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ABSTRACT

The consequences are examined of assuming that the oxidation rate of pyrites in an overburden dump is determined by the rate at which the oxygen required can be supplied from the top surface of the heap by diffusion through the pore space of the heap. It is shown that the oxidation reaction proceeds at a reaction front that moves away from the top surface of the heap at a rate determined entirely by the concentration of pyrites in the heap, the diffusion coefficient of oxygen in the pore space, the concentration of oxygen in the air and the ratio of the mass of oxygen to the mass of pyrites consumed in the oxidation.

Applied to White's overburden dump at Rum Jungle, the model indicates oxidation rates of the same order as those inferred from field measurement. It also predicts that at the present stage of that heap's development the reaction front lies between 3 and 5 m from the surface, depending on the porosity, which is assumed to be between 20 and 40 per cent, and that the front advances 7.5 to 13 cm per year. If the reaction is catalysed by iron-oxidising bacteria, then on the basis of the model the bacterial population will be greatest in this comparatively small region, zero in the anaerobic region below the front, and small in the upper levels of the heap.

(continued)

ABSTRACT (continued)

Estimates are also made of the temperature rise at the reaction front and the temperature distribution, assuming that the only heat loss is by conduction through the soil. However, heat loss to water passing through the heap could be significant and a more sophisticated treatment may be required.

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LEACHING; GASEOUS DIFFUSION; SOILS; IRON SULPHIDES; OXIDATION; RUM JUNGLE; MINING; LAND POLLUTION; WATER POLLUTION

CONTENTS

1. INTRODUCTION

Water flowing over and through some of the heaps of overburden material which have resulted from opencut mining at Rum Jungle, contains significant quantities of dissolved salts of the heavy metals such as copper, zinc and manganese [Davy 1975]. Since heavy metal concentrations of a few parts per million are toxic to most plant and aquatic life, waterways near the heaps and the heaps themselves are depleted of plant and animal life. This is a feature common to many mining areas throughout the world. The effect is most marked when the heaps contain appreciable (about a few per cent) quantities of iron pyrites. The dominant process [Dugan 1972] appears to be oxidation of pyrites to ferrous sulphate followed by further oxidation to ferric sulphate, which, in turn, oxidises any other metal sulphides present in the heap to soluble sulphates.

Bacteria present in the soil use the energy released in the oxidation process for their growth. In doing so they catalyse a series of chemical reactions and, under certain conditions [Lowson 1975a, Dugan 1972], considerably speed up the solublisation of the heavy metals. This heavy metal solublisation, which is clearly deleterious to the environment in the case of waste dumps, has been used successfully on a commercial scale to extract metals such as copper, nickel and uranium from low grade ores [Pings 1968]. It would therefore seem reasonable that any modelling which has been carried out to optimise parameters in commercial leaching of heavy metals, could be applied to heavy metal polluted water flowing from waste dumps. However, there is much that is not known, about both the biochemistry of the process and the mechanism by which reactants and reaction products are transported to and from sites in the heap where the oxidation occurs. In practice, little quantitative modelling exists, and optimisation of parameters on a commercial scale is done largely by trial and error, assisted to some extent by laboratory experiment.

Harris [1969] developed a model by analogy between a heap undergoing leaching and a porous catalysis particle. Two extremes were envisaged with an actual heap operating somewhere between these. At one extreme where the oxygen supply rate was assumed much slower than any chemical reaction, the leaching rate was inversely proportional to a characteristic length L. In the other extreme where the oxygen supply rate was assumed much faster than any chemical reaction rate, the leaching rate was independent of L. Unfortunately, it is not clear how to evaluate L which can refer either to individual particles in the heap or to the heap as a whole, or how to determine into which regime the leaching process falls. For this reason Harris' model is of qualitative rather than quantitative interest.

Roman *et al.*[1974] considered leaching of copper from a pile of material in which examination of individual particles had indicated the rate-controlling process was the rate of diffusion of leach liquor into the individual particles. As leach liquor passed down through the pile, it became steadily depleted and, as time increased, the reaction front in each particle penetrated further into the particle. Roman *et al.* used a numerical method for predicting the behaviour of leaching columns of this material and found good agreement between predicted and measured copper recovery fractions.

