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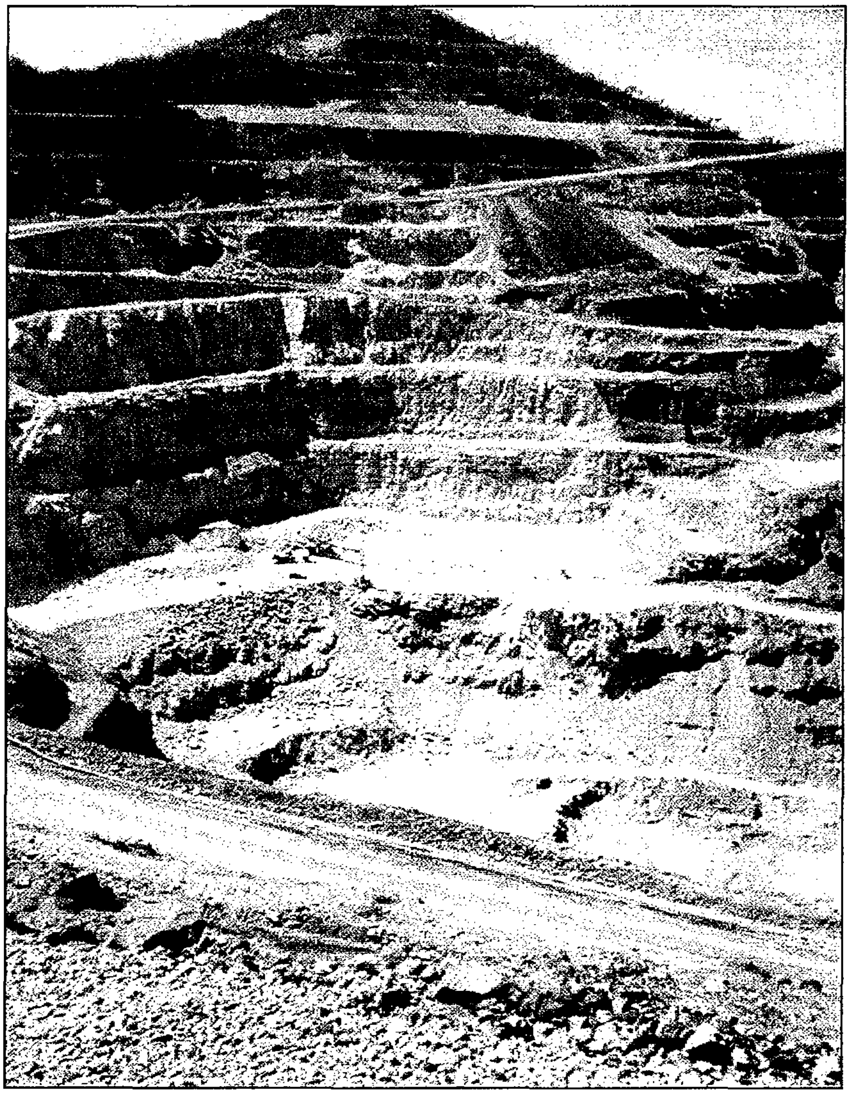

REPORT:
A Model for the Description of Oxidation in Sulfidic Waste Rock Dumps

by

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Prepared within the Managing Mine Wastes Project
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Contents

ABSTRACT

Basic mathematical equations which describe the processes of sulfide oxidation and gas and water transport in waste rock dumps are presented and discussed. The governing equations account for gas and water flow, vaporisation and condensation with latent heat effects, heat transport and mass balance. Gas, water and solid phases are assumed to be in local thermal equilibrium at all times. Air is approximated as an ideal three-component gas. Different semi-empirical relationships between physical values are used: Darcy's law for fluid flow, ideal gas law, the Van Genuchten formula for the relationship between degree of water saturation and pressure head, Mualem's formula for the relative hydraulic conductivity as a function of pressure head, etc. Some important global quantities, such as the fraction of sulfide sulfur oxidised and the global oxidation rate, are defined and considered as functions of time. The full set of equations is collected and presented in explicit form, convenient for further numerical modelling. The glossary of some technical terms and the table of definitions of the main parameters as well as their units and characteristic values are displayed.

1. Introduction.

The leaching of metals (such as copper, nickel, zinc, uranium, etc.) from some ores depends on the conversion (oxidation) of largely insoluble metal sulfides to much more soluble sulfates. The process can occur in large waste rock dumps of sulfidic material through which gas and water can infiltrate (Fig. 1).

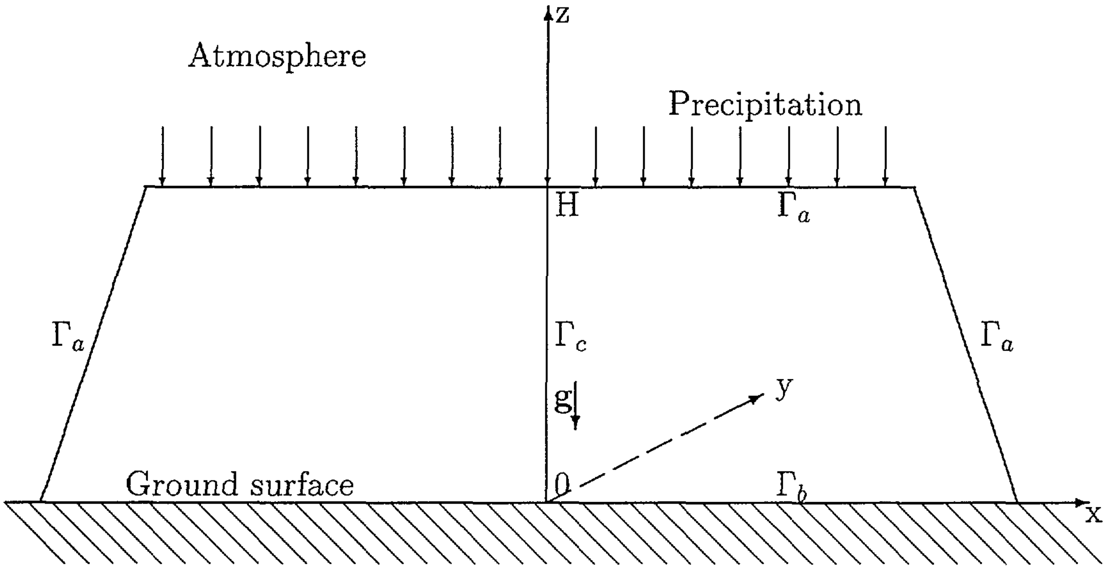


Fig. 1. A schematic vertical cross-section of a waste rock dump.

Water dissolves the metal sulfates and passes out through the base of the dump. Crucial to the solubilisation process is the bacterially catalysed oxidation of pyrite or other iron containing sulfide minerals (*Lawrence* et al., 1986; *Norris* and *Kelly*, 1987).

In waste rock dumps, which may measure from several metres to several tens of metres in height (typically about 20 m) and several hundreds of metres in width (typically about 600 m), oxygen initially enters the dump at the atmosphere–dump interface by the process of molecular diffusion. Initially, the oxidation reaction is confined to the surface layers of the dump. The heat released from pyrite oxidation will cause small changes in the air density within the dump. The same effect, but even more pronounced, arises from the oxygen depletion in the pore gas phase due to its consumption in the chemical reaction with pyrite. This, in turn, induces a convective air current within the dump and in so doing increases the rate of atmospheric oxygen transport into the dump and permits oxidation throughout the dump.

Davis et al. (1986a, 1986b, 1987) considered the case where oxygen transport was a two stage process: diffusion through the pore space of the dump followed by diffusion into reaction sites within particles comprising the dump. This model is applicable to columns and thin heaps where convection is negligible. *Cathles* and *Schlitt* (1980) considered a similar case but they assumed convection through the dump to be the only macroscopic transport process. Here, an advanced model which takes into account water transport inside the dump and the influence of the vaporisation process on a temperature balance is presented. Traditionally, the dump is modelled as a three phase system consisting of a rigid solid porous phase through which flow gas and water phases.

2. Balance laws.

Consider a two-dimensional model of a dump which is comprised of pyritic ore lying on a relatively impermeable and insulating ground surface, denoted by Γ_b, as depicted in Fig. 1. The sides and upper surfaces, which represent the atmosphere–dump interface, are denoted by Γ_a. It is assumed for simplicity that the physical properties of the solid matrix as well as the fluid components are isotropic in space, although this restriction is not essential.

