OXYGEN TRANSPORT AND PYRITE OXIDATION IN UNSATURATED COAL-MINE SPOIL[1]

by

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Abstract. An understanding of the mechanisms of oxygen (O_2) transport in unsaturated mine spoil is necessary to design and implement effective measures to exclude O_2 from pyritic materials and to control the formation of acidic mine drainage. Partial pressure of oxygen (Po_2) in pore gas, chemistry of pore water, and temperature were measured at different depths in unsaturated spoil at two reclaimed surface coal mines in Pennsylvania. At mine 1, where spoil was loose, blocky sandstone, Po_2 changed little with depth, decreasing from 21 volume percent (vol %) at the ground surface to a minimum of about 18 vol % at 10 m depth. At mine 2, where spoil was compacted, friable shale, Po_2 decreased to less than 2 vol % at depth of about 10 m. Although pore-water chemistry and temperature data indicate that acid-forming reactions were active at both mines, the pore-gas data indicate that mechanisms for O_2 transport were different at each mine. A numerical model was developed to simulate O_2 transport and pyrite oxidation in unsaturated mine spoil. The results of the numerical simulations indicate that differences in O_2 transport at the two mines can be explained by differences in the air permeability of spoil. Po_2 changes little with depth if advective transport of O_2 dominates as at mine 1, but decreases greatly with depth if diffusive transport of O_2 dominates, as in mine 2. Model results also indicate that advective transport becomes significant if the air permeability of spoil is greater than 10^{-9} m^2, which is expected for blocky sandstone spoil. In the advective-dominant system, thermally-induced convective air flow, as a consequence of the exothermic oxidation of pyrite, supplies the O_2 to maintain high Po_2 within the deep unsaturated zone.

Additional Key Words: advection, diffusion, numerical simulation, heat transfer

Introduction

Atmospheric oxygen (O_2) is required for pyrite oxidation and the consequent formation of acidic mine drainage (AMD). Gaseous or dissolved O_2 is necessary for the direct oxidation of pyrite and for the regeneration of ferric iron (Fe^{3+}), which is an important oxidant (Singer and Stumm 1970). Hence, an understanding of the mechanisms of O_2 transport in mine spoil is necessary to design and implement effective measures to control the formation of AMD.

Pyrite oxidation takes place mainly in the unsaturated zone of mine spoil. Although infiltrating water carries some dissolved O_2 into mine spoil, gaseous transport of O_2 generally is more effective than aqueous transport of O_2 because of the low solubility and low diffusivity of O_2 in water (Watzlaf 1992).

Gaseous O_2 transport through air-filled voids in spoil involves both processes of diffusion and advection. Diffusive transport is the movement of O_2 molecules from zones of high O_2 to zones of low O_2 concentration. Steep gradients in O_2 concentration can be formed between the exterior and interior of spoil because of relatively rapid O_2 consumption by oxidation reactions and slow diffusive transport of O_2. If air permeability is low, such as in compacted, shaly spoil, diffusive transport can be the major mechanism

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of O_2 transport. However, if air permeability of spoil is high, such as in blocky sandstone spoil, advective transport of O_2 by moving air can predominate. Thermal gradients within spoil can induce the inward (lateral) flow of oxygenated air to replace outward (upward) flowing air that is warmed by the exothermic oxidation of pyrite (Harries 1969). Advective transport can also result from rapid changes in barometric pressure and from displacement of air by ground water.

Approaches to controlling the formation of AMD include minimizing the exposure of pyrite to fresh air and oxygenated or Fe^{3+}-rich waters (Kleinmann and Erickson 1986; Barton-Bridges and Robertson 1989; Watzlaf 1992). However, the processes that form AMD in unsaturated spoil are complex and involve many hydrological, chemical, and biological factors (Williams et al. 1982). Numerical models have been developed to evaluate the interactions of these factors and the generation of AMD (Cathles and Apps 1975; Jaynes et al. 1984a,b; Pantelis and Ritchie 1992).

In this study, evaluations were made on the relative importance of diffusive and advective transport of O_2 on the distribution of O_2 in coal-mine spoil and the effect of O_2 supply on the formation of AMD. Composition of pore gas, temperature, and water quality were measured at different depths in spoils at two reclaimed surface coal mines in Pennsylvania. A two-dimensional numerical model that was developed to study the relation between O_2 transport and the rate of acid generation (Guo 1993) is used to explain the observed chemical compositions of pore-gas and pore-water samples from the mines.