Here the leaching of waste heaps under natural rainfall conditions is investigated with particular reference to White's overburden dump at Rum Jungle. All the reactants required in the oxidation process are assumed to be readily available, except for oxygen, which is supplied by diffusion through the pore space of the heap from the air at its surface. It will also be assumed that all the chemical reactions and transport processes involved are faster than the diffusion rate of oxygen. If the oxidation is catalysed by the bacteria, then these assumptions mean that the bacterial population is so large that any further rate of increase is determined by one rate-controlling mechanism, and that this mechanism is the supply of oxygen.

Of interest is the extent to which these assumptions dictate where in the heap the oxidation process takes place and how the oxidation site changes position with time. Also of interest is the dependence of the rates of consumption of oxygen and pyrites on such parameters as heap size, oxygen diffusion rate, heap porosity, etc. These consumption rates can be compared with actual measurements on the White's overburden dump to see if the model, which is physically reasonable, could possibly describe oxidation in such waste dumps.

2. THE MODEL

Consider the waste dump as a permeable slab with one face open to the atmosphere. This is a reasonable description of White's heap which is about 500 m across and 18 m deep. Since the rate of oxidation of pyrites in the heap is assumed to be governed entirely by the rate at which oxygen can be supplied by diffusion through the pore space of the heap from the air at the open surface, the reaction proceeds at a front [Crank 1956] which is initially at the surface, and whose distance (X) below this surface as a function of time is given by

$$X(t) = 2\alpha(Dt)^{\frac{1}{2}} \qquad (1)$$

where α is given by

$$\pi^{\frac{1}{2}} \rho_S \, \varepsilon \, \alpha \, e^{\alpha^2} \, \mathrm{erf}(\alpha) = C_O \qquad (2)$$

and D = diffusion coefficient of (in this case) oxygen through the pore space of the heap;

ρ_S = density of (in this case) sulphur in the heap being consumed in the oxidation;

ε = ratio of the mass of oxygen used to the mass of sulphur used in the oxidation reaction; and

C_O = concentration of oxygen at the surface of the slab.

The oxygen concentration as a function of depth below the surface is given by

$$C(x) = C_O[1-\mathrm{erf}(x/2\sqrt{Dt})/\mathrm{erf}(\alpha)] \quad .$$

For small α the expression 2 gives

$$\alpha = \sqrt{\frac{C_O}{2\rho_S\varepsilon}} \qquad (3)$$

and $$X(t) = \sqrt{\frac{2C_O Dt}{\varepsilon\rho_S}} = \mu \, t^{\frac{1}{2}} \qquad (4)$$

with $$\mu = \sqrt{2C_O D/\varepsilon\rho_S} \quad .$$

Since ε is the order of unity, it follows that α is small and takes the form (3) when the concentration of oxygen in air is less than the sulphur concentration in the overburden dump, a condition that holds in White's overburden dump where the average sulphur concentration is about 3% [Davy 1975].

When α is small, the oxygen concentration as a function of distance from the surface takes the simple form

$$C = C_O \, (1 - x/X(t)) \quad .$$

This expression can also be obtained by assuming that the front X(t) moves so slowly that diffusion can be assumed to be a steady state process with concentration C_O at the surface and zero at the front, $x = X$, where the chemical reaction is taking place. Solution of the steady state diffusion equation with these boundary conditions yields

$$C = C_O \, (1 - x/X) \quad . \qquad (5)$$

The rate of flow of oxygen through to the reaction surface is then

$$J = \frac{D \, C_O}{X} \text{ /unit area.} \qquad (6)$$

This can be equated with the amount of oxygen

$$\varepsilon \rho_S \frac{dX}{dt} \text{ /unit area} \tag{7}$$

required to advance the front at a rate dX/dt to give the differential equation

$$X \frac{dX}{dt} = \frac{D\,C_o}{\rho_S \varepsilon} \quad .$$

The solution of this equation with X = 0 at t = o gives the result (4).