The mathematical description that follows is based on macroscopic equations for multi-component flows through continuous reactive porous media. A system is considered that consists of oxygen in air in the gas phase, water in both the liquid and gas phase (as water vapour in air) and a solid phase. The ***bulk phase density,*** ρ_α, of each phase: gas, liquid (water) and solid ($\alpha = g,w,s$, respectively), is related to the intrinsic density, ρ_α^{in}, by

$$\rho_\alpha = \varepsilon_\alpha \rho_\alpha^{in}, \tag{1}$$

where the ***volume fractions of the*** α ***-phase,*** ε_α, must satisfy the relation

$$\varepsilon_g + \varepsilon_w + \varepsilon_s = 1. \tag{2}$$

Generally speaking, each α-phase is assumed to be comprised of N_α components. The ***concentration of component*** i ***in the*** α ***-phase*** (or ***the mass fraction of component*** i ***in the*** α ***-phase***) is written as $(\omega_\alpha)_i = (\rho_\alpha^{in})_i / \rho_\alpha^{in}$, ($i = 1, \ldots N_\alpha$), where the subscript α denotes the phase and the subindex i identifies the component within the phase. In particular, the mass concentration of a gas component i, $(\omega_g)_i$, can be expressed in terms of the components intrinsic gas density $(\rho_g^{in})_i$ by $(\omega_g)_i = (\rho_g^{in})_i / \rho_g^{in}$ with the associated identities

$$\sum_{i=1}^{N_g} (\omega_g)_i = 1, \quad \sum_{i=1}^{N_g} (\rho_g^{in})_i = \rho_g^{in}. \tag{3}$$

There are four major components in the gas phase (air), namely nitrogen $\sim 78\%$, oxygen $\sim 21\%$, argon $\sim 0.9\%$, carbon dioxide $\sim 0.033\%$. A fifth, water vapour may be present up to 3%, with reduced amounts of the other components.

The liquid phase is considered to be comprised of water only, while the solid phase is assumed to be comprised of sulfur and residual waste rock material (sand, clay, gravel, etc.). It is also assumed that chemical reactions can take place between different phases α but not between different species i within the same phase. Chemical reactions between species in the same phase can be taken into account, but such reactions will not be considered in this report.

The mass balance for component i in the gas phase can be obtained from the continuity equation (*Nield* and *Bejan*, 1999):

$$\frac{\partial[\rho_g(\omega_g)_i]}{\partial t} + \mathrm{div}\{\rho_g(\omega_g)_i(\mathbf{v}_g)_i - D_i\nabla[\rho_g(\omega_g)_i]\} = \left(S_g\right)_i, \qquad i = 1, \ldots N_g, \tag{4}$$

where $\left(\mathbf{v}_g\right)_i$ is the intrinsic velocity of individual gas component i, $\left(S_g\right)_i$ is the production (or consumption) rate of component i in the gas phase and D_i represents the ***diffusion coefficient in porous media*** for component i through the gas phase.

It is assumed that the diffusion coefficient in porous media, D_i**,** can be expressed as

$$D_i = \Lambda_g(\tau,\delta,\varepsilon_w)\hat{D}_i, \tag{5}$$

where $\hat{D}_i$ is the ***intrinsic coefficient of diffusion of component*** i in the gas phase and the ***porosity factor***, Λ_g, depends on the structure of porous material (pore ***tortuosity***, τ, and the ***constrictivity***, δ) and the volumetric water fraction, ε_w. The tortuosity accounts for the tortuous paths of real pores and the constrictivity accounts for the fact that the cross-section of a pore segment varies over its length.

There are several different empirical and semi-empirical formulae for the porosity factor, $\Lambda_g(\tau,\delta,\varepsilon_w)$ with some of them being fairly complex. A good review about the methods to estimate effective diffusion coefficients and the comparison between different analytical formulae and experimental data can be found in *Collin* and *Rasmuson* (1988). In our study, two of the simplest formulae for the diffusion of gas components are used. They can be considered, to some extent, as limiting dependencies which give upper and lower bounds of the function Λ_g [for the details see *Collin* and *Rasmuson* (1988)].

The upper bound estimate can be presented in the form:

$$\Lambda_g = \frac{\delta}{\tau^2}\frac{\varepsilon_g^2}{1-\varepsilon_s} = \frac{\delta}{\tau^2}(1-\varepsilon_s)(1-s)^2, \qquad (6)$$

where the ratio δ/τ^2 is taken at $\varepsilon_w = 0$ and ranges from 0.5 to 1; s is the ***degree of water saturation*** and can be defined as:

$$s \equiv \frac{\varepsilon_w}{\varepsilon_g + \varepsilon_w} = \frac{\varepsilon_w}{1-\varepsilon_s}. \qquad (7)$$

According to *Collin* and *Rasmuson* (1988), the relation (6) gives much too high values at higher moisture contents. The lower bound estimate corresponds to Currie's formula [again see *Collin* and *Rasmuson* (1988)]:

$$\Lambda_g = \frac{\delta}{\tau^2}\frac{\varepsilon_g^5}{1-\varepsilon_s} = \frac{\delta}{\tau^2}(1-\varepsilon_s)^4(1-s)^5. \qquad (8)$$

Both these dependencies are depicted in Fig. 2 on a semi-logarithmic scale.

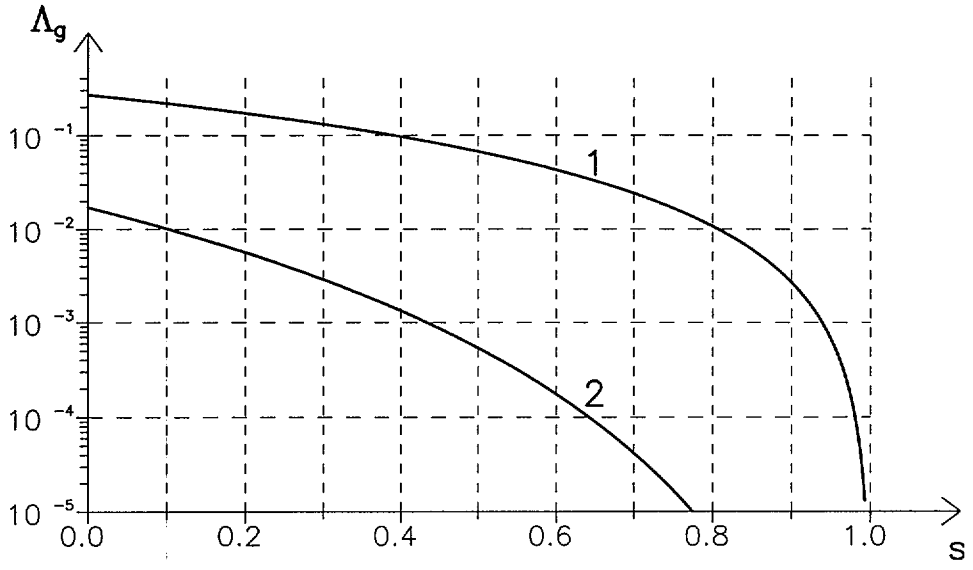


Fig. 2. Porosity factor, Λ_g, versus degree of water saturation s. Curve 1 corresponds to formula (6) while curve 2 corresponds to Currie's formula (8) with $\delta/\tau^2 = 0.67$, $\varepsilon_s = 0.6$.

Intrinsic diffusion coefficients for both oxygen and water vapour in air depend on the temperature, T, and pressure, p, (*Batchelor*, 1970) and can be represented as (Fig. 3)

$$\hat{D}_i = \delta_i \left(1 + \frac{T}{\Theta}\right)^{7/4} \frac{p_0}{p}, \qquad (i = 1,2), \tag{9}$$

where for oxygen $\delta_o = 1.78 \cdot 10^{-5}$ m^2 s^{-1}, for water vapour $\delta_v = 2.19 \cdot 10^{-5}$ m^2 s^{-1}, $\Theta = 273.16^\circ$C, $p_0 = 1$ atm and the temperature is measured in Celsius. Here and in the subsequent text, the subindices "o" and "v" are used instead of "1" and "2" for convenience to denote gas components, oxygen and water vapour, respectively.

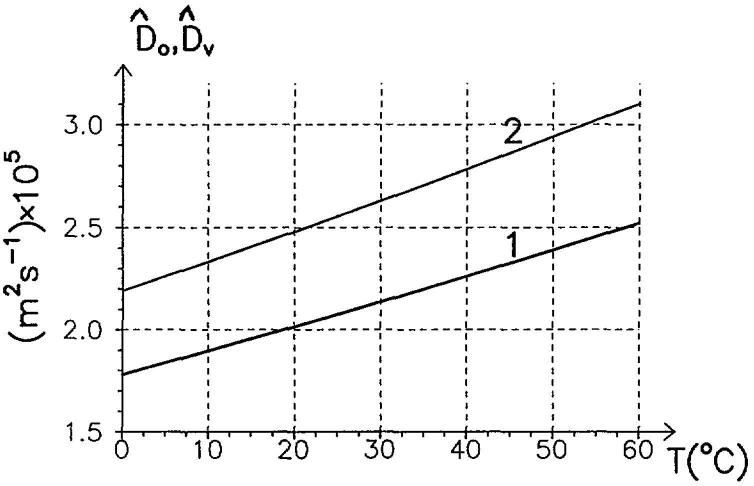


Fig. 3. Temperature dependence of the intrinsic diffusion coefficients for oxygen (1) and for water vapour (2).

