes from 1mm to 10cm. These values are thought to be appropriate for White's dump. The predicted curve is taken at 25yrs because it is approximately 25yrs since White's dump was constructed. Both the theoretical and experimental curves show a spatial distribution down the dump with a similar "width" of the distribution for the first 9.5m. Also, the peak values of the two distributions are nearly equal. Although, the "width" and peak values of the predicted distribution and the experimental distribution are
Figure 7.1  The spatially distributed heat source within the dump. Comparison of the experimental result with numerical prediction at 25 yrs after the creation of the dump obtained, using a pyrite density of 3.3% by weight, and a porosity of 40%.
comparable, the shapes of the two profiles differ in detail. The experimental result shows a general decrease in the magnitude of the heat source with depth down the dump to 9.5 m, from a maximum amplitude of approximately $0.95 \text{W m}^{-3}$ at 1.5 m depth. The theoretical curve, however, has an increasing profile from the surface of the dump to the peak of the distribution at a depth of 7.5 m; decreasing from that point to a negligible amount at 9 m. The near surface heat source strength predicted by the model is only $\sim 0.25 \text{W m}^{-3}$ at 1.5 m, which is as much as an order of magnitude down on the experimental result. In general though, the model predicts a heat source distribution that lies within an order of magnitude of the experimental distribution.

Closer quantitative prediction of the experimental heat source distribution is possible if values of parameters within the model are allowed to vary. Increasing the minimum cut-off point of the particle size distribution, for example, yields a less-peaked heat source distribution (see Figure 6.10), more in line with the experimental result of Figure 7.1. Also, the peak of the predicted distribution is closer to the surface of the dump for a calculation with a lower porosity or higher pyrite content (see Figure 6.9). Further, using a particle size distribution, less heavily weighted towards particles of small size, the model again predicts a flatter heat source distribution. Varying parameters in this way is not wholly unreasonable, due to the heterogeneous nature of waste rock dumps, however in Figure 7.1 only the one calculation is presented for those parameter values thought to be applicable, at least in an average
sense, to White's overburden dump at Rum Jungle.

Although the model prediction, for the heat source distribution, a microscopic property of the dump, is not good in detail, the model may well be adequate for prediction of average properties of the dump such as the total sulphate production rate. Harries and Ritchie (1981) give two estimates of the $SO_4$ production rate. Based on the mean value of the total heat production, estimated from the temperature profiles for each of the probe holes, and equation (4.3.1), they estimated the total sulphate production rate of the dump to be $1.9 \times 10^{-7} \text{kg s}^{-1} \text{m}^{-2}$. The other estimate, which assumes that $SO_4$ concentration in spring water flowing from the base of the dump is typical of all water flowing through the dump, and that 80% of annual rainfall flows through the dump (the other 20% being run-off and evaporation), was found to be $6.34 \times 10^{-7} \text{kg s}^{-1} \text{m}^{-2}$ which is of the same order as the first estimate. In comparison the model predicts, for a waste rock dump with a 3.3% pyrite content, a 40% porosity and a particle size distribution with range 1mm to 10cm, at 25yrs after the formation of the dump, that the sulphate production rate integrated over the height of the waste pile is approximately $5.6 \times 10^{-7} \text{kg s}^{-1} \text{m}^{-2}$ which is certainly of the right order.

As recently as January 1982 a further three holes were drilled through White's heap using the percussion drilling technique. Tubing was inserted after drilling to allow sampling of the soil atmosphere at prescribed depths through sampling ports. The gas sampling holes lie close to holes A, B and D and are referred to as holes A_g, B_g.
and D_g. To date four individual readings have been taken at each of the prescribed depths down the dump in each of the three gas probe holes. Results for the individual holes A and B are reasonably consistent within themselves, however, from hole to hole there is a wide variability both for oxygen concentration and carbon dioxide measurements (see Harries and Ritchie, 1983). Oxygen profiles for hole D_g show a large variation (even diurnally) and therefore hole D_g results are not included for comparison.

Figure 7.2 shows experimental values of oxygen concentration within the pore space of the dump for the two probe holes A_g and B_g taken in September of 1982, as well as the oxygen profile predicted by the present theoretical model. In general the two experimental curves decrease in value from the top surface of the dump. The hole A_g profile decreases to around 5m in depth before increasing again, to a value close to atmospheric oxygen concentration, at depth 12m. Hole B_g exhibits mostly a decreasing profile but the curve is far from that of hole A_g and the oxygen profile for hole B_g is concave upwards for nearly the total depth of the dump. The experimental profiles therefore differ markedly.

The theoretical curve presented in Figure 7.2 is calculated for the same parameter values used to obtain the heat source distribution in Figure 7.1. The predicted oxygen concentration profile is curvilinear over the whole depth of the dump due to the presence of oxidising particles, whether large or small, in all regions of the dump. The calculated oxygen profile does not lie close to either of the
Figure 7.2 The oxygen concentration within the pore space of the dump as a function of depth. Comparison of experimental profiles for holes Ag and Bg with the numerical result.
experimental curves depicted in Figure 7.2, although qualitatively it is similar to the profiles for hole $A_g$ (for a short distance) and hole $B_g$. The predicted curve is well off quantitatively, but the oxygen gradients of the theoretical curve and that of hole $A_g$, in the 1.5m to 5m range, are at least comparable. It is possible, however, to reproduce the oxygen profile given for hole $B_g$ if, for example, the pyrite density is increased to 10% or the porosity reduced to 20%. We do not pursue this investigation further here since we have no data suggesting such increases in density or reductions in the porosity around hole $B_g$, and, because, the model was originally developed to predict the response of the oxidising waste pile based on known data, not to fit the experimentally obtained response. What may be more appropriate is, if experimental data, such as pyrite density or dump porosity, could be measured for regions around the individual holes in White’s dump. Model calculations, using values of parameters found locally to the holes, would then be more appropriate for prediction of observations given for the individual holes.

We note also that consistent with the results, seen in Figure 7.2 for hole $A_g$, is the theory that oxygen is being supplied from elsewhere other than the top surface of the dump. This is because hole $A_g$ shows a sharp rise in its oxygen profile to a maximum near the 12m mark. Observe from Map 2.3 that hole $A_g$ is reasonably close to the sides of the dump, relative to $B_g$, and therefore diffusion of oxygen from the sides of the dump would raise the oxygen
concentration within the region of hole A. Also, because heat is produced via the oxidation of pyrites, it is reasonable to suggest that convection may play a role if a pathway from the sides or base of the dump exists for oxygen to traverse in reaching reaction sites within the dump. Indeed, if a linear temperature profile is assumed from the outside of the dump to the hottest region of the dump at about 15m in depth in hole A (a temperature of approximately $56^\circ$C), the mass flux of oxygen to reaction sites under convection can be calculated as $3.6 \times 10^{-8} \text{kg s}^{-1} \text{m}^{-3}$ which is comparable to both the oxidation rate assuming diffusional transport of oxygen and that calculated from experimental results (see Section 4.1). The model given here, could be extended to include the convection of oxygen by temperature gradients and, the model then, may go further in predicting the experimental observations, however, experimental data particular to the individual holes would still be necessary, for such a model to predict microscopic phenomena which is peculiar to individual regions of the dump.

7.3 Strategy for Dump Rehabilitation

Rehabilitation proposals for the abandoned overburden dumps at Rum Jungle vary from, bulldozing the overburden material back into the flooded opencuts, to sealing the waste dumps to exclude oxygen and/or water. What is not clear, however, is the effectiveness of such measures in stopping or even limiting the oxidation process, and therefore, pollution production. Most strategies for rehabilitation attempt to retard the oxidising process in order to keep pollutant
production below prescribed levels, as is the case for the proposal we consider in detail below. However, the pyritic oxidation process, if accelerated, would cause a higher sulphate production rate, but over a shorter period of time, thus requiring less time spent in active monitoring of the mine site. Such a rehabilitation proposal may be worth investigating, however it is not considered further here.

We consider in detail, in this section, a rehabilitation strategy aimed at limiting the pyritic oxidation rate within a waste rock dump. In reducing the oxidation rate, and therefore the overall sulphate production rate, we have only two parameters within the model that may vary; the porosity and the pyrite density of the dump. Little can be done to vary the pyrite content of the dump, but it is possible to change the porosity, at least near the top surface of the dump. Suppose, for our rehabilitation strategy, we propose to compact the surface of the dump so that the porosity, and the associated diffusivity, is reduced in the top 0.5m of the dump. The lower porosity in this region would then restrict the diffusion of oxygen to reaction sites within the dump and apparently slow the production rate of pollutants.