The gas transport process could be likened to gas transport through a permeable slab with one face open to the atmosphere and with a pump at the other face capable of preferentially removing oxygen as fast as it is supplied to that face. It could be argued that the decrease in pressure at the pumped face will lead to gas transport driven by a pressure gradient and that this could lead to a faster rate of mass transfer than diffusion driven by a concentration gradient. It has been shown elsewhere [Ritchie 1977] that the pressure gradient is, in fact, small since it is determined by a balance between the back diffusion rate of unpumped nitrogen and the input rate of nitrogen from air flow onto the open face of the slab. The oxygen transport can be described as diffusion with a diffusion coefficient slightly enhanced (by ∿ 20%) by gas flow. As the discussion below makes clear, the increase in the diffusion coefficient is small compared to uncertainties introduced by other factors.

3. PARAMETERS IN THE MODEL

Values for C_o, ε and ρ_S in equation 4 can be fairly well defined, but the value for the diffusion coefficient D, which depends on the porosity of the heap, presents more of a problem.

The value for ε, the ratio of oxygen to sulphur used, is determined by the chemical equation which describes the oxidation process. The major oxidation reaction is the oxidation of iron pyrites to ferrous sulphate and can be described by the equation

$$FeS_2 + H_2O + \frac{7}{2} O_2 \rightarrow FeSO_4 + H_2SO_4 \quad . \tag{8}$$

Although further oxidation of the ferrous sulphate to ferric sulphate occurs, the ferric sulphate oxidises other metal sulphides to sulphates in reactions which can be described by equations of the form

$$MnS + 2O_2 \rightarrow MnSO_4 \quad , \tag{9}$$

and which leave only small net production of ferric sulphate.

Since the concentration of other metal sulphides in White's dump is about an order of magnitude lower than that for iron pyrites, it is reasonable to take reaction 8 as the one which defines ε. Clearly equations 8 and 9 are simplifications of the bacterially catalysed reactions taking place, but are sufficient for the present purpose of evaluating ε.

Chemical analysis of bulked, crushed auger drill samples from White's dump [Lowson 1975b] yielded a sulphur concentration of 3.27%. This is the value that has been used for ρ_S.

The results of Papendick and Runkles [1965], who have measured the diffusion coefficient of oxygen in soil as a function of soil porosity, have been reproduced in Figure 1. No direct measurements have been made of the porosity of White's dump, but estimates ranging from 11% to 40% from a variety of sources are given in Table 1. Of these, the value of 37%, derived from the ratio of the average density of the heap to the density of the rocky material that came from the opencut, is perhaps the most reliable.

4. PREDICTIONS OF THE MODEL

4.1 Movement of the Reaction Front and Usage of Oxygen and Pyrites

Figure 2a shows the position of the reaction front as a function of time assuming porosities of 20, 30 and 40%. Since White's heap has been in existence for about 20 years, the present position of the front should be between 3 and 5 m from the surface. If the height of the heap is taken as 18 m which is the maximum height of the heap above the former land surface, it will be some 250 to 700 years before the reaction front reaches the bottom of the heap.

The mass of oxygen (Figure 2b) predicted to be consumed in a year by a 20-year old heap lies between 1800 and 3000 t. This is to be compared with preliminary estimates of 2700 to 4500 t [Clancy & Ritchie 1975] and estimates of 2800 to 5300 t in one year of average rainfall derived from more detailed measurements carried out during the 1975-76 wet season [Clancy & Ritchie 1977].

Figure 2b also shows the distance the front moves in a year. For a 20-year old heap, this lies between 7.6 and 13 cm, with an upper limit of 23 cm set by the diffusion coefficient of oxygen in air. This result means that the iron pyrites oxidising reaction described by equation 8 is confined in any one year to a very thin layer for a mature heap. If the reaction is catalysed by iron-oxidising bacteria, then the bacterial population is also confined to this very thin layer.