One can consider the set of N_g independent equations (4) for N_g unknown functions $(\omega_g)_i$ and then, to determine the function ρ_g with the help of the relationships (1) – (3). However, sometimes it is more convenient to consider only $N_g - 1$ independent equations of set (4) for $N_g - 1$ functions $(\omega_g)_i$ and one more independent equation for the function ρ_g, which can be obtained by summation of all equations (4) over i by taking into account the relationships (3):

$$\frac{\partial \rho_g}{\partial t} + \mathrm{div}(\rho_g \mathbf{v}_g) = S_g \equiv \sum_i (S_g)_i + \mathrm{div}\left\{\sum_i D_i \nabla\left[\rho_g (\omega_g)_i\right]\right\}, \tag{10}$$

where $\mathbf{v}_g \equiv \frac{1}{\rho_g^{in}} \sum_{i=1}^{N_g} (\rho_g^{in})_i (\mathbf{v}_g)_i$ is the mass-averaged intrinsic velocity of gas flow through the porous medium. Note that in groundwater flow theory the intrinsic velocity for gas or liquid phase, $\mathbf{v}_\alpha$, is related to the so-called Darcy or seepage velocity, $\mathbf{V}_\alpha$, by the relationship $\mathbf{V}_\alpha = \varepsilon_\alpha \mathbf{v}_\alpha$ (*Nield* and *Bejan*, 1999). However, in this report only the intrinsic velocity is used for each phase. The last term on the right-hand side of (10), $\mathrm{div}\left\{\sum_i D_i \nabla\left[\rho_g (\omega_g)_i\right]\right\}$, can usually be omitted so that $S_g = \sum_i (S_g)_i$. This means that in the case of relatively small concentration gradients, the total ***diffusive*** flux of gas components is equal to zero, while the particular fluxes of individual components are non-zero (in essence, this will be a diffusion mechanism). However, the flux associated with the average velocity $\mathbf{v}^g$ is caused by external forces and not by diffusion processes.

In this study a gas phase system comprised of *three main* components is considered: oxygen, water vapour and the remaining portion of the gas phase, the latter of which is approximated by nitrogen gas. Oxygen, water vapour and nitrogen are denoted components $i = 1$, 2 and 3, respectively, and have mass concentrations $\omega_o \equiv (\omega_g)_1$, $\omega_v \equiv (\omega_g)_2$, $\omega_n \equiv (\omega_g)_3$.

For the liquid phase (which is assumed to be comprised of water only), the mass balance equation is

$$\frac{\partial \rho_w}{\partial t} + \mathrm{div}(\rho_w \mathbf{v}_w) = -S_w(\varepsilon_w, T), \tag{11}$$

where the function $S_w(\varepsilon_w, T)$ describes the water depletion (production) due to vaporisation (condensation) process within the waste material and will be specified in the next section. In principle, some more sink terms could be added to the right hand side of this equation (e.g., the term responsible for water depletion due to chemical reaction of sulfur oxidation) but for simplicity the model is restricted to one water depletion/production term only, as described above.

The intrinsic water density, ρ_w^{in}, is a constant with a high accuracy (its dependence on temperature, pressure, salinity, etc. is negligible), therefore (11) can be reduced to an equation for the volumetric water content, ε_w:

$$\frac{\partial \varepsilon_w}{\partial t} + \operatorname{div}(\varepsilon_w \mathbf{v}_w) = -\frac{S_w(\varepsilon_w, T)}{\rho_w^{in}}. \tag{12}$$

The solid phase is assumed to be rigid which means that $\mathbf{v}_s = 0$. Additionally, no diffusive transport occurs in the solid phase and only a single reactive species, sulfur, is considered so that $(\omega_s)_1 \equiv \omega_s$. The balance equation for the sulfur concentration, ω_s, is

$$\rho_s \frac{\partial \omega_s}{\partial t} = -S_s(\omega_o, \omega_s, T), \tag{13}$$

where $S_s(\omega_o, \omega_s, T)$ is the rate of consumption of the reactant in the solid phase.

3. Water evaporation and condensation in porous media.

The rate of vapour production, $S_v(\varepsilon_w, T)$, is equal to the rate of water depletion, $S_w(\varepsilon_w, T)$ allowing these functions to be specified. The quantity of water vapour in a gas phase is usually characterized by the ***humidity***, h, which is the ratio of vapour density to the saturated vapour density at the particular pressure and temperature:

$$h \equiv \frac{\rho_v^{in}}{(\rho_v^{in})_{sat}} = \frac{\rho_g \omega_v R(T + \Theta)}{\varepsilon_g \mu_v P_v(T)}, \tag{14}$$

where $R = 8.314\ \mathrm{m^2\,kg\,K^{-1}s^{-2}\,mol^{-1}}$ is the universal gas constant, T is the temperature in Celsius, $\mu_v = 18.016\cdot 10^{-3}\ \mathrm{kg\,mol^{-1}}$ is molecular mass of water vapour and $P_v(T)$ is the equilibrium saturated vapour pressure as a function of temperature (see Table 1 and Fig. 4).

Table 1. Saturated vapour pressure versus temperature.

$T(°C)$	$P(Pa)$	$T(°C)$	$P(Pa)$	$T(°C)$	$P(Pa)$
0	611.29	20	2338.8	40	7381.4
1	657.16	21	2487.7	41	7784.0
2	706.05	22	2644.7	42	8205.4
3	758.13	23	2810.4	43	8646.3
4	813.59	24	2985.0	44	9107.5
5	872.6	25	3169.0	45	9589.8
6	935.37	26	3362.9	46	10094.0
7	1002.1	27	3567.0	47	10620.0
8	1073.0	28	3781.8	48	11171.0
9	1148.2	29	4007.8	49	11745.0
10	1228.1	30	4245.5	50	12344.0
11	1312.9	31	4495.3	51	12970.0
12	1402.7	32	4757.8	52	13623.0
13	1497.9	33	5033.5	53	14303.0
14	1598.8	34	5322.9	54	15012.0
15	1705.6	35	5626.7	55	15752.0
16	1818.5	36	5945.3	56	16522.0
17	1938.0	37	6279.5	57	17324.0
18	2064.4	38	6629.8	58	18159.0
19	2197.8	39	6996.9	59	19028.0

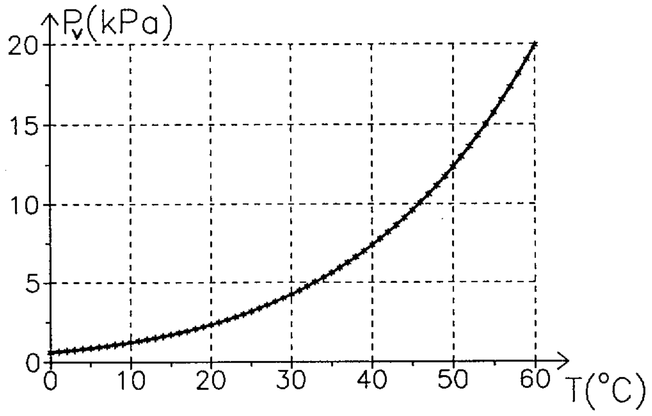


Fig. 4. Saturated vapour pressure as a function of temperature (see Table 1).

The ideal gas law has been used in the formula (14) for water vapour at saturation, i.e., at 100% humidity: $p_v^{in} = \frac{\rho_v^{in}}{\mu_v} R(T+\Theta)$.

The humidity in porous media, in turn, can be represented through the temperature, T, and the ***pressure head***, ψ, by a simple formula (*Campbell*, 1977):

$$h = \exp\left[\frac{\mu_v g \psi}{R(T+\Theta)}\right]. \tag{15}$$

Combining (14) and (15) and using (2) one can obtain

$$\rho_g \omega_v = \frac{(1-\varepsilon_s-\varepsilon_w)\mu_v P_v(T)}{R(T+\Theta)} \exp\left[\frac{\mu_v g \psi}{R(T+\Theta)}\right]. \tag{16}$$

This means that the vapor density can be expressed algebraically through the other field variables, temperature, pressure head and volumetric water content (solid volume fraction, ε_s, is assumed constant). In other words, it means that the vapor in unsaturated pore space is always at local equilibrium with water due to the relatively fast process of diffusion relaxation (characteristic time scale of the relaxation can be readily estimated to be less than $5 \cdot 10^{-2}\,\mathrm{s}$). However, vapour density can be unstationary on larger temporal scales (of order $1\,\mathrm{s}$ and greater) and can vary in space.

Inasmuch as vapour density is presented by formula (16), one can invert the mass balance equation for vapour and consider it as a definition of the source function $S_w(\varepsilon_w, T)$:

$$S_w(\varepsilon_w, T) = \frac{\partial \rho_g \omega_v}{\partial t} + \mathrm{div}\left[\rho_g \omega_v \mathrm{v}_g - D_v \nabla(\rho_g \omega_v)\right]. \tag{17}$$

4. Models of source terms for sulfur depletion.

The depletion of pyrite is assumed to occur by way of a single reaction, described by the rate formula $S_s(\omega_o,\omega_s,T) = S_o(\omega_o,\omega_s,T)/\beta_g$, where $S_o(\omega_o,\omega_s,T)$ is the rate of consumption of oxygen and β_g is the mass of oxygen consumed per mass of sulfur in the oxidation reaction.