For the above proposal, the model equations of Chapter 4, assuming a single particle size throughout the dump, remain largely the same, except that we now solve the coupled system of equations for a different porosity and diffusivity in the first 0.5m of the dump, that is, we allow the diffusion coefficient for oxygen to
vary discontinuously with depth down the dump. Across the 0.5m depth the mass flux of oxygen is conserved and the continuity of oxygen concentration within the pore space of the dump is retained. The boundary conditions at the 0.5m mark can therefore be written mathematically as

\[ D_0 \frac{\partial^2 u}{\partial x^2}(x + 0.5^-, t) = D_1 \frac{\partial^2 u}{\partial x^2}(x + 0.5^+, t), \quad (7.3.1) \]
\[ u(x + 0.5^-, t) = u(x + 0.5^+, t), \quad (7.3.2) \]

where \( D_0 \) is the diffusion coefficient of oxygen corresponding to the low porosity of the top 0.5m of the dump.

The numerical technique of Section 6.2 is again employed to solve the resulting system of equations but only after the discretised form of the equations is made symmetric, in order to use the Cholesky LDL^T decomposition. Note that the LU decomposition could just as easily be used for the non-symmetric system, however, in this case, it is a simple task to make the system symmetric, and a bonus is a saving in storage space in the computer (not that storage space is a limiting factor).

Figure 7.3 shows the dimensionless oxygen concentration profiles, for different porosities within the top 0.5m of the dump, as well as, the oxygen profile for a 40% porosity throughout the dump. The porosity of the dump below the 0.5m mark was taken to be 40% in each case. All curves illustrated in Figure 7.4 are for a pyrite density of 3%, a single particle size of 1mm (which is reasonable for this analysis) and time equal to 25yrs. As expected the lower the porosity
Figure 7.3 The spatially dependent oxygen profiles after 25 yrs of oxidation of the dump with a particle size of 1mm. Comparison of calculations for different porosities in the top 0.5m of the dump.
in the top 0.5m of the dump, the less oxygen penetrates to depth within the dump. It is clear there is an appreciable difference between the oxygen profiles with discontinuous oxygen gradient and the oxygen profiles for a dump of 40% porosity throughout. This difference is evident, even for a dump with a 20% porosity in the top 0.5m, which is only a factor of two down in porosity. Note that below the 0.5m mark all three curves are nearly parallel.

Reducing the porosity in the top 0.5m of the dump produces large changes, not only in the oxygen profiles, but also in other output parameters, such as the heat source distribution, however, our main interest lies in investigating how such a rehabilitation strategy affects pollutant production levels in an oxidising waste rock dump. The total sulphate production rate, under reasonable assumptions, can be considered a measure of the pollution load presented by the overburden dump to the environs of the mine site. In Figure 7.4 we illustrate the integrated sulphate production rate predicted by the model for the same parameter values used in Figure 7.3. As expected, a calculation done assuming a lower porosity (diffusivity) in the top 0.5m of the waste pile produces a lower rate of sulphate production integrated over the height of the dump, than a calculation for a dump with a 40% porosity throughout, but only until the dump with the higher porosity ceases reacting. The difference in pollution production, and therefore environmental impact, is greatest close to the creation of the waste dump, lessening with increasing time. The total sulphate production rate of the less porous dump, in fact,
Figure 7.4 The integrated sulphate production rate as a function of time assuming a dump comprised of 1mm sized particles. Comparison of calculations for different porosities in the top 0.5m of the dump.
asymptotically approaches the production rate for the dump with 40% porosity throughout. A dump with lower porosity, while evidenced by a lower SO$_4$ production rate, also has a longer reactive lifetime than a more porous dump. An unaltered dump with 40% porosity throughout, for example, finishes oxidising in approximately 250yrs whereas when the porosity is reduced to 7.5%, in the top 0.5m of the dump, the time span for the dump to be totally oxidised is lengthened to 377.6yrs a 50% increase. It is clear then from Figure 7.4 that even when reducing the diffusivity by a factor of ten in the top 0.5m of the dump, we achieve only a small reduction in the total sulphate production rate, with the disadvantage of an extension in the lifetime of the dump as a pollution source.

The rehabilitation scheme suggested above which proposes a lowering of the porosity of the top portion of a waste rock dump in order to restrict access of oxygen to reaction sites within the dump, when considered via the model of Chapter 4, predicts a lowering of the total pollutant load presented to the environment in the vicinity of a waste rock dump, however, the reduction in pollutant output is at the expense of the prolonged reactive life span of the oxidising waste heap. The reduction gained can only be termed marginal since, for as much as a tenfold decrease in diffusivity, only a small decrease in total sulphate production is obtained and the reduction in SO$_4$ production decreases with time. This marginal change must be assessed in the light of critical toxicity levels of pollutants which affect both aquatic and plant life, nearby to the
reacting waste piles. Also an assessment, of the effort required to compact the surface material on a waste dump, should be made, with a view to cost efficiency. It may well be that, for the rehabilitation strategy suggested here, too little a reduction in the overall pollution load of the dump is produced, to warrant the expenditure necessary in producing that reduction.
CHAPTER 8

GENERAL SUMMARY AND CONCLUSIONS

A physically reasonable mathematical model has been developed (see Chapter 4) describing the oxidation of pyritic mine waste. Special reference has been made to the waste rock comprising White's overburden dump at Rum Jungle, however, the model is generally applicable to wastes at other mine sites where pyritic oxidation is a problem.

Unlike the simple semi-infinite model of Ritchie (1977), which assumes a homogeneous slab structure for the overburden dump, we consider, in the "dual region" model developed in Section 4.2, that the pyritic oxidation reaction proceeds within particles of the dump thus taking account of the two-phase (gas-solid) particulate structure inherent within fragmented waste rock material. A feature exclusive to the "dual region" model is the prediction of a spatially dependent heat source distribution which is in accord with experimental findings. In contrast the simple model can only predict a δ-function for the heat source distribution within the dump. Also the oxygen concentration within the pore space of the dump for the "dual region" model (assuming a single particle size) exhibits a linear profile from the surface of the dump, through the totally reacted region \(R(t) = 0\), to the position of the planar moving front \(X(t)\) within the dump, and then decreases in a curvilinear fashion through the high oxidation rate zone \(0 < R(t) < 1\). The oxygen profile for the simple model, however, decreases linearly from the surface of the
dump to a zero concentration at the planar reaction front \( X(t) \) (see Appendix A). Therefore accounting for the particulate structure of the dump, as spherical oxidising particles, has introduced into the slab model a partially reacted region below \( X(t) \) where particles are at all stages of oxidation, unlike the homogeneous model which assumes a totally unreacted region below \( X(t) \). Note that the "dual region" model is also consistent with the simple model since the results of the dual region model approach those of the simple model when the particle size tends towards zero.

The model equations of Chapter 4 were considered mathematically in three ways. Firstly, equations governing diffusion and reaction within a single particle of the dump, when exposed to the atmosphere, were investigated using a new analytic series solution technique. When evaluated, for parameter values appropriate to White's dump, the non-steady state series solution was shown to lie close to the pseudo-steady result. The pseudo-steady result was taken to be true of all particles within the dump allowing an important simplification to be made to the overall model equations. Secondly, approximate analytic expressions were obtained in Chapter 5 by approximation of the position of the moving reaction front within particles of the dump. For the approximate upper bound case this gave rise to a planar moving boundary formulation, involving different partial differential equations either side of a planar moving interface which were largely decoupled from the actual position of the reaction front \( (R(x,t)) \) within individual particles of the dump. Analytic
expressions for parameters of interest such as the heat source distribution were obtained for the approximate upper bound case and numerically evaluated. Finally, the model equations of Chapter 4 were considered numerically.

The approximate upper bound result is accurate qualitatively for all physical parameters displayed, for a dump assumed to be composed of one size particles, but it is most accurate for the total SO₄ production rate, the position of the planar moving front within the body of the dump, the oxygen concentration profile within the pore space of the dump and in predicting the time to completely react the waste dump. Since the approximate result is quickly and easily evaluated it is useful, both for investigating the response of the dump model to changes in parameter values, as well as for prediction of the response of the dump over large periods of time. Indeed, to find the time to fully oxidise a waste rock dump the numerical scheme would take of the order of hours of CPU time on a computer, whereas the approximate results of Chapter 5 gives an analytic expression for this parameter (shown in Section 6.3 to be accurate when compared to the numerical result) which is trivial to evaluate.