4.2 Temperature Distribution in the Heap

The chemical reaction described by equation 8 releases energy, some of which is used by the bacteria which catalyse the reaction, and the rest of which is liberated as heat. The temperature distribution as a function of time and distance to be expected from the moving source of heat is [Carslaw & Jaeger 1950]

$$\nu = \nu_o + \frac{\rho_s \gamma}{\rho c} \; \frac{1}{4\sqrt{\pi\kappa}} \int_0^t \frac{d\tau}{\tau^{\frac{1}{2}}} \; \frac{\mu}{(t-\tau)^{\frac{1}{2}}} \left\{ \exp -\left[\frac{(x-\mu\tau^{\frac{1}{2}})^2}{4\kappa \; (t-\tau)} \right] - \exp -\left[\frac{(x+\mu\tau^{\frac{1}{2}})^2}{4\kappa \; (t-\tau)} \right] \right\} \tag{10}$$

where ν_o = ambient temperature at the surface of the heap,

γ = heat released/g of sulphur used in oxidation equation 8,

ρ = density of the material of waste dump,

c = specific heat of the material,

κ = K/c,

K = thermal conductivity of material of waste dump,

μ = $\sqrt{2 \; C_o \; D/\rho_s \varepsilon}$.

Equation 10 is not amenable to analytical solution and it is, in fact, simpler to use numerical methods [Clancy 1977] to solve the corresponding partial differential equation. Figure 3 shows the shape of the temperature distribution as a function of time for unit heat source ($\rho_s\gamma = 1$) and 100% porosity ($D = D_o$). It can be seen that the maximum temperature increase above ambient occurs as expected at the reaction front, and that this temperature difference is independent of time.

An analytic expression can be found for this temperature difference at the reaction front $x = \mu\tau^{\frac{1}{2}}$ since substitution of this into equation 10 considerably simplifies the integral. After some algebra (see Appendix A), the temperature difference can be expressed in terms of

$$\Delta\nu = \nu - \nu_o = \frac{\rho_s \gamma}{\rho c} \; \beta^2 \; \frac{2}{\sqrt{\pi}} \left\{ \int_0^{\beta^2} \frac{e^{-p} dp}{p^{\frac{1}{2}}(p+\beta^2)} - \frac{\pi}{2\beta} \; e^{\beta^2} \mathrm{erfc}(\beta) \right\} \tag{11}$$

where $\beta = \mu/2\sqrt{\kappa}$.

If β is less than one, which is true for reasonable values of μ and κ, then equation 11 can be expressed as

$$\Delta\nu = 2\beta^2 \; \frac{\rho_s \gamma}{\rho c} = \gamma \frac{C_o D}{\varepsilon K} \; . \tag{12}$$

Equation 11 shows clearly that the temperature at the front is independent of time. It is also clear from equation 12 that the temperature rise is independent of the sulphur density, the specific heat of the material of the heap and the density of the material, provided β is less than one, that is, provided the reaction front moves more slowly than heat propagating from it.

The temperature rise is proportional to the oxygen diffusion coefficient and hence is much more sensitive to the uncertainty in heap porosity than are quantities such as the rate of movement of the front and the amount of oxygen consumed. There is also some uncertainty in γ, the specific heat released, since no measurements have been made of the energy used by the thiobacilli in oxidation of pyrites. An upper limit is set by the specific heat of 4.73 kcal/g of sulphur consumed in the reaction described by equation 11. With this value for γ and assuming the thermal conductivity of the material of the heap to be typically 2.3×10^{-3} cal/cm/s/°C [Carslaw & Jaeger 1950], the maximum temperature rise lies between 21°C and 7°C for porosities between 20 and 40%.

5. DISCUSSION

The model, which assumes that the rate at which oxidation proceeds within a heap is limited by the rate at which atmospheric oxygen can be supplied by diffusion through the pore space within the heap, predicts an annual oxygen consumption of the same order as that indicated by measurement of pollution levels in water emanating from the heap. It is reasonable to conclude that since the process is physically possible, it is a likely oxidation process. It should be emphasised that this does not necessarily mean that this is the only oxidation mechanism. It seems most likely that there are a number of different mechanisms for oxygen transport, each of which dominates in turn in a given leaching system.

The model predicts that the reaction front has moved some 3 to 5 m below the surface in the 20 years that have elapsed since White's overburden dump was laid down. It also predicts that the present yearly oxygen consumption of about 1800 to 3000 t will drop by only a factor of two in the next 60 years.