There are several expressions which have been used for the ***intrinsic oxidation rate (IOR)***, $S_o(\omega_o,\omega_s,T)$. Essentially, they are based on two main models:

The monod model (MM-model):

$$S_o(\omega_o,\omega_s,T) = S_{\max} A(T) \exp\left[-\frac{E_a}{R(T+\Theta)}\right]\left(\frac{\omega_o}{\Omega_o}\frac{\sigma_1+1}{\sigma_1+\omega_o/\Omega_o}\right)\left(\frac{\omega_s}{\Omega_s}\frac{\sigma_2+1}{\sigma_2+\omega_s/\Omega_s}\right), \tag{19}$$

where $S_{\max}$ is the maximum value of IOR; σ_1, σ_2 are empirical constants; Ω_o and Ω_s are the initial oxygen and sulfur mass fractions, respectively (Ω_o coinsides with the oxygen mass fraction at mean ambient conditions in atmosphere); E_a is the ***activation energy*** ($\mathrm{J\,mole^{-1}}$). The factor $A(T)$ is a smooth function of temperature equalling unity for $T < T_{sick}$ and monotonically decreases to zero for $T_{sick} \le T \le T_{kill}$, where T_{sick} is the temperature at which catalytic activity of microorganisms begins to diminish and T_{kill} is a temperature at which microorganisms cease to be effective as catalysts. Qualitatively this is depicted in Fig. 5a.

The bilinear model (LL-model) is fairly simple one:

$$S_o(\omega_o,\omega_s,T) = S_{\max} A(T) \exp\left[-\frac{E_a}{R(T+\Theta)}\right]\frac{\omega_o}{\Omega_o}\frac{\omega_s}{\Omega_s}. \tag{20}$$

A sketch of function $S_o(\omega_o,\Omega_s,T)$ versus ω_o at fixed arguments $\omega_s = \Omega_s$ and $T < T_{sick}$ is depicted in Fig. 5b for both abovementioned models. Qualitatively the same functions describe the dependencies of $S_o(\Omega_o,\omega_s,T)$ on the second argument, ω_s, at fixed other arguments $\omega_o = \Omega_o$ and $T < T_{sick}$.

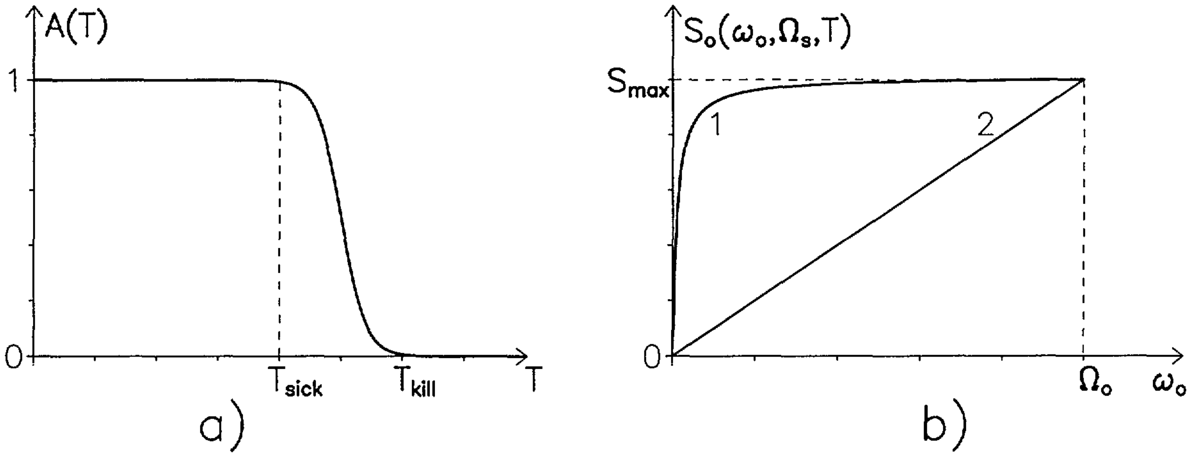


Fig. 5. a) A sketch of the function $A(T)$. b) A sketch of the functions $S_o(\omega_o,\Omega_s,T)$ for $T < T_{sick}$ and $E_a = 0$: 1 – monod model, 2 – bilinear model.

In addition to these MM- and LL-models two other models are also possible, ML- and LM-models, which are, in essence, combinations of the monod (M) model for the oxygen and linear (L) model for sulfur and vice versa.

5. Thermal conductivity.

Now we consider the equation of energy balance, which reduces to the equation of heat transport. It could be readily derived for the elementary volume of porous medium comprising all phases, gaseous, liquid and solid, by summation of particular heat equations for separate phases. Assuming that all phases are locally in thermodynamic equilibrium and have the same temperature, one can obtain following to (*Nield* and *Bejan*, 1999):

$$(\rho_g c_g + \rho_w c_w + \rho_s c_s)\frac{\partial T}{\partial t} + (\rho_g c_g \mathbf{v}_g + \rho_w c_w \mathbf{v}_w)\nabla T =$$

$$\mathrm{div}\left[(\kappa_g(T) + \kappa_w(T) + \kappa_s(T))\nabla T\right] + \beta_h S_s(\omega_o, \omega_s, T) - \beta_w S_w(\varepsilon_w, T), \qquad (21)$$

where c_α is the ***specific heat capacity*** of the α-phase (gas, water or solid) at a constant pressure, $\kappa_\alpha(T)$ is the ***coefficient of thermal conductivity*** of the corresponding phase (which in general is a function of temperature), β_h is the ***heat of reaction per mass of sulfur*** associated with the oxidation reaction, β_w is the ***latent heat of vaporisation per mass of water***. The thermal conductivity of gas (air) and water as functions of temperature are presented in Table 2 and Fig. 6.

Table 2. Thermal conductivity of air and water as functions of temperature.

T(°C)	0	10	20	30	40	50	60
κ_g(W °C^{-1}m^{-1})	0.0241	0.0248	0.0254	0.0262	0.0269	0.0276	0.0284
κ_w(W °C^{-1}m^{-1})	0.561	0.58	0.5984	0.6154	0.6305	0.6435	0.6543

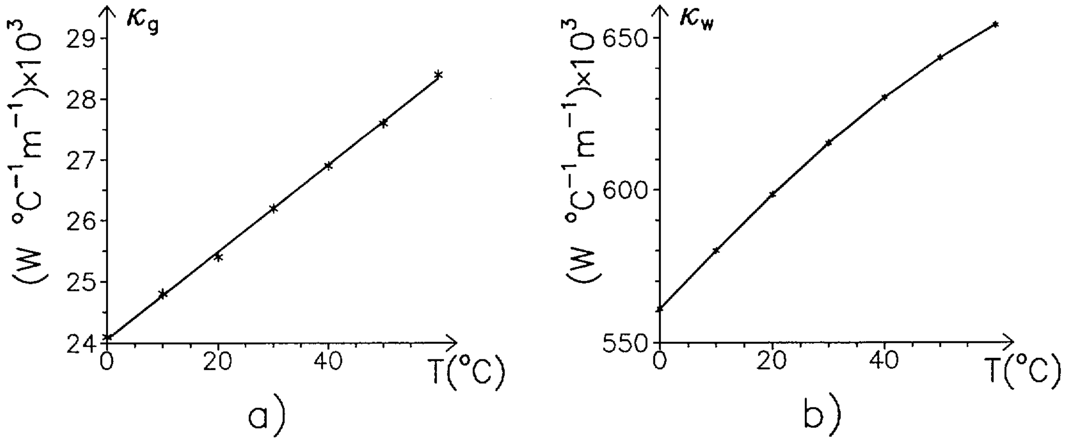


Fig. 6. Thermal conductivity of air (a) and water (b) as functions of temperature.

In contrast, the thermal conductivity of a solid phase is practically constant within the temperature range from 0 to 60°C and is approximately equal to

$\kappa_s = 1.5$ W °C^{-1} m^{-1} [depending on the composition of solid phase and ranges from 0.71 to 3.31 W °C^{-1} m^{-1} (*Ritchie*, 1994)].

In Table 3 and Fig. 7, the heat of vaporisation of water versus temperature is presented.

Table 3. The heat of vaporisation of water (per unit mass) versus temperature.