The inclusion of a range of particle sizes within the model equations produced substantially different results for microscopic parameters such as the heat source distribution and oxygen concentration profiles, when compared to those obtained assuming a single particle size. Therefore in comparing model predictions
with experimental measurement, from oxidising pyritic material, a
calculation done assuming only one sized particle (or an "average"
sized particle) throughout the dump would prove inadequate and results
pertaining to a distribution of particle sizes, appropriate to the
waste material under consideration, should be adopted. An increase
in the lower limit cut-off size in a calculation for a range of
particle sizes produced a flatter heat source distribution with a
greater "width" and with the peak of the distribution positioned at a
shallower depth. Similarly, increasing the upper limit cut-off size
gave a less peaked heat source distribution with an extended "width",
but in this case the peak was positioned further towards the base of
the dump (see Section 6.5). Note, however, that assuming a single
particle size throughout the dump is still accurate (within a few
percent) for average properties of the dump such as the integrated
SO$_4$ production rate within the mid-range of the dump's reactive
lifetime.

Model predictions were found to be qualitatively similar to
experimental measurement and estimation when physicochemical data
appropriate to White's dump, especially the particle size distribution,
were included in the calculation. The model, however, was unable to
predict some detailed characteristics of the experimental results.
For example, an important achievement of the model was the prediction
of the spatial dependence of the heat source distribution, which
when compared to the heat source distribution for hole A, shows a
similar "width" and maximum peak, even though the shapes of the two
profiles differ (see Section 7.2). As indicated, this is in stark contrast to the \( \delta \)-function predicted by the simple dump model.

It is clear from experimental observation that other transport mechanisms have some role to play in movement of oxygen within oxidising pyritic material, whether it be by convection (as alluded to in Section 7.2) or pressure gradients due to windflow around overburden rock piles. Quantification and inclusion of such transport mechanisms in an overall model of the pyritic oxidation process is left for further research. Even then, with an all encompassing model, the availability of physicochemical data particular to a region of observation would affect, to a degree, the accuracy of predictions of observable phenomena from that region. This is a factor that should be borne in mind when predicting such quantities, as the oxygen concentration at depth within the dump or the spatial heat source distribution for White's overburden dump, since only average values of the pyrite density and porosity of the dump are available. By the same argument, the model presented here does not include minute detail of the particles of the dump such as a non-sphericity factor or a factor accounting for the non-uniform distribution of pyrites within particles (see Roach and Prosser, 1978). Therefore an experimental programme aimed at obtaining data specific to probe holes on White's dump would complement the extension and refinement of the mathematical model.

Of immediate interest, however, should be the extension of the model to include other possible physical transport mechanisms evident
within a waste rock dump. This is because the prediction of some experimental results, such as the rise in oxygen concentration down hole Ag below a depth of 5m, is not possible using the present diffusion rate-limited model. A goal therefore for future research in this area should be qualitative agreement between the model and experimental results before excessive refinement of the model is undertaken or indeed before physicochemical data particular to regions of the waste material are sought.
APPENDIX A

The equations governing the model of Ritchie (1977) can be written as (Jost, 1960; Crank, 1975)

\[ \frac{\partial u^*}{\partial t^*}(x^*, t^*) = D_1 \frac{\partial^2 u^*}{\partial x^2}(x^*, t^*), \quad 0 < x^* < X^*(t^*), \quad (A.1) \]

with the boundary conditions given by

\[ u^*(0, t^*) = u_0, \quad u^*(X^*(t^*), t^*) = 0, \quad (A.2) \]

and

\[ D_1 \frac{\partial u^*}{\partial x^*}(X^*(t^*), t^*) = -\varepsilon \rho_S \frac{dX^*}{dt^*}(t^*), \quad X^*(0) = 0, \quad (A.3) \]

where \( X^*(t^*) \) is the position of the planar moving reaction front within the dump (m) and the other symbols are defined in Chapter 4. The usual method of solution (see Crank, 1975) assumes \( u^*(x^*, t^*) \) is given by

\[ u^*(x^*, t^*) = A \text{erf}\left(\frac{x^*}{2\sqrt{D^*}t^*}\right) + B \text{erfc}\left(\frac{x^*}{2\sqrt{D^*}t^*}\right), \quad (A.4) \]

where \( D^* = D_1/\rho_1 \), which upon substitution into (A.3) yields the position of the moving boundary \( X^*(t^*) \) as

\[ X^*(t^*) = 2\alpha \sqrt{D^*} t^*, \quad (A.5) \]

while the constants \( A \) and \( B \) are found using boundary conditions (A.2), and \( \alpha \) is found from the transcendental equation

\[ \sqrt{\pi} a e^{-a^2} \text{erf}(a) = \frac{\rho_1 u_0}{\varepsilon \rho_S}, \quad (A.6) \]

where \( \text{erf}(x) \) is the error function defined as

\[ \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-z^2} dz, \quad (A.7) \]
and \( \text{erfc}(x) = 1 - \text{erf}(x) \). Having found the constants \( A \) and \( B \) we can write the solution for \( u^*(x^*, t^*) \), equation (A.4), as

\[
\begin{align*}
u^*(x^*, t^*) &= u_0 \left( 1 - \frac{\text{erf}(x^*/2D't^*)}{\text{erf}(\alpha)} \right),
\end{align*}
\]  

(A.8)

which is the same expression as that obtained by Ritchie (1977) except \( D' \) here replaces \( D \).

An alternate derivation of this solution can be found (see Davis and Hill, 1982a; Appendix P) where new transform variables are introduced, which fix the moving boundary, given by

\[
\xi = \frac{x^*}{X^*(t^*)}, \quad \tau = X^*(t^*), \quad (A.9)
\]

and also

\[
\phi(\xi) = u^*(x^*, t^*). \quad (A.10)
\]

Equations (A.1) to (A.3) therefore become

\[
\begin{align*}
\varepsilon \rho \phi''(\xi) &= \rho_1 \phi'(1) \xi \phi'(\xi), \quad (A.11) \\
\phi(0) &= u_0, \quad \phi(1) = 0, \quad (A.12)
\end{align*}
\]

and

\[
D_1 \phi'(1) = -\varepsilon \rho \xi \phi'(\xi), \quad \tau(0) = 0, \quad (A.13)
\]

where the dash denotes differentiation with respect to \( \xi (\phi' = d\phi / d\xi) \). The ordinary differential equation (A.11) can then be easily integrated subject to (A.12) to yield

\[
\phi(\xi) = u_0 \left( 1 - \frac{\text{erf}(\alpha \xi)}{\text{erf}(\alpha)} \right), \quad (A.14)
\]
where $\alpha$ is defined as

$$\alpha^2 = -\frac{p_1\phi'(1)}{2\epsilon \rho_s}.$$  \hspace{1cm} \text{(A.15)}

Upon differentiating (A.14) with respect to $\xi$, putting $\xi = 1$, and then using (A.15) we obtain the transcendental equation (A.6) for $\alpha$. It is clear also that equation (A.5) is obtained directly using this method by integrating (A.13) and using definition (A.15). We note that the above technique also allows an analytic solution to be found when the initial position of the moving boundary is non-zero whereas assuming a solution of the form (A.4) necessitates a numerical solution for such a problem.
REFERENCES


Barrie, D.R. The Heart of Rum Jungle; The History of Rum Jungle and Batchelor in the Northern Territory of Australia, Published by S. and D. Barrie, Batchelor, Northern Territory, 1982.


Zhongxiang, C. and Lishang, J. Exact solution for the system of flow equations through a medium with double-porosity, Scientia Sinica 23(7), 880-896, 1980.


Reprints of papers 1, 2, 3, 4 and 6 are included in Appendix P (inside back cover).

Papers 1, 2, 3 removed for copyright reasons
Oil recovery from water-wet fractured reservoirs is investigated. Water saturation in the fissures is governed by an integro-differential equation which involves an arbitrary function of time, \( F(t) \). This function must be determined experimentally and represents the production of oil per unit volume of the matrix. Various theoretical and physical aspects of this problem are discussed and closed form expressions are given for the solution of the linearised integro-differential equation corresponding to different choices of \( F(t) \). The solution for the standard choice of \( F(t) \), namely involving an exponential function, is included. The solutions obtained are illustrated numerically.

INTRODUCTION

Oil recovery by flooding of fractured reservoirs is clearly an important area of study. At present, interest centres primarily on two aspects of the problem. The first is a thorough understanding of the whole physical process and, for example, how quantities such as the 'flooding rate' affect subsequent oil delivery. The second is the determination of the appropriate physical characteristics of the fluid used for flooding (such as surface tension and viscosity) which maximise the quantity of oil attainable in a given time. In this paper some theoretical aspects of this general problem are considered. For convenience we refer to the process as water flooding of fractured reservoirs although of course the actual fluid may not be simply water. The general theory depends upon a function of time \( F(t) \) which describes the production of oil per unit volume of the matrix and which is assumed known from experimental results. The purpose of this paper is to give the general integro-differential equation governing the process for arbitrary \( F(t) \) and to give solutions for particular functions \( F(t) \).