Of perhaps greatest interest is the prediction that the oxidation reaction is confined to a layer only about 7.5 to 13 cm thick in any one year at this stage in the heap's lifetime. This means that any bacteria that catalyse the oxidation of iron pyrites will be confined to this comparatively small region. In practice, the non-homogeneity of the heap, and the fact that diffusion rates into boulders may well be even slower than diffusion of oxygen through the pore space of the heap, mean that some pyrites and hence some bacteria may be left behind the diffusion rate-limited reaction front.

The estimated temperature rise is proportional to the oxygen diffusion coefficient (see equation 12) rather than to the square root of this quantity, and hence more sensitive to the uncertainty of the heap porosity than to such quantities as the position of the reaction front and the consumption rate of oxygen. It should also be noted that the temperature rise was calculated on the assumption that the only heat loss mechanism was conduction and that the magnitude of this loss was determined by maintaining the surface of the heap at ambient temperature. The average run-off fraction is known to be about 10% [Clancy & Ritchie 1977]. If a large fraction of the rest of the annual rainfall on the heap is assumed to pass through the heap and acquire the temperature of the reaction front, the heat required is comparable with the heat generated by the reaction in a year. This means that heat transported by water flowing through the heap must also be included when estimating the temperature distribution in the heap.

6. ACKNOWLEDGEMENT

Discussions with Dr. B.E. Clancy on the problem are gratefully acknowledged.

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APPENDIX A

THE TEMPERATURE AT THE REACTION FRONT

When $x = \mu t^{\frac{1}{2}}$ the temperature is given by

$$\nu = \nu_o + \frac{\rho_s \gamma}{\rho c} \frac{\beta}{2\sqrt{\pi}} \int_o^t \frac{d\tau}{\tau^{\frac{1}{2}}(t-\tau)^{\frac{1}{2}}} \left\{ \exp - \left[\beta^2 \frac{(t^{\frac{1}{2}}-\tau^{\frac{1}{2}})^2}{(t-\tau)} \right] - \exp - \left[\beta^2 \frac{(t^{\frac{1}{2}}+\tau^{\frac{1}{2}})^2}{(t-\tau)} \right] \right\} . \tag{A1}$$

Using the changes of variable

$$p = \beta^2 \frac{(t^{\frac{1}{2}}-\tau^{\frac{1}{2}})^2}{(t-\tau)} ,$$

and $$p = \beta^2 \frac{(t^{\frac{1}{2}}+\tau^{\frac{1}{2}})^2}{(t-\tau)} ,$$

respectively, in the integrals that arise from the terms in the square brackets, the expression A1 becomes

$$\nu = \nu_o + \frac{\rho_s \gamma}{\rho c} \frac{\beta^2}{\sqrt{\pi}} \left\{ \int_o^{\beta^2} \frac{e^{-p}dp}{p^{\frac{1}{2}}(p+\beta^2)} - \int_{\beta^2}^{\infty} \frac{e^{-p}dp}{p^{\frac{1}{2}}(p+\beta^2)} \right\}$$

$$= \nu_o + \frac{\rho_s \gamma}{\rho c} \frac{2\beta^2}{\sqrt{\pi}} \left\{ \int_o^{\beta^2} \frac{e^{-p}dp}{p^{\frac{1}{2}}(p+\beta^2)} - \frac{1}{2} \int_o^{\infty} \frac{e^{-p}dp}{p^{\frac{1}{2}}(p+\beta^2)} \right\} . \tag{A2}$$

Now $$\int_o^{\infty} \frac{e^{-p}dp}{p^{\frac{1}{2}}(p+\beta^2)} = \frac{\pi}{\beta} e^{\beta^2} \operatorname{erfc}\beta . \tag{A3}$$

Moreover, since for values of μ and κ which would be applicable to White's heap, $\beta = \frac{\mu}{2\sqrt{\kappa}} < 1$, the exponential and erfc functions in equation A3 can be expanded as a power series in β. Similarly, the exponential in the first integral of equation A2 can be expanded to give:

$$\int_o^{\beta^2} \frac{e^{-p}dp}{p^{\frac{1}{2}}(p+\beta^2)} = \sum_{n=0} (-1)^n \frac{2\beta^{2n-1}}{n!} \int_o^{\pi/4} \tan^{2n}\theta d\theta .$$

Using these expansions

$$\int_o^{\beta^2} \frac{e^{-p}dp}{p^{\frac{1}{2}}(p+\beta^2)} - \frac{\pi}{2\beta} e^{\beta^2} \operatorname{erfc}\beta = \sqrt{\pi} - 2\beta + \ldots$$

to give $\nu = \nu_o + 2\beta^2 \frac{\rho_s \gamma}{\rho c}$

to second order in β .