T (°C)	0	25	40	60
$\beta_w \times 10^{-6}$ (J · kg^{-1})	2.503	2.444	2.408	2.36

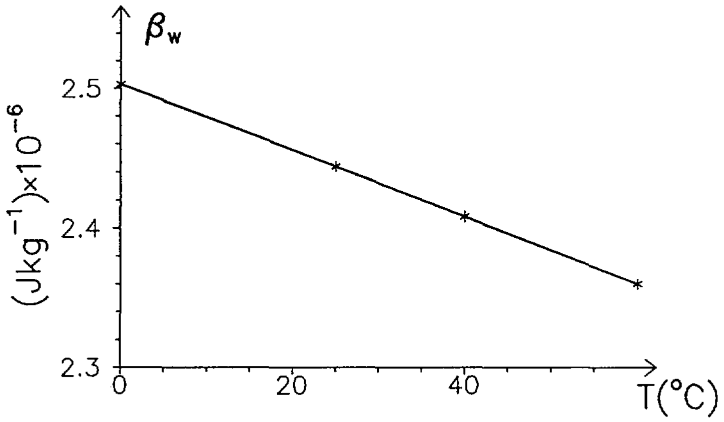


Fig. 7. The heat of vaporisation of water versus temperature (see Table 3).

6. Darcy's law for gas flow.

Gas flow in porous media strongly depends on the degree of water saturation. When the degree of water saturation is relatively small, $s \le 0.8$, the gas phase is continuous and can flow freely through the porous medium. However, when the degree of water saturation is large enough, $s \ge 0.9$, the gas phase becomes disconnected and occluded (*Fredlund* and *Rahardjo*, 1993). In this case, it is assumed that the average advective gas velocity is equal to zero ($\mathbf{v}_g = 0$), but that gas diffusion still occurs through the pore-water. There is no sharp threshold between these two limiting cases, and gas motion is fairly complex in the transition range, $0.8 \le s \le 0.9$. However, it is assumed, for simplicity, that the boundary between free and diffusive motions is sharp and occurs at $s_c = 0.85$.

At a small degree of water saturation, $s \le 0.85$, gas flow through the porous media is described by Darcy's law (*Nield* and *Bejan*, 1999):

$$\mathbf{v}_g = -\frac{K_{in} k_g(s)}{\varepsilon_g \rho_g^{in} \nu_g} \left(\nabla p_g^{in} + \rho_g^{in} g \nabla z \right). \tag{22}$$

Here K_{in} (in m^2) is the ***intrinsic coefficient of medium permeability*** at zero degree of water saturation (i.e., for completely dry medium). It is determined only by the intrinsic structure of the medium and does not depend on the nature of the fluid. Its values are given in the Table 5 at the end of the Report. The other parameter, $k_g(s)$, is the ***relative coefficient of permeability*** of unsaturated medium with respect to gas phase, and depends on the degree of water saturation, s, and can be approxi-mated by the Brooks and Corey formula [see (*Fredlund* and *Rahardjo*, 1993)]:

$$k_g(s) = (1-s)^2 (1 - s^{1+2/\lambda}), \tag{23}$$

where $\lambda \approx 4.17$ is a fitting parameter. This dependence is shown in Fig. 8.

Further, $\nu_g(T)$ is the kinematic viscosity of the gas phase (air) which is temperature dependent (see Table 4 and Fig. 9); g is the acceleration due to gravity; p_g^{in} is the ***total gas pressure***: $p_g^{in} = \sum_{i=1}^{N_g} \left(p_g^{in}\right)_i$, and $\left(p_g^{in}\right)_i$ is the ***partial gas pressure of the each gas component***. It is assumed that the ideal gas law applies for the component i

$$\left(p_g^{in}\right)_i = \frac{R}{\mu_i}\left(\rho_g^{in}\right)_i (T+\Theta), \qquad i=1,\ \dots\ N_g, \tag{24}$$

where R is the universal gas constant, μ_i *is* a ***molecular weight of the component*** i (in $\mathrm{kg\,mol^{-1}}$) and the temperature, T, is measured in degrees Celsius. By summation over i we get

$$p_g^{in} = \rho_g^{in}(T+\Theta)R\sum_{i=1}^{N_g}\frac{(\omega_g)_i}{\mu_i}. \tag{25}$$

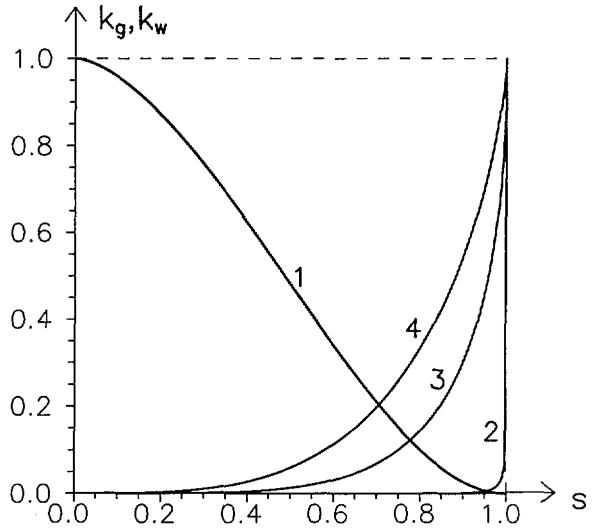


Fig. 8. Curve 1: dependence of the coefficient of relative permeability of unsaturated medium with respect to gas phase, $k_g(s)$, on the degree of water saturation, s. Curves 2, 3, 4: analogous dependences of the coefficient of relative hydraulic permeability with respect to water phase, k_w, for different values of parameter n [see formula (30) below]: 2 – $n=1.1$ ($m=0.091$); 3 – $n=2.0$ ($m=0.5$); 4 – $n=3.5$ ($m=0.714$).

Table 4. Dependencies of the kinematic viscosities of air, $\nu_g(T)$, and water, $\nu_w(T)$, on the temperature (Batchelor, 1970).

T (°C)	0	5	10	15	20	25	30	40	50	60
$\nu_g \cdot 10^5 (m^2 s^{-1})$	1.32		1.41	1.45	1.5		1.6	1.69		1.88
$\nu_w \cdot 10^6 (m^2 s^{-1})$	1.787	1.514	1.304	1.138	1.004	0.894	0.802	0.659	0.554	0.475

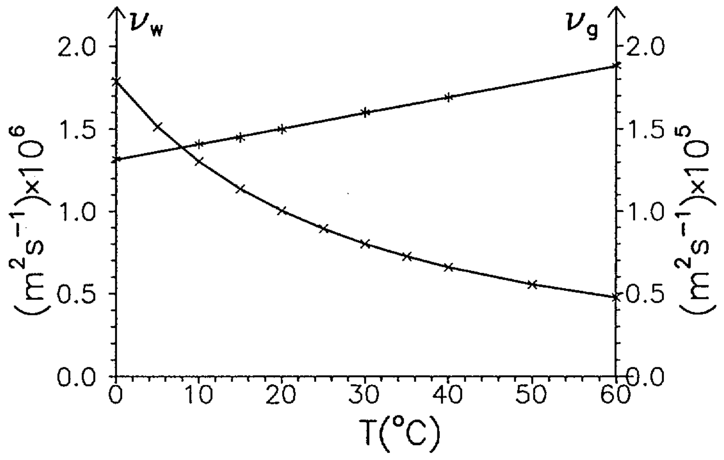


Fig. 9. Dependencies of the kinematic viscosity of air, $v_g(T)$, (asterisks) and water, $v_w(T)$, (crosses) on the temperature (see Table 4).

In many cases the gas density, ρ_g^{in}, can be considered as a constant, which leads to some simplification. Similarly, the last term in equation (22), $\rho_g^{in} g \nabla z$, can often be omitted due to its small relative magnitude with respect to the previous term, ∇p_g^{in}, representing the gradient of gas pressure. However, whenever convective processes become important, neither can the gas density be considered as a constant, nor can the gradient of the gravitational pressure, $\rho_g^{in} g \nabla z$, be neglected. More detail about the conditions of convection and approximations used are given by *Nield* and *Bejan* (1999).

7. Richards' equation.

For the liquid phase (water motion) Darcy's law has a similar form to gas flow (*Fredlund* and *Rahardjo*, 1993):

$$\mathbf{v}_w = -\frac{g K_{in} k_w(s)}{\varepsilon_w v_w(T)} \nabla(\psi + z). \tag{26}$$

Here K_{in} is the same as the intrinsic coefficient of medium permeability given above; $k_w(s)$ is the ***coefficient of relative water (or hydraulic) permeability*** of unsaturated media (its dependence on s is discussed below); $v_w(T)$ is the ***coefficient of the kinematic water viscosity*** (its dependence on the temperature is reflected in the Table 4 and in the Fig. 9); $\psi \equiv \frac{p_w^{in}}{\rho_w^{in} g}$ is the ***pressure head*** and z is the ***gravitational (or the elevation) head*** which is equal to the elevation from some arbitrary reference level.