Production of oil in a fractured reservoir is achieved through the displacement of oil by water due either to pressure gradients (imposed artificially) or by imbibition (see de Swaan\(^1\)). Imbibition is the exchange mechanism resulting from capillary forces, whereby oil in a matrix system is displaced by water from a fissured system. Here we propose a generalised imbibition term involving an arbitrary function \( f(t) = \frac{dF(t)}{dt} \) which describes the rate at which oil is released by capillary action. The function \( f(t) \) is generally found experimentally by immersing a section of matrix block in water, thus imposing a constant unit saturation at the surface of the block, and then observing the response of the block in releasing oil and absorbing water. For a varying saturation at the block surface an integro-differential equation arises involving a convolution integral for \( f(t) \). Under certain assumptions we give solutions of the basic integro-differential equation for a variety of \( f(t) \) including the standard exponential case. These solutions exhibit delayed travelling wave phenomena.

Buckley and Leverett\(^1\) put forward a theory attempting to describe the mechanism by which displacement of oil from a reservoir is effected. Their theory, however, does not take into account the imbibition effect in fractured reservoirs. The equations describing a fluid which flows either through fissures in the reservoir or through the porous matrix blocks (separated by fissures) were first described in a series of papers by Barenblatt and co-workers\(^3-5\) who termed it 'double porosity'. Aifantis\(^6-8\) extended this concept and developed a 'multiporosity theory' of which the equations of Barenblatt are a particular case. These authors do not take into account the oil production from capillary action. Aronofsky et al.\(^9\) point out that in fact 'imbibition ... may become with time, a significant element of the production mechanism'. This is especially true for instance if the water advance is very slow, or if the fractured reservoir has many large fractures. Combining the Buckley and Leverett theory with theories associated with the imbibition term\(^1,9\), we can produce basic equations describing fluid displacement from a medium with double porosity. A similar equation can also be found in a review article by Streltsova-Adams\(^10\) and a paper by Boulton and Streltsova-Adams\(^11\).

Most authors\(^1,9-11\) when considering the form of the imbibition term take the function \( F(t) \) describing oil production per unit volume of matrix, to be given by

\[
F(t) = R(1 - e^{-\lambda t}) \quad (\lambda > 0)
\]

Aronofsky et al.\(^9\) indicate the desirability of more general \( F(t) \) for more accurate fitting of experimental data. Strictly speaking all that is required of the function is that it is a non-decreasing function of time, converging to a finite limit as time goes to infinity and is zero at time equal to zero. Using equation (1), some authors\(^1,9-11\) have derived an intensity of imbibition term \( q(x, t) \) written as

\[
q(x, t) = R\lambda \int_0^t \frac{\partial \sigma_1}{\partial t}(x, \tau) e^{-\lambda (t-\tau)} d\tau
\]

The imbibition equation in its most general form, however, should be given by (see Appendix I)

\[
q(x, t) = \int_0^t \frac{\partial \sigma_1}{\partial t}(x, \tau) f(t-\tau) d\tau
\]
where \( f(t) \) is a continuously monotonic function physically representing the rate at which a volume of oil is produced per unit volume of matrix.

In the following section we give the general form of the integro-differential equation for water saturation both in the fractured system and in the matrix system, and consider two simple examples for the intensity of deliverance \( f(t) \). Closed form solutions for particular examples of the function \( f(t) \) are given in subsequent sections. Approximate results for general \( f(t) \) and numerical results are given in the final two sections.

**MODEL AND SIMPLE EXAMPLES**

The equations governing two phase one-dimensional flow in the fissure system (see Appendix A) are given by

\[
\frac{\partial s_1}{\partial t} + \frac{w_0}{\mu} \frac{\partial s_1}{\partial x} + \int_0^t \frac{\partial s_1}{\partial \tau} (x, \tau) f(t - \tau) d\tau = 0
\]

\( s_1(x, 0) = 0, \quad s_1(0, t) = 1 \) \( \tag{3} \)

The matrix system is considered only a 'source' supplying the fracture system with oil. Therefore the equations governing water saturation in the matrix system are

\[
\frac{\partial s}{\partial t} - \frac{\partial s}{\partial x} f(t - \tau) d\tau = 0
\]

\( s_1(0, t) = 0 \) \( \tag{4} \)

Taking Laplace transforms with respect to time, equations (3) and (4) yield

\[
\hat{s}_1(x, p) = \frac{p}{p^2 - \mu \rho \rho_0} \hat{s}_1(x, p)\exp{\left(-\frac{\mu \rho \rho_0}{\mu} p^2 x\right)}
\]

\( \tag{5} \)

\[
\hat{s}_1(x, p) = \frac{p}{p^2 - \mu \rho \rho_0} \hat{s}_1(x, p) + \psi^{-1} f(p) \hat{u}(x, p)
\]

\( \tag{6} \)

where the Laplace transform with respect to \( t \) of an arbitrary function \( u(x, t) \) is denoted by \( \hat{u}(x, p) \) and

\[
\hat{u}(x, p) = \int_0^\infty e^{-pt} u(x, t) dt
\]

Now from equation (5), we can write the general solution for the water saturation, for any intensity of deliverance \( f(t) \), in the form of a travelling wave, thus

\[
s_1(x, t) = \begin{cases} 0, & t < \alpha x \\ h(x, t - \alpha x), & t \geq \alpha x \end{cases}
\]

\( \tag{7} \)

where \( \alpha = \mu \phi \rho_0 / w_0 \) and the function \( h(x, t) \) is defined in terms of its Laplace transform \( \hat{h}(x, p) \) (see Oberhettinger and Badii \( \text{Vol. 12, p. 3} \) namely

\[
\hat{h}(x, p) = p^{-1} \exp{-\mu \phi \rho_0 f(p)/w_0}
\]

\( \tag{8} \)

Let us consider firstly the trivial example of the intensity of deliverance \( f(t) \) given by \( f(t) = 0 \). This gives the solution for the simplified Buckley–Leverett equation, viz.

\[
s_1(x, t) = H(t - \alpha x) = \begin{cases} 0, & t < \alpha x \\ 1, & t \geq \alpha x \end{cases}
\]

\[
S_1(x, t) = S_1^0
\]

Physically this solution represents a singly porous system. Therefore we can either consider the water saturation in the fissures \( s_1(x, t) \) as the solution throughout the reservoir or we can assume that all oil that is recoverable is in the fissured system and there is no loss to the matrix of water from the fissures. The solution \( s_1(x, t) \) depicts a wave of constant height one, travelling in the positive \( x \) direction with velocity \( \alpha^{-1} \). Note that at time \( t = \alpha x \) we have an instantaneous saturation at position \( x \).

Now consider the intensity of deliverance given by \( f(t) = R \delta(t) \), where \( \delta(t) \) is the Dirac delta function. The solutions to equations (3) and (4) then become

\[
s_1(x, t) = H(t - (\alpha + \beta) x) = \begin{cases} 0, & t < (\alpha + \beta) x \\ 1, & t \geq (\alpha + \beta) x \end{cases}
\]

\[
S_1(x, t) = (R/\rho) H(t - (\alpha + \beta) x)
\]

\[
S_1^0 = \begin{cases} S_1^0, & t < (\alpha + \beta) x \\ S_1^0 + (R/\rho), & t \geq (\alpha + \beta) x \end{cases}
\]

where \( \beta = R \rho_0 / w_0 \). We see that we have a similar result as for the case \( f(t) = 0 \) except that now we have a wave travelling through the matrix systems well, and the wave front in both the fissures and the matrix blocks is delayed a further time interval \( \beta x \). It is not until time \( t \geq (\alpha + \beta) x \) that we obtain maximum saturation. The lower velocity \( (\alpha + \beta)^{-1} \) causing the extra delay is brought about through the imbibition of water out of the fissures into the matrix blocks over a time span of exactly \( \beta x \). That is, it takes \( \beta x \) extra time units to maximise saturation in matrix blocks at position \( x \) by imbibition.

Both of these simple examples indicate a sharp interface between the wet and dry zones, there being no intermediate values for the water saturation between zero and one in the fissures, of \( S_1^0 \) and \( S_1^0 + (R/\rho) \) in the matrix blocks. The second of these examples does, to a certain extent, hint at the physical effect imbibition will have on solutions to equations (3) and (4). It shows that imbibition will cause a delay in the complete saturation of a position \( x \), both in the fissures and in the matrix. The magnitude of the extra delay and the form it takes depends on the form of the function \( f(t) \). In the following sections we consider other forms for \( f(t) \).