TABLE 1

ESTIMATES OF POROSITY OF WHITE'S HEAP

Data Source	Porosity Estimates
1. Comparison of volume of opencut at 3.53×10^6 m^3 with volume of heap at 3.95×10^6 m^3. [Lowson 1975b]	0.11
2. Comparison of volume of opencut corrected for volume of ore removed, at 0.204×10^6 m^3, with volume of heap. [Lowson 1975b] Note: The weight of material removed from the opencut at 9.35×10^6 t is much greater than the estimated weight of material in the heap at 6.60×10^6 t.	0.18
3. Comparison of original rock density of 2.65 with heap density of 1.67. [Lowson 1975b]	0.37

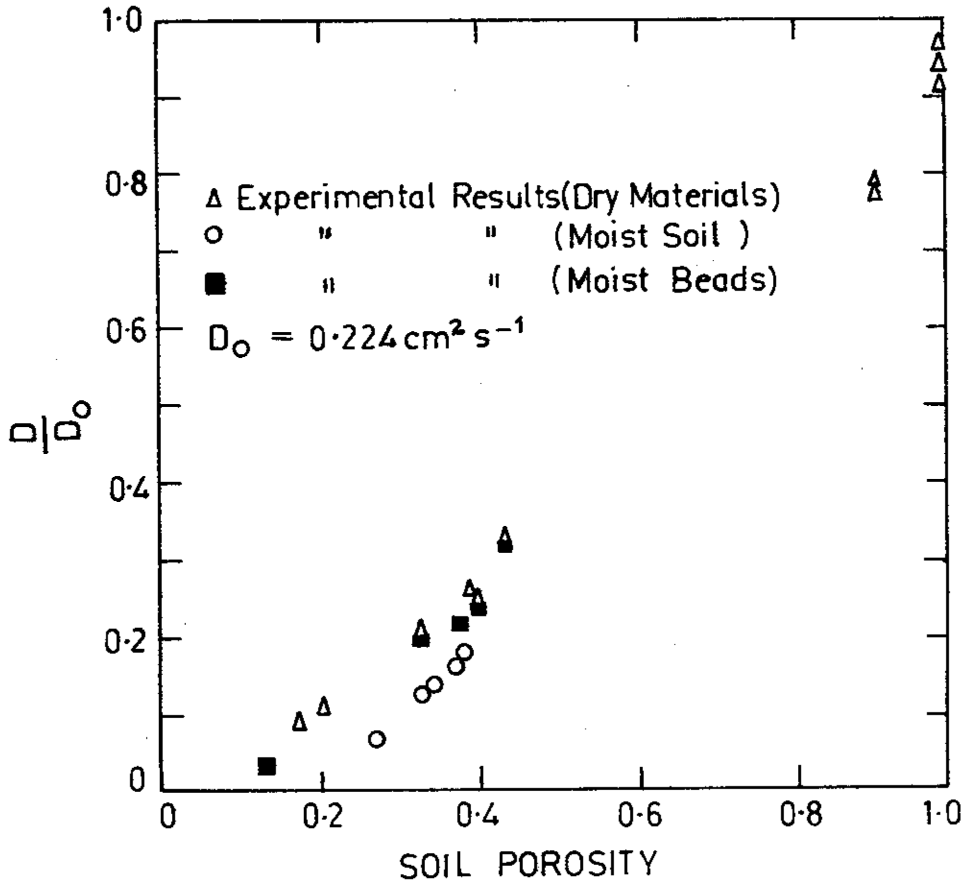

FIGURE 1. RELATIONS BETWEEN RATIO OF OXYGEN DIFFUSION RATES IN POROUS MEDIA AND IN AIR, D/D_o, AND POROSITY (After Papendick, R.I. & Runkles, J.A. (1965) Soil Science, 100 :251)