Substituting (26) into equation (12) leads to the Richards' equation (*Richards*, 1931; *Miyazaki*, 1993):

$$\frac{\partial \varepsilon_w}{\partial t} - gK_{in}\mathrm{div}\left[\frac{k_w(\varepsilon_w)}{v_w(T)}\nabla(\psi + z)\right] = -\frac{S_w(\varepsilon_w, T)}{\rho_w^{in}}. \tag{27}$$

To complete the set of equations, two additional relations must be added:

(a) the relation between the volumetric water content, ε_w, and the pressure head, ψ, (the so-called ***water retention curve***); and

(b) the relation between the relative hydraulic permeability, k_w, and the pressure head, ψ.

There are several different formulations which can be used for these relationships. One of them is the commonly used relationship between the degree of water saturation, s, (or volumetric water content, ε_w) and the pressure head, ψ, which is based on the Van Genuchten formula (*Van Genuchten*, 1980):

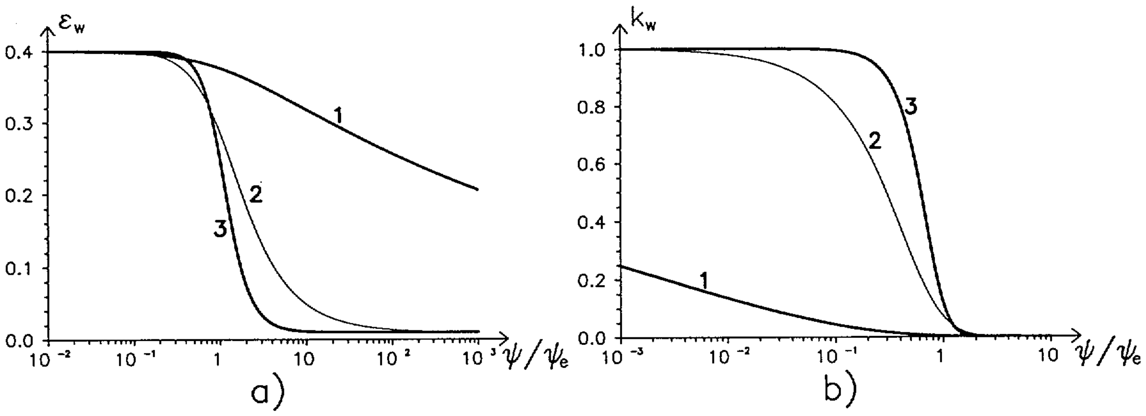
$$s \equiv \frac{\varepsilon_w}{1-\varepsilon_s} = \frac{1}{\left[1+\left(\psi/\psi_e\right)^n\right]^m}, \tag{28}$$

where ψ_e is some characteristic value of head (an empirical parameter related to the mean pore size) and, in general, exponents m and n are also empirical parameters. Sometimes (fairly often) the following relationship between these parameters is used just for simplicity: $m = 1 - 1/n$, where n is a parameter related to the pore-size distribution. In Fig. 10a the dependence of ε_w on ψ is depicted for different values of n.

The relative hydraulic permeability as a function of pressure head is often described by Mualem's formula (*Mualem*, 1976):

$$k_w = \frac{\left\{1-(\psi/\psi_e)^{n-1}\left[1+(\psi/\psi_e)^n\right]^{-m}\right\}^2}{\left[1+(\psi/\psi_e)^n\right]^{m/2}}. \tag{29}$$

This plotted in Fig. 10b.



a) b)

Fig. 10. a) Dependence of volumetric water content ε_w on pressure head ψ for different values of n : 1 – n = 1.1 (m = 0.091); 2 – n = 2.0 (m = 0.5); 3 – n = 3.5 (m = 0.714). b) Dependence of relative hydraulic permeability k_w on pressure head ψ for the same values of n.

Combining the last two equations leads to the dependence of relative coefficient of water permeability, k_w, on the degree of water saturation, s, (which in turn depends on the volumetric water content in the medium):

$$k_w(s) = s^{1/2}\left[1-\left(1-s^{1/m}\right)^m\right]^2. \tag{30}$$

This dependence is depicted in Fig. 8 for three different values of m.

The basic set of equations is now complete and we shall present in the Appendix the collection of all equations in the form convenient for numerical computations.

8. Static equilibrium gas conditions.

It is convenient to remove the hydrostatic terms in the gas pressure and to solve for the pressure perturbation relative to hydrostatic equilibrium. To this end, let T_0 be the ambient temperature in Celsius assumed to be constant in space and time and $\left(\Omega_g\right)_i$ is the concentration of the gas components at $t = 0$ which is supposed to be equal to that in the ambient space at all time.

The total gas pressure can be represented as the sum

$$p_g^{in}(\mathbf{r},t) = p_0 + p_{eq}(z) + \tilde{p}(\mathbf{r},t), \tag{31}$$

where p_0 is some constant value, $p_{eq}(z)$ is the relative gas pressure at hydrostatic equilibrium and $\tilde{p}(\mathbf{r},t)$ is the gas pressure perturbation relative to equilibrium (with $\tilde{p}(\mathbf{r},0)=0$, $\mathbf{r}$ is the spatial radius-vector). The same formula is also valid for the gas density:

$$\rho_g^{in}(\mathbf{r},t)=\rho_{eq}(z)+\tilde{\rho}(\mathbf{r},t) \tag{32}$$

with $\tilde{\rho}(\mathbf{r},0)=0$.

The static equilibrium relative gas pressure $p_{eq}(z)$ is related to the ambient static equilibrium gas density $\rho_{eq}(z)$ by

$$\frac{dp_{eq}(z)}{dz}=-g\rho_{eq}(z). \tag{33}$$

This identity follows from equation (26) assuming steady state and a zero flux boundary condition applied at the lower surface. The equation can be rewritten in the form, taking into account the ideal gas law:

$$\frac{dp_{eq}(z)}{dz}=-g\frac{p_0+p_{eq}(z)}{R(T_0+\Theta)\Sigma}, \tag{34}$$

where $\Sigma=\sum_{i=1}^{N_g}\frac{(\Omega_g)_i}{\mu_i}$. Then, denoting $p_{eq}(0)=0$ the usual barometric formula is obtained

$$p_{eq}(z)=p_0\left(e^{-gz/R(T_0+\Theta)\Sigma}-1\right). \tag{35}$$

It follows from equation (35) and the ideal gas law (25) that the static equilibrium gas density is

$$\rho_{eq}(z) = \rho_0 e^{-gz/R(T_0+\Theta)\Sigma}, \qquad \text{where} \qquad \rho_0 = \frac{p_0}{R(T_0+\Theta)\Sigma}. \tag{36}$$

These two last formulae represent the equilibrium static distributions of the main gas characteristics, pressure and density, as functions of height.

9. Boundary and initial conditions.

Let Γ_a denote the dump–atmosphere interface and Γ_b denote the dump–base interface (see Fig. 1). Let $\mathbf{n}$ denote the unit outward normal vector to the entire boundary Γ which is the closure of $\Gamma_a \cup \Gamma_b$. The following boundary conditions are then applied.

At the upper boundary $\left(\mathbf{r} \in \Gamma_a, \quad t \geq 0\right)$:

$$\omega_o(\mathbf{r}) = \Omega_o, \qquad \omega_v(\mathbf{r}) = \Omega_v, \qquad T(\mathbf{r}) = T_0, \tag{37}$$

and at the bottom boundary $\left(\mathbf{r} \in \Gamma_b, \quad t \geq 0\right)$:

$$(\mathbf{n}, \nabla\omega_o) = 0, \qquad (\mathbf{n}, \nabla\omega_v) = 0, \qquad a(T - T_b) + b(\mathbf{n}, \nabla T) = 0, \tag{38}$$

where Ω_o, Ω_v are constants (see Table 5 below), T_b is the tempera-ture at the bottom of the dump, a and b are weight coefficients: $b = 0$ corres-ponds to the fixed temperature at the bottom (Dirichlet boundary condition for the temperature); $a = 0$ corresponds to zero heat flux at the bottom (Neumann boundary condition for the temperature gradient); and the general case, $a \neq 0,\ b \neq 0$, gives a mixed type boundary condition when a heat flux at the boundary is not zero but depends on the ambient temperature. The second condition (38) is used when water is draining heat from the base of the dump.

This is a good approximation when advective water transport is dominant across the boundary.

The boundary conditions for the gas pressure are given by

$$\begin{aligned} p_g^{in} &= p_0 + p_{eq}(z) + (1 - e^{-t/\tau_u})\tilde{p}_u^{in}(\mathbf{r},t) \qquad \mathbf{r} \in \Gamma_a, \qquad t > 0, \\ p_g^{in} &= p_0 + p_{eq}(z) + (1 - e^{-t/\tau_l})\tilde{p}_l^{in}(\mathbf{r},t) \qquad \mathbf{r} \in \Gamma_b, \qquad t > 0, \end{aligned} \tag{39}$$

where $\tilde{p}_u^{in}(\mathbf{r},t)$, $\tilde{p}_l^{in}(\mathbf{r},t)$ are the prescribed gas pressure perturbations at the upper and lower boundaries, respectively.