**HEAVISIDE INTENSITY OF DELIVERANCE**

If oil is released from a single block at a constant rate for a period \( t_0 \) then the function \( f(t) \) takes the form

\[
f(t) = (R/t_0) H(t_0 - t)
\]

and

\[
f'(t) = (R/t_0)(1 - e^{-t_0})
\]

On substituting this equation into (6) and (8) and with

\[
\text{Trans IChemE, Vol. 60, 1982}
\]
\[ \tau = t - \alpha x \] we obtain \[ S_1(x, t) = S_1^0 \] for \( \tau < 0 \) and
\[ S_1(x, t) = S_1^0 + \eta e^{-\beta x} \sum_{n=0}^{N} \frac{(\beta x)^n}{n!} \left[ \tau -(N+1)t_0 \right] \frac{(\beta x)^n}{n!} \]

\[ h(x, t) = e^{-\beta x} \sum_{n=0}^{N} \frac{(\beta x)^n}{n!} \]

for \( Nt_0 \leq \tau < (N+1)t_0 \) where \( N = 0, 1, 2, \ldots \).

These solutions describe a travelling wave, increasing in saturation discontinuously for each interval of time \( t_0 \). We note that for each portion of the reservoir there is a balance between imbibition of water into the matrix and the rate at which water is flowing into the portion. The solutions indicate that an ever decreasing volume of oil per time interval \( t_0 \), is being imbibed out of the matrix blocks by water. For large time \( (t \to \infty) \) both the matrix blocks and the fissures become completely saturated with water, \( S_1(x, t) \to 1 \) and \( S_\infty(x, t) \to S_\infty + 1 \).

We also note that the water saturation both in the fissures and matrix decreases monotonically with increasing distance \( x \). This indicates that the matrix blocks and fissures downstream are subject to variable water and oil saturations, dependent on the imbibition process between the fissures and the blocks upstream.

**EXponential INTENSITY OF DELIVERANCE**

The form considered most often\(^1,9-11\) for \( f(t) \) is given by the exponential function
\[ f(t) = R_0 e^{-\lambda t} \quad (\lambda > 0) \]

Substituting the Laplace transform of \( f(t) \) into equation (8) and inverting gives
\[ h(x, t) = J(\beta x, \lambda t) \]

where the function \( J(x, t) \) is defined by
\[ J(x, t) = 1 - e^{-\lambda t} \int_{0}^{t} e^{-\lambda (t-\tau)} (2\sqrt{\tau \tau}) d\tau \]

Properties of the function \( J(x, t) \), as well as the derivation of the solution \( h(x, t) \), are given briefly in Appendix B. Inverting equation (6) using (11) gives the saturation of water in the matrix system,
\[ S_1(x, t) = S_1^0 \]

for \( \tau < 0 \) while
\[ S_1(x, t) = S_1^0 + (R/\psi) [1 - J(\lambda(t-\alpha x), \beta x)] \]

Unlike the example in the previous section where saturation increased due to discrete jumps for each time interval \( t_0 \), we now have a continuous monotonically increasing function of time. Physically this indicates that for increasing time the water saturation in the fissure and matrix systems increases smoothly and achieves total saturation for large time \( t \). De Swaan\(^1\) also gives the solution for the saturation in the fissures for the exponential intensity of deliverance. However, it should be noted his final result contains a minor error [namely, in our notation, \( h(x, t) \) is given instead of \( h(x, t-\alpha x) \) as in equation (7)].

**GAMMA INTENSITY OF DELIVERANCE**

The gamma function intensity of deliverance has not been considered previously, and can be written as
\[ f(t) = \frac{R_0^a}{\Gamma(a)} t^{a-1} e^{-\lambda t} \quad (0 < a < 1, \lambda > 0) \]

This function permits a more precise analytical approximation to experimental data since we now have a function of two parameters \( a \) and \( \lambda \). After substitution of the Laplace transform of equation (14) into equation (8) and inverting we obtain
\[ h(x, t) = (D + \lambda)^2 \int_{0}^{t} e^{-\lambda t} \int_{0}^{z} G(0; a-1; -\beta \lambda (z-u)^a) \]

\[ \times G(0; a; -\beta \lambda x(z-u)^a) \]

where \( G(v; u; z) \) is the generalised Bessel function, the definition and properties of which and the derivation of equation (15) are given in Appendix C. The water saturation in the matrix is also given in Appendix C.

**UPPER AND LOWER BOUND SOLUTIONS FOR GENERAL \( f(t) \)**

Rewriting the imbibition term \( q(x, t) \) given in equation (2), for the general form of the intensity of deliverance \( f(t) \), gives
\[ q(x, t) = f(0) S_1(x, t) + \int_{0}^{t} S_1(x, \tau) f'(t-\tau) d\tau \]

Now since the water saturation in the fissures \( S_\infty(x, \tau) \) increases gradually with time we note that \( 0 \leq S_\infty(x, \tau) \leq S_\infty(x, t) \) for \( \tau \gtrless t \). Multiplication of this inequality by \( f'(t-\tau) \), integrating with respect to \( \tau \) and adding \( f(0) S_1(x, t) \), gives
\[ f(0) S_1(x, t) \geq q(x, t) \geq f(t) S_1(x, t) \]

The left hand side of inequality (17) shows that replacing \( S_\infty(x, \tau) \) in (16) by zero will exaggerate the imbibition effect and therefore the result obtained minimises the solution. Similarly, putting \( S_\infty(x, \tau) = S_\infty(x, t) \) it is shown by the right hand side of (17) to have a reduced imbibition effect and therefore the result maximises the solution.

Letting \( S_\infty(x, \tau) = 0 \) in equation (16) the minimising solution can therefore be given by
\[ S_1(x, t) = \begin{cases} 0, & t < \alpha x \\ e^{-\beta x}, & t \geq \alpha x \end{cases} \]

Also for \( S_\infty(x, \tau) = S_\infty(x, t) \) we obtain the maximising solution
\[ S_1(x, t) = \begin{cases} 0, & t < \alpha x \\ \exp\left(-\frac{\alpha x}{\alpha x} \int_{0}^{\alpha x} f(u+t-\alpha x) du\right), & t \geq \alpha x \end{cases} \]

Thus for arbitrary \( f(t) \) the solution of (3) is bounded above and below by (19) and (18) respectively. These bounding solutions are illustrated graphically in Figure 4 and discussed in the following section.

Trans IChemE, Vol. 60, 1982
NUMERICAL RESULTS AND CONCLUSIONS

Taking $R = 0.1$, $\phi = 0.01$, $\psi = 0.15$ and $S_i^0 = 0.2$, calculations were made for different values of the ratio $\zeta = \mu/W_0$. Throughout, for the exponential function $f(t)$, $\lambda = 2.7$ is taken to be the parameter value. Solutions of water saturation in the fissures, for the exponential and gamma functions $f(t)$ (equations 12 and 15 respectively), are shown in Figure 1 with $\zeta = 5.0$. It can be seen that the water saturation in the fissures decreases with distance $x$ and increases with time $t$ to complete saturation as time becomes large. Figure 2 illustrates the behaviour of the water saturation in the matrix system for $\zeta = 5.0$ whereby water saturation increases with time due to the imbibition of water into the matrix system from the fissures system. In Figure 3 we compare water–oil ratios, as they vary with time, for the gamma and exponential solutions. The curves relating to the gamma intensity of deliverance in Figures 1 and 3 are given for $\alpha = 0.5$ and $\lambda = 2$ where $\alpha$ and $\lambda$ were chosen arbitrarily to facilitate a comparison between the exponential and gamma solutions. No fit to experimental data was attempted to obtain $\alpha$ and $\lambda$ but this would be a relatively simple task in an initial evaluation of an oil recovery project.

The minimising and maximising solutions as outlined in the previous section [equations (18) and (19) respectively] are illustrated in Figure 4. We can observe that the minimising solution does not respond at all to variations in time since oil is being imbibed into the fissures out of the matrix blocks at a constant rate. This produces a water saturation distribution along the fissures which is static. The phenomenon not accounted for in the maximising solution is the extra loss of water from the fissures brought about by the delayed yield from storage of oil due to variations in the water saturation at previous time $t$. The maximising solution, however, does account for the eventual depletion of oil from the matrix blocks and therefore approximates the solution quite well, especially for larger water injection rates.