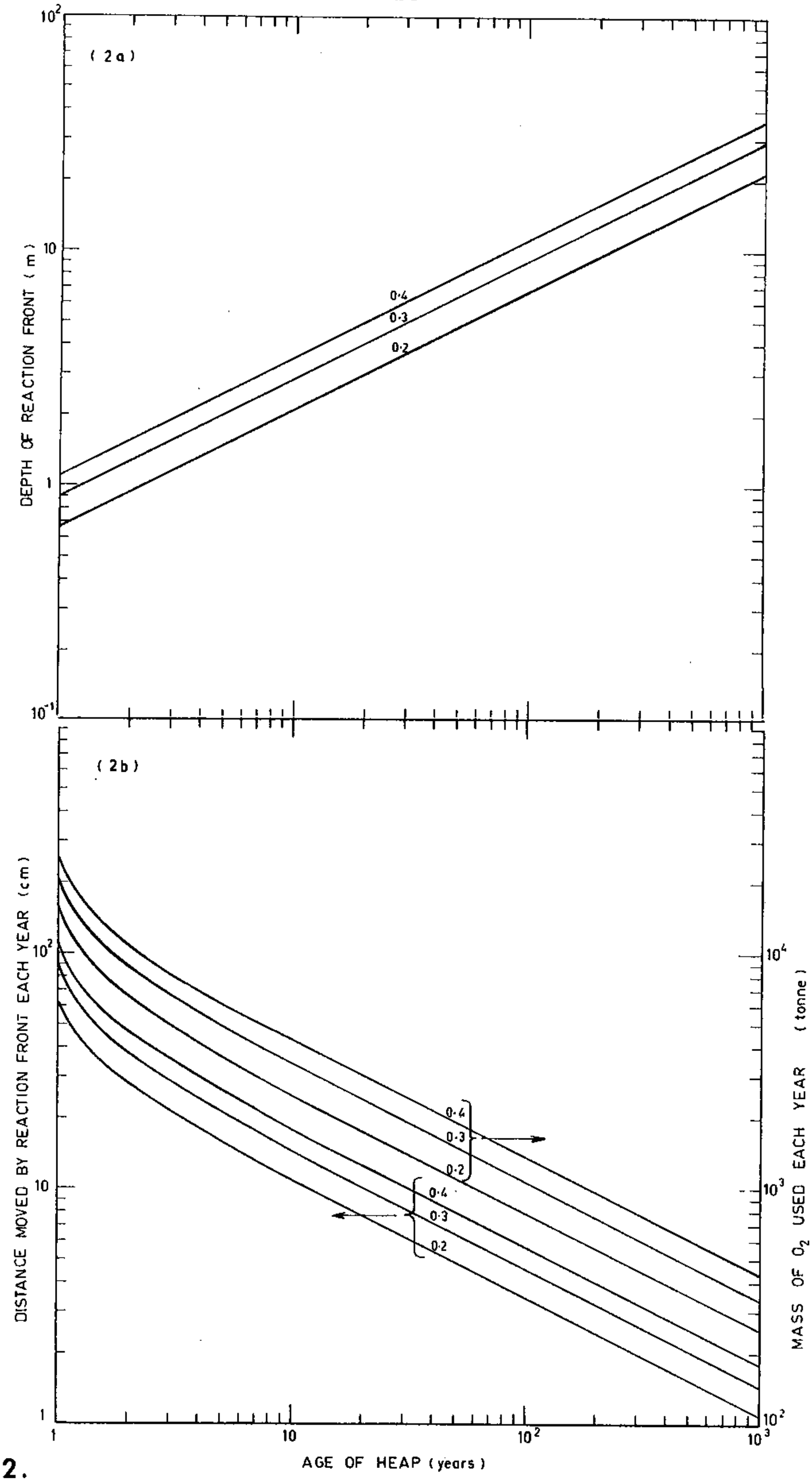

FIGURE 2.