For these boundary conditions to be consistent with the initial conditions, the terms $(1 - e^{-t/\tau_u})$ and $(1 - e^{-t/\tau_l})$ are included artificially to allow the forcing pressure perturbations to be increased from zero in the initial period of the numerical simulations. The parameters τ_u and τ_l are arbitrary time parameters which are selected to effect the required pressure in a sufficiently short time period.

The initial conditions at $t = 0$ for the main variables within the bulk of the dump, $\mathbf{r} \in V$, are

$$\begin{aligned} &\omega_o = \Omega_o, \qquad \omega_v = \Omega_v, \qquad \omega_s = \Omega_s, \qquad T = T_0, \\ &\varepsilon_w = E_w, \qquad \psi = \psi_0(z), \qquad p_g^{in} = p_0 + p_{eq}(z), \qquad \rho_g^{in} = \rho_{eq}(z). \end{aligned} \tag{40}$$

All these constant quantities are presented in the Table 5 below. The initial concentration of the nitrogen, Ω_n, related with the initial concentrations of oxygen, Ω_o, and water vapour, Ω_v: $\Omega_n = 1 - \Omega_o - \Omega_v$. In a particular case of zero water infiltration rate through the dump, function $\psi_0(z) \equiv -z$, while in the general case of arbitrary infiltration rate it is a more complex function.

10. Global quantities.

There are at least two important quantities that are of special interest in monitoring of the progress of oxidation in the dump.

The first quantity is called the ***fraction of sulfide sulfur oxidised***, $F_s(t)$, and is a measure of the total sulfide mass depleted in the dump at any given time:

$$F_s(t) = \frac{\int\limits_V \rho_s(\Omega_s - \omega_s)d\mathbf{r}}{\int\limits_V \rho_s \Omega_s d\mathbf{r}} \tag{41}$$

The second quantity is the ***global or overall oxidation rate (GOR) of sulfur*** ($\mathrm{kg\ m^{-2}\ s^{-1}}$). It represents the rate of oxidation of reactive sulfur in a dump vertical column of unit lateral area per second, and is defined as:

$$GOR(t) \equiv -\frac{\partial}{\partial t}\int\limits_0^H \rho_s \omega_s dz = \int\limits_0^H S^s(\omega_o^g, \omega_s^s, T)dz\,. \tag{42}$$

All these quantities can be determined and plotted in a process of numerical solution of the full set of equations. These values are directly related to the production rate of sulfate ($\mathrm{SO_4}$) in the heap. According to the stoichiometric relationship:

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

the rate of sulfate production is three times greater than the *GOR* (*Ritchie*, 1994).

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12. Glossary of some technical terms.

Activation energy, E_a ($\mathrm{J\,mol^{-1}}$), – a parameter in the Arrehenius form of the temperature dependence of a chemical or biological reaction rate.

Advection – fluid flow driven by a pressure gradient.

Air coefficient of permeability, $k_g(s)$ ($\mathrm{m\,s^{-1}}$), – a coefficient that appears in Darcy's law for gas phase in porous media [(see (18)]. It depends on the degree of water saturation of the medium, s, or on the volumetric water content, ε_w.

Bulk density, ρ_α ($\mathrm{kg\,m^{-3}}$), – the mass per unit volume of piled material. The index $\alpha = g, w, s$ denotes gas, water or solid phases, respectively.

Coefficient of thermal conductivity, κ_α ($\mathrm{J\,s^{-1}\,C^{-1}\,m^{-1}}$), – the ratio of diffusive heat flux to the temperature gradient.

Concentration of component i **in the** α**-phase** (e. g., concentration of oxygen in the air) is the ratio $\omega_i^\alpha = \rho_i^\alpha / \rho^\alpha$, ($i = 1, \dots N_\alpha$), where the superscript α denotes the phase and the subscript i identifies the component within the phase. In essence it is the mass fraction of component i in the α-phase.

Convection – a special case of advection where the pressure gradient is caused by a temperature gradient.

Diffusion – fluid flow driven by a concentration gradient. It is a particular case of the transport phenomenon.

Diffusion coefficient, $\hat{\mathrm{D}}_\alpha$ ($\mathrm{m\,s^{-1}}$), – the ratio of the diffusive flux of any species (oxygen, nitrogen, etc.) to the concentration gradient.

Flux – the quantity crossing unit area per unit time. The quantity can be an entity such as water, heat, mass, etc.

Fractional volume of species, ε_α, – the fraction of the total volume taken up by the species α. The bulk density of the species α is related to its intrinsic density, ρ^α, by the formula $\rho_\alpha = \varepsilon_\alpha \rho^\alpha$.

Global oxidation – the global sulfur oxidation rate integrated over the time from pile construction until the time of interest. It is the total quantity of sulfide sulfur oxidised up to the time of interest. It is frequently expressed as a fraction of the initial contained sulfide sulfur.

Global (or overall) oxidation rate (GOR) – the oxygen consumption rate integrated over those spatial variables over which the consumption rate is assumed to vary in the pile.

Global sulfur oxidation rate – the sulfide sulfur oxidation rate integrated over those spatial variables over which the sulfur oxidation rate is assumed to vary in the pile.

Gravitational (elevation) head, $z\ (\mathrm{m})$, – elevation of the point relative to some arbitrary reference level.

Heat of reaction per mass of sulfur, $\beta_h \approx 2.19 \cdot 10^7\ \mathrm{J\,kg^{-1}}$, – amount of heat released in the process of oxidation of unit mass of pyrite.

Humidity, h (dimensionless), – is the ratio of vapour density to the saturated vapour density at the particular pressure and temperature: $h \equiv \rho_v^g / \rho_{vs}^g$.

Infiltration – water percolation in a soil or in waste rock dumps (usually from rainfall).

Infiltration rate $(\mathrm{m^3\,m^{-2}\,s^{-1} \equiv ms^{-1}})$ – the bulk rate of flow of water infiltrating the pile through the unit area in a unit time.

Intrinsic coefficient of medium permeability, $K_i\ (\mathrm{m^2})$, – a coefficient that appears in Darcy's law for fluid flow in porous media. It is determined only by the intrinsic structure of the medium and does not depend on the nature of the fluid. For the gas phase it is the ratio of gas flux with respect to pressure gradient in *completely dry medium*, whilst for water phase it is the ratio of water flux with respect to pressure gradient in *completely water saturated medium.*

Intrinsic oxidation rate (IOR) – the rate of consumption of oxygen by sulfidic material at a point in a pile. The IOR can be a function of a number of parameters but for consistency it should be a function only of the variables appearing in the mathematical model used to describe oxidation in a pile of sulfidic material. It is assumed to be a property of bulk sulfidic material. The sulfide sulfur oxidation rate is related to the IOR by the stoichiometry relationship of sulfide oxidation.

Latent heat of vaporisation of water, $\beta_w \approx 2.45 \cdot 10^6$ J kg^{-1}, – amount of heat released in the process of evaporation of unit mass of water.

Saturated water content, ε_w^s (dimensionless), – the volumetric water content of completely water saturated porous medium when all void space of the medium is filled by water.

Specific heat, c_α (m^2 s^{-2} C^{-1}), – the quantity of heat required to raise unit mass of the species α through unit temperature.

Table 5. Parameter definition and characteristic values
(angular brackets stand for some mean values).

Quantity	Definition	Dimensions	Value/range
c_g	specific heat of air	m^2 s^{-2} °C^{-1}	$1.01 \cdot 10^3$
c_s	specific heat of solid phase	m^2 s^{-2} °C^{-1}	866
c_w	specific heat of water	m^2 s^{-2} °C^{-1}	$4.18 \cdot 10^3$
g	acceleration due to gravity	m s^{-2}	9.8
m	free parameter (in general) of the Van Genuchten formula [see (28)]	dimensionless	$m = 1 - 1/n$ in our study
n	free parameter of the Van Genuchten formula [see (28)]	dimensionless	$1.1 \div 3.5$
$p^g_{u,l}$	gas pressure perturbations applied at the upper (u) and lower (l) heap boundaries [see (39)]	Pa	$-10^2 \div +10^3$
s_c	conditional threshold value of the degree of water saturation: at $s \le s_c$, the gas phase in porous media is assumed continuous and free, while at $s > s_c$, the gas phase is assumed occluded	dimensionless	0.85 in our study
$\langle \hat{D}_o \rangle$	coefficient of oxygen diffusion in air	m s^{-1}	$2.0 \cdot 10^{-5}$
$\langle \hat{D}_v \rangle$	coefficient of vapour diffusion in air	m s^{-1}	$2.5 \cdot 10^{-5}$
E_a	activation energy	J mol^{-1}	$0 \div 7 \cdot 10^4$
E_w	initial water volume fraction	dimensionless	$0.1 \div 0.4$
H	height of a dump	m	$20 \div 70$
K_i	intrinsic coefficient of medium permeability	m^2	$10^{-20} \div 10^{-7}$
R	universal gas constant	J °C^{-1} mol^{-1}	8.314
$S_{\max}$	maximum rate of sulfur depletion due to oxygen, see (19)	kg(S) m^{-3} s^{-1}	10^{-6}
T_b	temperature at the bottom of a dump	°C	$5 \div 15$
T_{kill}	temperature at which reactions cease to be catalysed, see Fig. 5	°C	60
T_{sick}	temperature at which catalysed reactions begin to retard, see Fig. 5	°C	40
T_0	ambient temperature	°C	$0 \div 40$
β_g	mass of oxygen used per mass of sulfur in the oxidation reaction	dimensionless	1.746
β_h	heat of reaction per mass of sulfur associated with oxidation reaction [see (21)]	J kg^{-1} (S)	$2.19 \cdot 10^7$
β_w	latent heat of vaporisation per mass of water [see (21)]	J kg^{-1}	$2.45 \cdot 10^6$
ε_g	gas volume fraction in the dump material	dimensionless	$0 \div 0.4$
ε_s	solid volume fraction in the dump material	dimensionless	$0.6 \div 0.8$
ε_w	water volume fraction in the dump material	dimensionless	$0.01 \div 0.4$
$\langle \kappa_g \rangle$	coefficient of thermal conduction for air	J s^{-1} °C^{-1} m^{-1}	$2.24 \cdot 10^{-2}$

Table 5. (continuation).