It becomes evident from Figures 5 and 6 that the strategy for water flooding of a fractured reservoir must be a compromise. These figures show that for a high
injection rate (a low $\zeta$ value) the matrix blocks will deliver their oil quickly but the penalty is a high water–oil ratio. Slower injection rates (high $\zeta$ values) bring about a higher percentage recovery of oil per volume of water injected (that is less water is expended to recover a unit volume of oil) but the production rate becomes very slow.

**APPENDIX A**

The one-dimensional system of equations describing flow through the fracture system (assuming water and oil are immiscible and incompressible, and neglecting gravitational effects) are given (see Bear\textsuperscript{13}, p. 459) by

\[
\begin{align*}
\frac{dp}{dx} &= \frac{k}{\mu} \frac{\partial s_1}{\partial x} - \frac{q(x, t)}{\mu} = -\phi \frac{s_1}{\partial t}, \\
\frac{\partial s_1}{\partial x} - q(x, t) &= -\phi \frac{s_2}{\partial t}, \\
\end{align*}
\]

(A1a-e)

Upon adding (A1c) and (A1d) and integrating we obtain $w_1 + w_2 = w(t)$ where $w(t)$ is an arbitrary function of time, describing the injection rate of water. Dividing equation (A1a) by the addition of (A1a) and (A1a) gives the fractional flow for water in the fissures, thus

\[
\frac{w_1}{w_1 + w_2} = \frac{s_1}{s_1 + s_2} = \frac{k_1(s_1)}{k_2(s_1)}
\]

(A2)

To form a closed system of equations we need an expression for $q(x, t)$ in terms of the water saturation in the fissures $s_1(x, t)$. If we were to consider the lowering of the water saturation in the fissures by a small amount $\delta s_1$ say, between the times $t$ and $t + \delta t$ then we would expect two responses, namely: a volume of oil instantaneously released from storage, and delayed yield from storage for any time $t (t > \tau)$. The volume of oil instantaneously
released from storage is incorporated in the first term of equation (A1c) and we may write the delayed yield at time \( t \) as \( \delta J \equiv f(t - r) \) where \( f(t) \) is the intensity of deliverance of the oil, having a zero limit for large time and such that

\[
\int_{0}^{\infty} f(t) \, dt = R
\]

Therefore the rate of imbibition at time \( t \) is given by

\[
g(x, t) = f(t - r) \, \tilde{S}_1(x, r)
\]

which becomes equation (2) after rearrangement. Upon combining equations (2), (A1c) and (A2) we obtain the general equation describing water saturation in the fissures, namely

\[
\frac{\partial \tilde{S}_1}{\partial t} + w(t) g(S_1) \frac{\partial \tilde{S}_1}{\partial x} = 0
\]

Upon combining equations (2), (A1c) and (A2) we obtain the general equation describing water saturation in the fissures, namely

\[
\frac{\partial \tilde{S}_1}{\partial t} + w(t) g(S_1) \frac{\partial \tilde{S}_1}{\partial x} = 0
\]

We now proceed to a particular form for \( g(S_1) \). Ignoring capillary effects in the fissures, the relative permeabilities can be taken as

\[
k_1(S_1) = S_1, \quad k_2(S_1) = 1 - S_1
\]

Therefore the fractional flow equation becomes

\[
g(S_1) = \left[ 1 - \mu(1 - S_1) \right]^{-1}
\]

which when expanded for \( S_1 < \mu |1 - \mu|^{-1} \) gives

\[
g(S_1) = S_1 + \left( 1 - \frac{1}{\mu} \right) S_1^2 + \left( 1 - \frac{1}{\mu} \right)^2 S_1^3 + \ldots
\]

Now taking the first order approximation to \( g(S_1) \)

\[
g(S_1) = \frac{S_1}{\mu}
\]

and also assuming a constant injection rate, \( w(t) = w_0 \), equation (A3) simplifies to give equation (3). We remark that the linearised form (A4) for \( g(S_1) \) is also applicable if the ratio \( \mu \) of the viscosities is close to unity.

**APPENDIX B**

For the exponential intensity of deliverance \( f(t) \), \( \tilde{h}(x, p) \) is given by

\[
\tilde{h}(x, p) = p^{-1} \exp \left\{ - \beta x (p + \lambda)^{-1} \right\}
\]

Upon rearranging the exponent and noting that the inverse Laplace transform of \( p^{-1} \) is unity, and the Laplace inverse of \( \exp \{- \beta x (p + \lambda)^{-1} \} \) is

\[
(\beta x)^{1/2} t^{-1/2} e^{-\lambda t} I_0(2\sqrt{\beta x t})^{1/2}
\]

we obtain a convolution integral which when integrated by parts, and using Bessel's equation, gives

\[
h(x, t) = 1 - e^{-\lambda t} \int_{0}^{\infty} e^{-\lambda t} I_0(2\sqrt{\beta x t}) \, dt
\]

and thus \( h(x, t) = J(\beta x, \lambda t) \).

**APPENDIX C**

For the gamma intensity of deliverance the Laplace transform \( \tilde{h}(x, p) \) is given by

\[
\tilde{h}(x, p) = p^{-1} \exp \left\{ - \beta x (p + \lambda)^{-1} \right\}
\]

Rearrangement gives

\[
\tilde{h}(x, p) = \frac{(p + 2\lambda + \lambda^2/p)(p + \lambda)^{-1}}{\exp \left\{ - \beta x (p + \lambda)^{-1} \right\} (p + \lambda)^{-1}} \times \exp \left\{ \beta \lambda x (p + \lambda)^{-1} \right\}
\]

Note that

\[
\mathcal{L}^{-1} \left\{ (p + \lambda)^{-(v + 1)} \exp \left\{ - x (p + \lambda)^{-1} \right\} \right\} = t^{-v} G(v; \mu; xt^\mu)
\]

where \( \mathcal{L}^{-1} \) is the inverse Laplace transform operator and

\[
G(v; \mu; z) = \sum_{n=0}^{N} \frac{(-z)^n}{n!} G(1 + v + \mu n)
\]

Using identity (C2) for the appropriate terms in equation (C1) we obtain a double convolution which when simplified gives equation (15). Similar methods for the water saturation in the matrix yield

\[
S(x, t) = S_1^0 + \frac{R \lambda^2}{(x - z) e^{-\lambda x}} \int_{0}^{x} G(0; a - 1; \beta x u^{-1}) \times G(0; a; -\beta \lambda x u^{-1}) \, du \, dz
\]

for \( x > 0 \) where \( G(a, z) \) is the incomplete gamma function defined by

\[
\gamma(a, z) = \int_{0}^{z} t^{a-1} e^{-t} \, dt, \quad R(a) > 0.
\]

The generalised Bessel function \( G(v; \mu; z) \) as defined in (C3) is related to the Bessel function of the first kind through the equation

\[
J_v(2z^{1/2}) = z^{v/2} G(v; 1; z)
\]

Also we have the result

\[
\frac{dG}{dz}(v; \mu; z) = -G(v + \mu; \mu; z)
\]

Trans IChemE, Vol. 60, 1982
SYMBOLS USED

\( a \) parameter appearing in equation (14), \((0 < a < 1)\)

\( D (= \frac{\partial}{\partial t}) \) formal differentiation in equation (15)

\( f(t) \) rate of production of oil per unit volume of matrix

\( F(t) \) production of oil per unit volume of matrix

\( g(s_1) \) fractional flow for water in the fissures

\( G(v; \mu; z) \) generalised Bessel function defined by equation (C3)

\( h(x, t) \) function defining water saturation in fissures [equation (7)]

\( H(t) \) Heaviside unit step function

\( I_0(z) \) modified Bessel function of the first kind of order zero

\( J(x, t) \) function associated with exponential \( f(t) \) (see Appendix B)

\( \kappa_1(s_1) \) relative permeability of water

\( \kappa_2(s_1) \) relative permeability of oil

\( m \) permeability

\( n \) dummy zero or positive integer

\( N \) zero or positive integer

\( P \) Laplace transform variable

\( p \) pressure in the fissures

\( q \) intensity of imbibition

\( R \) total volume of oil available per unit volume of matrix

\( s_1 \) water saturation in the fissures

\( s_1 \) oil saturation in the fissures \((s_1 + s_2 = 1)\)

\( S_1^0 \) initial water saturation in the matrix

\( S_1 \) water saturation in the matrix

\( t_0 \) fixed time period

\( t \) time

\( w_0 \) constant water injection rate

\( w_1 \) volume flow rate of water per unit cross-sectional area

\( w_2 \) volume flow rate of oil per unit cross-sectional area

\( w(t) \) water injection rate

\( x \) position vector

\( x \) position

\( u, z \) dummy variables

Greek letters

\( \alpha \) so that \( \alpha \) is velocity of travelling wave

\( \beta \) constant associated with delta function \( f(t) \)