(a) POSITION OF REACTION FRONT AS A FUNCTION OF THE AGE OF THE HEAP FOR VARIOUS POROSITIES

(b) DISTANCE FRONT MOVES AND MASS OF O_2 CONSUMED IN A YEAR AS A FUNCTION OF THE AGE OF THE HEAP

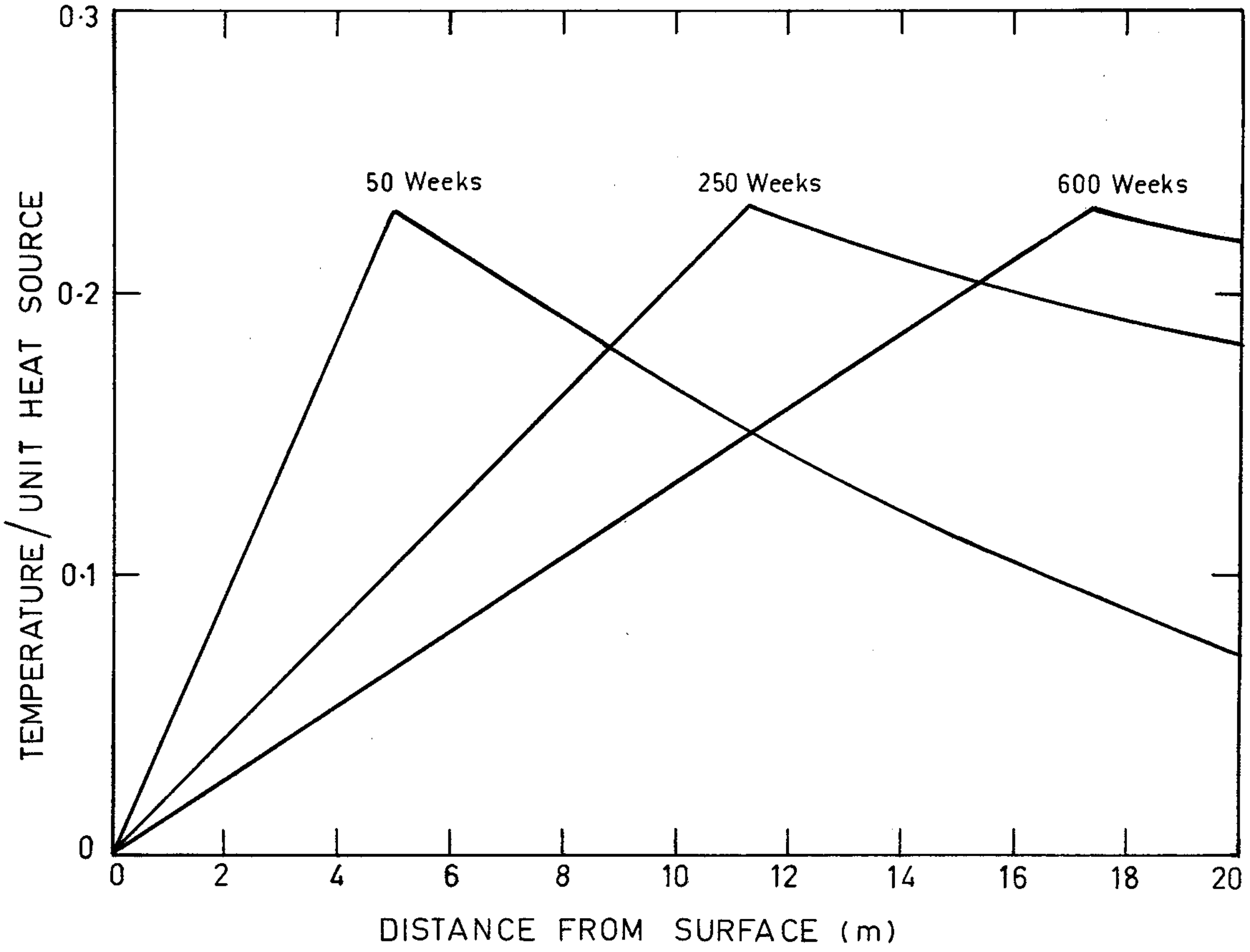

FIGURE 3. TEMPERATURE DISTRIBUTION AT VARIOUS TIMES IN THE LIFETIME OF THE HEAP