Quantity	Definition	Dimensions	Value/range
$\langle \kappa_w \rangle$	coefficient of thermal conduction for water	$\mathrm{J\,s^{-1}\,{}^{o}C^{-1}m^{-1}}$	$6.2 \cdot 10^{-1}$
$\langle \kappa_s \rangle$	coefficient of thermal conduction for soil	$\mathrm{J\,s^{-1}\,{}^{o}C^{-1}m^{-1}}$	1.5
$\langle \nu^g \rangle$	kinematic viscosity of air (see Table 4)	$\mathrm{m^2\,s^{-1}}$	$1.5 \cdot 10^{-5}$
$\langle \nu^w \rangle$	kinematic viscosity of water (see Table 4)	$\mathrm{m^2\,s^{-1}}$	10^{-6}
ρ_s	bulk density of solid phase	$\mathrm{kg\,m^{-3}}$	1500
ρ_0^g	atmospheric density of gas phase	$\mathrm{kg\,m^{-3}}$	1.2
ρ^w	intrinsic density of water	$\mathrm{kg\,m^{-3}}$	1000
σ_1	intrinsic oxidation model parameter, see (15)	dimensionless	$0.01 \div 0.05$
σ_2	intrinsic oxidation model parameter, see (15)	dimensionless	$0.01 \div 0.05$
$\tau_{u,l}$	time parameters associated with the boundary gas pressures [see (39)]	s	$3.6 \cdot 10^5$
ψ_c	characteristic value of pressure head	m	$-(0.073 \div 0.26)$
Ω_o	initial mass fraction of oxygen in gas phase	dimensionless	0.22
Ω_s	initial mass fraction of sulfur in solid phase	dimensionless	0.01
Ω_v	initial mass fraction of vapour in gas phase	dimensionless	0.0065
$\left. \left\langle \frac{\delta}{\tau^2} \right\rangle \right\|_{\varepsilon_w = 0}$	mean value of the tortuosity factor in the dry material	dimensionless	0.67

Appendix: The full set of governing equations.

The full consistent set of equations, which is used in the model, is collected here for convenience.

For the gas phase:

From (4) we have the oxygen mass balance equation:

$$\frac{\partial \rho_g \omega_o}{\partial t} + \operatorname{div}\left[\rho_g \omega_o \mathbf{v}_g - D_o \nabla\left(\rho_g \omega_o\right)\right] = - S_o(\omega_o^g, \omega_s^s, T)\,. \tag{A1}$$

The vapour component of the gas phase is related to the pressure head, temperature and volumetric water content by equation (16):

$$\rho_g \omega_v = \frac{(1-\varepsilon_s - \varepsilon_w)\mu_v P_v(T)}{R(T+\Theta)} \exp\left[\frac{\mu_v g \psi}{R(T+\Theta)}\right]. \tag{A2}$$

This relationship allows to determine the source term for water depletion/production from the continuity equation (17):

$$S_w = \frac{\partial \rho_g \omega_v}{\partial t} + \operatorname{div}\left[\rho_g \omega_v \mathbf{v}_g - D_v \nabla(\rho_g \omega_v)\right]. \tag{A3}$$

For the whole gas phase it follows from (10) that

$$\frac{\partial \rho_g}{\partial t} + \operatorname{div}\left(\rho_g \mathbf{v}_g\right) = -S_o(\omega_o, \omega_s, T) + S_w \tag{A4}$$

with the additional expression (19) or (20) for the intrinsic oxidation rate, $S_o(\omega_o^g, \omega_s^s, T)$, and the expression (A3) for the water depletion/production, S_w.

Gas velocity is given in accordance with the model described in Section 6:

$$\mathbf{v}_g = \begin{cases} 0, & \text{if } \dfrac{\varepsilon_w}{1-\varepsilon_s} > 0.85; \\ -\dfrac{K_{in}(1-\varepsilon_s-\varepsilon_w)^3}{\rho_g \nu^g(T)(1-\varepsilon_s)^2}\left[1-\left(\dfrac{\varepsilon_w}{1-\varepsilon_s}\right)^{1+2/\lambda}\right]\left(\nabla\tilde{p}^g + \dfrac{\tilde{\rho}_g g}{1-\varepsilon_s-\varepsilon_w}\nabla z\right), & \text{otherwise} \end{cases} \tag{A5}$$

with the additional equation for gas pressure [equation (25)]:

$$p_g^{in} = \rho_g^{in}(T+\Theta)R\sum_{i=1}^{N_g}\frac{(\omega_g)_i}{\mu_i}. \tag{A6}$$

For the liquid phase:

The mass balance equation (11) leads to the Richards' equation (27):

$$\frac{\partial\varepsilon_w}{\partial t} - gK_{in}\mathrm{div}\left[\frac{k_w(\varepsilon_w)}{\nu_w(T)}\nabla(\psi+z)\right] = -\frac{S_w}{\rho_w^{in}} \tag{A7}$$

with the source term on the right-hand side of (A3). Additionally, empirical relationships come from Van Genuchten (28) and Mualem's (29) formulae have been used:

$$\frac{\psi}{\psi_c} = \left[\left(\frac{\varepsilon_w}{1-\varepsilon_s}\right)^{-\frac{n}{n-1}} - 1\right]^{\frac{1}{n}}, \tag{A8}$$

$$k_w(\varepsilon_w) = \left(\frac{\varepsilon_w}{1-\varepsilon_s}\right)^{\frac{1}{2}}\left\{1-\left[1-\left(\frac{\varepsilon_w}{1-\varepsilon_s}\right)^{\frac{n}{n-1}}\right]^{\frac{n-1}{n}}\right\}^2. \tag{A9}$$

Water velocity field is given by formula (26) with the help of expressions (A8) and (A9):

$$\mathbf{v}^{w} = -\frac{gK_{in}k_{w}(\varepsilon_{w})}{\varepsilon_{w}\nu_{w}(T)}\nabla[\psi(\varepsilon_{w}) + z]. \tag{A10}$$

<u>For the solid phase:</u>

The equation follows directly from equation (13):

$$\frac{\partial \omega_{s}}{\partial t} = -\frac{S_{o}(\omega_{o},\omega_{s},T)}{\rho_{s}\beta_{g}} \tag{A11}$$

with the additional expression for the intrinsic oxidation rate, $S_{o}(\omega_{o}^{g},\omega_{s}^{s},T)$, which can be described by one of the models: MM, LL, ML or LM [see equations (19), (20)].

<u>For the temperature:</u>

It is assumed that the temperature is the same locally for all phases and is given by:

$$\left(\rho_{g}c_{g} + \rho_{w}c_{w} + \rho_{s}c_{s}\right)\frac{\partial T}{\partial t} + \left(\rho_{g}c_{g}\mathbf{v}_{g} + \rho_{w}c_{w}\mathbf{v}_{w}\right)\nabla T =$$

$$\mathrm{div}\left[\left(\kappa_{g}(T) + \kappa_{w}(T) + \kappa_{s}(T)\right)\nabla T\right] + \frac{\beta_{h}}{\beta_{g}}S_{o}(\omega_{o},\omega_{s},T) - \beta_{w}S_{w}(\varepsilon_{w},T), \tag{A12}$$

with the additional expression for the intrinsic oxidation rate, $S_{o}(\omega_{o}^{g},\omega_{s}^{s},T)$ and the expression (A3) for the water depletion/production rate, S_{w}.

Given that the solid volume fraction, ε_{s}, is constant in the dump, the gas volume fraction, ε_{g}, in the dump can be evaluated using equation (2).

So, finally we have the following 6 main variables: $\omega_o, \omega_v, \omega_s, \rho_g, \varepsilon_w, T$ and a corresponding consistent set of equations for them is represented by equations (A1) – (A12).