\( \beta^* \) constant associated with Heaviside \( f(t) \)

\( \beta^\prime \) constant associated with exponential \( f(t) \)

\( \beta^\prime\prime \) constant associated with gamma \( f(t) \)

\( \beta^\prime\prime\prime \) constant associated with minimising water saturation solution

\( \gamma(a, z) \) incomplete gamma function (see Appendix C)

\( \Gamma(z) \) gamma function

\( \delta(t) \) Dirac delta function

\( \xi (= \mu / w_o) \) constant associated with maximising water saturation solution and used in the Figures

\( \eta (= R / \psi t_0) \) constant associated with Heaviside \( f(t) \)

\( \lambda \) parameter associated with exponential and gamma \( f(t) \)

\( \mu_1 \) viscosity of water

\( \mu_2 \) viscosity of oil

\( \mu \) constant associated with exponential \( f(t) \) and gamma \( f(t) \) (see Appendix B)

\( \psi \) porosity of matrix

\( \phi \) porosity of matrix

Subscripts

1 refers to water

2 refers to oil

REFERENCES


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ADDRESS

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A Mathematical Model of Pyritic Oxidation in Waste Rock Dumps

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SUMMARY
Mathematical equations are formulated which describe a model of pyritic oxidation within a waste rock dump, where it is assumed that oxygen transport is the rate limiting step in the oxidation process and that oxygen transport is by gaseous diffusion through the pore space of the dump, followed by diffusion into oxidation sites within the particles that comprise the dump. A pseudo-steady state assumption is made with respect to diffusion within the particles and the resulting equations are solved numerically. Variables, such as the spatial heat source and the oxygen concentration distributions are evaluated and their dependence on other parameters of the model noted. Comparisons are made with both experimental measurements and with the predictions of a simpler diffusion rate-limited model of pyritic oxidation. The present model is in much better qualitative agreement with experimental values than the simpler model.

1 INTRODUCTION

Iron pyrites is a common mineral which is frequently associated with minerals of economic significance such as copper, nickel, zinc, coal and uranium. When exposed to the action of air and water, it oxidises and leads to the high acidity and high trace metal concentrations found in runoff and seepage water from mine waste residues containing pyritic material (Raicevic, 1979; Hore-Lacey, 1979; Olson et al., 1979). During the lifetime of the mine, water collection and water treatment can ensure adequately high water quality standards for surface waters leaving the mine site and minimise the environmental impact of such waters. However, as 50-60% of the rainfall incident on a waste rock dump can find its way to the local ground water (Harries and Ritchie, 1982), there is a need to reduce pollution levels in water that percolates through pyritic mine wastes. Furthermore, the pyritic oxidation process can continue long after the mine site has been abandoned, with the consequent need to devise long-term, cost effective measures to reduce pyritic oxidation and associated water pollution to acceptable levels. There is therefore a need to understand the mechanisms involved in pyritic oxidation and to quantify the rate controlling steps in these mechanisms in a given situation.

The chemical reactions describing pyritic oxidation, and the role played by the bacteria that catalyse some of these reactions, have been described elsewhere (Brierley 1978). In this paper, it will be assumed that all the nutritional requirements for bacterial growth are freely available, that the oxidation reaction proceeds as fast as reactants are fed to the oxidation sites, and that all the reactants for the oxidation of pyrites are freely available with the exception of oxygen. It will be further assumed that oxygen is supplied from the atmosphere exterior to the mine wastes and is transported to the oxidation sites by a diffusion process. The mine wastes that are presently under investigation are the piles of overburden material that arose from open-cut mining of the uranium ore bodies at Rum Jungle, Northern Territory, where high trace metal concentrations (predominantly copper) in runoff and seepage water have led to an adverse impact on flora and aquatic fauna in the environs of the mine site (Davy 1975).
2 NOTATION

\( u^*(x^*, t^*) \) = the concentration of oxygen within the pore space of the dump

\( q^*(x^*, t^*) \) = the rate of volume loss of oxygen from the pore spaces

\( p \) = the porosity of the dump

\( D_1 \) = the diffusion coefficient of oxygen in the pore space

\( u_0 \) = the concentration of oxygen at the surface of the dump (concentration in the air)

\( L \) = the height of the dump

\( x^* \) = the vertical coordinate (depth in the dump)

\( t^* \) = the time

\( v^*(x^*, r^*, t^*) \) = the concentration of oxygen within a particle within the dump

\( r^* \) = the radial distance within a particle

\( a \) = the radius of the particle

\( D_2 \) = the diffusion coefficient of oxygen in water

\( a_m \) = the interfacial area per unit volume of water

\( R^*(x^*, t^*) \) = the position of the moving boundary within the particle

\( c \) = the mass of oxygen used per mass of sulphur in the oxidation reaction

\( \rho_s \) = the density of sulphur within the particle

\( k_L \) = the mass transfer coefficient

\( \gamma \) = a proportionality constant encompassing both Henry's law and the gas law

Dimensionless quantities

\( u = u^*/u_0 \) ; \( v = v^*/\gamma u_0 \); \( R = R^*/a \); \( X = x^*/L \);

\( r = r^*/a \); \( t = (\gamma u_0 D_2 t^*)/(\rho_s a^2) \)

\( k_1 = \frac{D_2}{D_1} \frac{u_0^2}{\rho_s a} \frac{1}{a^2} \)

\( k_2 = \frac{\gamma u_0 a D_2}{a D_1} \)

\( k_3 = D_2/(k_L a) \)

\( \delta = (u_0 D_2)/(\rho_s a) \)

3 THE MATHEMATICAL MODEL

3.1 Derivation of Equations

Since White's heap is approximately 18 m high and 500 m diameter, it is reasonable to model the dump as a slab, impervious at the base and with the surface open to the atmosphere. In the preceding section we concluded that diffusion might be a feasible mechanism for the supply of oxygen to the reaction sites within the dump, therefore the equation governing oxygen diffusion into the pore space of the dump can be written as

\[ \frac{3 u^*}{D_1 t^*} = D_1 \left( \frac{\partial^2 u^*}{\partial x^*^2} \right) = q^*, \]

with boundary and initial conditions given as

\[ u^*(0, t^*) = u_0, \quad \frac{\partial u^*}{\partial x^*} (L, t^*) = 0, \]

\[ u^*(x^*, 0) = 0. \]

Consider now the loss term \( q(x^*, t^*) \) in (1). Account must be taken of how the pyrites is being oxidised and where the reaction sites are situated in the waste heap. Recognising that the dump has a particulate microstructure we assume that the oxidation of the pyritic material occurs within the particles of the dump. If these are assumed to be spherical we can write the loss term as

\[ q(x^*, t^*) = a_m D_2 \frac{v^*}{a} (x^*, a, t^*) \]

It is assumed that since water is necessary, both for the oxidation of pyrites and for the bacteria that catalyse the reaction, the oxidation sites are in an aqueous phase. For a perfectly spherical particle of radius \( a \)

\[ a_m = 3(1-p)/a, \]

but in practical terms (4) must be considered a lower bound on the correct value of \( a_m \) for the particles of the dump.

Also, since we are particularly interested in the consequences of assuming a diffusion rate-limited model (that is the rate of diffusion of oxygen to the reaction site is slower than the rate of reaction of the pyrites) we require a shrinking core or moving boundary formulation for the particles of the dump. This assumption divides the particle into two regions - an outer reacted region and a shrinking unreacted core separated by a clearly defined boundary (the experimental evidence of Roman et al (1974) supports this assumption). The equations governing oxygen transport and reaction within the particle can therefore be written as

\[ \frac{3 v^*}{D_1 t^*} = D_2 \left( \frac{\partial^2 v^*}{\partial r^*^2} + \frac{2 v^*}{r^*} \right) \]

\[ R^*(x^*, R^*, t^*) = 0, \]

with the moving boundary conditions given by

\[ \frac{3 v^*}{D_1 t^*} = - \frac{3 R^*}{r^*} \quad \text{at} \quad R^* = R^*. \]

While the initial condition is

\[ R^*(x^*, 0) = a. \]

The model now lacks only a boundary condition at the outside of the particle, linking oxygen concentrations in the pore spaces of the dump with those in the particle. The assumption that oxidation occurs in the aqueous phase leads us to consider a gas-liquid interface across which oxygen must be transported to reach the reaction site within the particle. The rate at which oxygen is transported from the pore spaces into the particles is assumed to be proportional to the difference between the concentration of oxygen (within the water) and the maximum solubility of oxygen, \( v^*(x^*, t^*) \) in water at the partial pressure of oxygen in the pore space.
surrounding the particle. This is expressed mathematically as
\[ D_2 \frac{\partial v}{\partial r} = k_L (v_o - v^*) \] at \( r = a \), (8)

It can be shown, using reasonable assumptions, that
\[ v_o = vu^* \] (9)

Equations (1) - (9) now define a physically reasonable model of the dump. We proceed in the next subsection to make the system dimensionless, to consider the magnitude of the parameters involved, and to make a simplifying approximation.

3.2 Approximate, Dimensionless Model

Using the dimensionless variables defined above, (1) - (9) become
\[ k_1 \frac{\partial \bar{u}}{\partial \bar{t}} = \frac{\partial^2 \bar{u}}{\partial \bar{x}^2} - k_2 \frac{\partial \bar{v}}{\partial \bar{r}} \] for \( 0 < \bar{x} < 1 \), (10)
\[ \delta \frac{\partial \bar{v}}{\partial \bar{t}} = \frac{\partial^2 \bar{v}}{\partial \bar{x}^2} + \frac{2 \bar{v}}{\partial \bar{r}} \] for \( \delta < \bar{r} < 1 \), (11)

with boundary conditions
\[ \bar{u}(0,t) = 1, \quad \frac{\partial \bar{u}}{\partial \bar{x}}(1,t) = 0, \] (12)
\[ k_3 \frac{\partial \bar{v}}{\partial \bar{r}} = \bar{u} - \bar{v} \] at \( \bar{r} = 1 \), (13)
\[ \bar{v}(x,0,t) = 0, \] (14)
\[ \frac{\partial \bar{v}}{\partial \bar{r}} = \bar{R} \] at \( \bar{r} = 0 \), (15)
and initial conditions
\[ \bar{u}(x,0) = 0, \quad R(x,0) = 1. \] (16)

Estimates of the parameters in the model are tabulated in Table I with references to the less obvious sources of the data. From Table I we find that \( \delta \sim 10^{-5} \) which is sufficiently small to neglect

\textbf{TABLE I}

\begin{center}
\begin{tabular}{|c|c|c|}
\hline
Parameter & Value or Range of Values & Source of Data \\
\hline
\( D_1 \) & \( 4.48 \times 10^{-6} \) m\(^2\) s\(^{-1}\) & AAEC/E429 \\
\( D_2 \) & \( 2.07 \times 10^{-9} \) m\(^2\) s\(^{-1}\) & Perry (1950) \\
\( p \) & 0.4 & AAEC/E429 \\
\( u_o \) & 0.26 kg m\(^{-3}\) & AAEC/365 \\
\( L \) & 18 m & \ \\
\( a \) & 3 \times 10^{-3} - 5 \times 10^{-2} m & \ \\
\( a_m \) & \( 3(1 - p)/\alpha \) m\(^{-1}\) & \ \\
\( \alpha \) & 1.746 & \ \\
\( \rho_s \) & 16.7 - 167.0 kg m\(^{-3}\) & AAEC/E365 \\
\( k_L \) & 1 \times 10^{-6} \) m s\(^{-1}\) & \ \\
\( \gamma \) & 0.03 & \ \\
\hline
\end{tabular}
\end{center}

the left hand side of equation (11). Bischoff (1963), in fact, concluded that this pseudo-steady state assumption for a moving boundary in a sphere is valid for \( \delta \sim 10^{-3} \), therefore the approximation here is a good one. Using this simplifying approximation in equation (11) and solving for \( v(x,r,t) \), with the boundary conditions (13) and (14), we obtain
\[ v(x,r,t) = \frac{u(x,t)}{R R(1 - k_3 R)}, \] (17)

where \( k_4 = 1 - k_3 \). Upon substitution of (17) into (15) and (10), we obtain a simplified dimensionless system of equations given by
\[ k_1 \frac{\partial \bar{u}}{\partial \bar{t}} = \frac{\partial^2 \bar{u}}{\partial \bar{x}^2} - k_2 \frac{\partial \bar{u}}{\partial \bar{r}} \] for \( 0 < \bar{x} < 1 \), (18)
\[ \frac{\partial \bar{R}}{\partial \bar{t}} = - \frac{\bar{u}}{R R(1 - k_4 R)}, \] (19)

subject to the boundary and initial conditions
\[ \bar{u}(0,t) = 1, \quad \frac{\partial \bar{u}}{\partial \bar{x}}(1,t) = 0, \] (20)
\[ u(x,0) = 0, \quad R(x,0) = 1. \] (21)

Equations (18) and (19), with the associated boundary and initial conditions (20) and (21), are amenable to numerical solution using DIFSUB, a computer package written by Gear (1971), designed to integrate a set of ordinary differential first order equations over one step at each call. To facilitate the use of the package, the first term on the right hand side of equation (18) was discretised in \( x \) using central differences to produce simultaneous ordinary differential equations to solve at each point down the dump at each time step. The routine uses an Adams predictor-corrector method. All results were obtained using the Central computer at the AAEC’s Lucas Heights Research Laboratories.

4 RESULTS

Figure 1 shows the spatial heat source distribution predicted by the present model for different size

The calculated spatial heat source as a function of depth for various particle radii; the dashed line is the simple model.
particles. Also shown is the distribution predicted by the simpler model in which the dump is assumed to be a homogeneous, porous slab. The values assumed for the oxygen diffusion coefficient in the pore space of the dump, the dump porosity, the sulphur density in the dump and the age of the dump are the same for both models (see Table II). The obvious difference between the two models is that, whereas the simple model predicts a 6-function distribution for the heat source, the present model predicts a distributed source in which the width of the distribution depends on the size of the particles comprising the dump; the smaller the particles, the smaller is the region of the dump involved in the oxidation process and hence in heat production.

The spatial distribution of the oxygen concentration in the pore space of the dump is shown in Figure 2. The age assumed for the dump and the values of the parameters used in the calculations were the same as those used to produce the results shown in Figure 1. The concentration predicted by the simple model decreases in a near linear fashion from the surface of the dump to the reaction front, whereas the concentration predicted by the present model for small size particles (3.0 mm) decreases linearly to the point where the whole volume of the particle is oxidised, then decreases in a curvilinear fashion. When the particle radius is 50 mm, none of the particles are wholly oxidised in the time span considered, and the oxygen concentration decreases curvilinearly over the whole depth of the dump.

Of interest is the position of the moving boundary within the particles both as a function of time and as a function of the depth of the particle within the dump. Figure 3 shows the position of the moving boundary as a function of time for a dump with 3% sulphur (compared to 3.3% for White’s dump) and a particle radius of 10 mm. It can be seen that, as was expected, the further the particle is from the surface of the dump the greater is the time it remains unreacted. It is also clear that once a particle starts to react, the further it is from the surface of the dump, the slower is the rate at which the reaction front moves towards the centre of the particle. The sensitivity of the rate of oxidation of the particles to the values of the various parameters in the model and the consequent sensitivity of heat output and oxygen concentration distributions will be explored in more detail at a later stage.

The spatial temperature distribution has been monitored in White’s dump for several years in probe holes that extend through the depth of the dump. Temperatures vary quite markedly from region to region with a maximum in one part of this dump of about 55°C. The heat source distribution has been evaluated in the region of the probe holes from the measured temperature distributions (Harries and Ritchie 1981) and that in the region of the hottest hole is shown in Figure 4. Information on the heat source distribution in the top metre or so of the surface of the dump is lacking, partly because the temperatures were measured generally at one metre intervals, and partly because the temperature variation due to insolation was estimated at 1.0 m from the surface to remove the effect of temperature variations with a period of less than about one
month. The heat source distribution shows no measurable change over the wet/dry season cycle that is a marked feature of that part of the Northern Territory, but there has been a slow decrease in the heat output which has reduced the temperature by about 1°C in the region of maximum temperature. (Daniel, Harries and Ritchie 1981). The heat source distribution predicted by the present model for a dump aged 10 and 25 years is also shown in Figure 4; the values for the other parameters in the model were the same as those used to produce the results of Figure 3. As White's dump was started in 1954 and completed in 1958, 25 years is an appropriate value for the age of the dump when comparing predicted heat source distributions with measured distributions.

It can be seen from Figure 4 that the present model predicts a heat source distribution which is of the same order as that measured in the field and in much better qualitative agreement than that predicted by a model which assumes the dump to be a homogeneous, porous slab. Averaging the predicted spatial distributions for particles of different radius over the distribution of particle sizes found within the dump will further improve the qualitative agreement. The model also predicts the spatial variation of oxygen concentration in the pore space of the dump; this can be compared with later experimental measurements of this quantity.

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7 REFERENCES