Field Studies of Oxygen in Mine Spoil

The availability of O_2 in mine spoil is controlled by the dynamic balance between the rate of O_2 consumption and the rate of O_2 supply. Consumption of O_2 results from pyrite oxidation, biological respiration, and other reactions. The rate at which O_2 is replenished at reaction sites is controlled largely by the air permeability, moisture content, temperature, the O_2 partial pressure (Po_2) gradient, and the strength of air convective flow within surrounding spoil. Therefore, the availability of O_2 in mine spoil can vary spatially and temporally.

Field investigations of O_2 in unsaturated spoil have been conducted at several surface coal mines in western Pennsylvania. Although active pyrite oxidation and AMD were problems at all these mines, the spatial distribution of Po_2 in pore-gas samples was extremely variable among and within the mines. Jaynes et al. (1983) reported fairly high Po_2. Po_2 in several boreholes decreased from 21 vol % at the ground surface to greater than 10 vol % at a depth of 12 m. At a second mine, Fielder (1989) reported Po_2 as high as 15 vol % down to 9.1 m; however, in adjacent spoil containing pyritic refuse, Po_2 was less than 1 vol %. At another mine, Lusardi and Erickson (1985) reported annual mean values of Po_2 as low as 1.3 vol % and as high as 10.2 vol % at a depth of 4.6 m in different boreholes. Data for two additional mines that were collected by the authors are representative of these extreme ranges and are described below.

Mine 1. Advective-Transport Dominant

Mine 1 is a reclaimed, abandoned surface coal mine on a broad hilltop (40°55′30″N, 78°22′30″W) in southern Clearfield County (Guo 1993). During 1968-85, the lower Kittanning coal was mined. The lower Kittanning coal and a rider seam with associated coaly shale were pyritic and had total sulfur concentrations of 3.8 and 5.4 weight percent (wt %), respectively. Spoil material was predominantly blocky sandstone and siltstone. Many boulder size fragments, with diameters greater than 1 m, were distributed throughout the spoil, and large voids were encountered during drilling. Seepage water in a roadcut along the western boundary of the mine was identified as AMD from the mine.

In 1989, a total of 35 boreholes (2-20 m deep) were drilled in spoil at the site. A control hole was drilled in an adjacent, unmined area. Piezometers were installed in the boreholes for measurement of the temperature in mine spoil and for ground-water sampling. Nested gas samplers were installed adjacent to the piezometers in 13 of these boreholes. Gas sampling ports were placed at depths of 0.9 m, 1.5 m, 4.6 m, 6.1 m, 9.1 m, 10.7 m, and deeper (Guo et al. 1994). Pore-gas and water sampling were conducted monthly for 1 and 2 years, respectively.

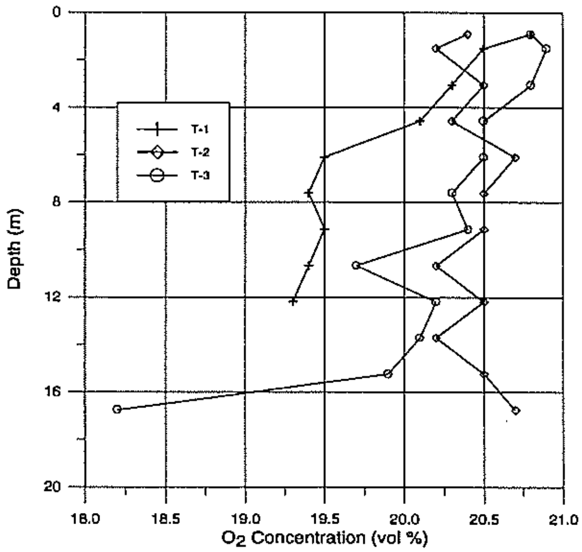

Figure 1. Concentrations O_2 in pore-gas samples from three boreholes (T-1, T-2 and T-3) in unsaturated spoil at mine 1 in Clearfield Co., PA October, 1989.

The chemistry of ground water and seepage water indicates that acid-generating reactions are ongoing at this mine. Water from a perennial seep (N1) had a median pH of 3.4 and had concentrations of sulfate, dissolved iron, dissolved manganese, and acidity, respectively, of 2,200, 45, 52 mg/L, and 290 mg/L as $CaCO_3$ (Durlin and Schaffstall 1993).

Pore-gas O_2 concentrations at mine 1 were found to exceed 18 vol % throughout the spoil during the entire year of monitoring. Several depth profiles of Po_2 are presented in Figure 1. Corresponding low concentrations of CO_2 ranged from 0.03 to 1.2 vol %. The amplitude of seasonal variations in Po_2 and Pco_2 was small.

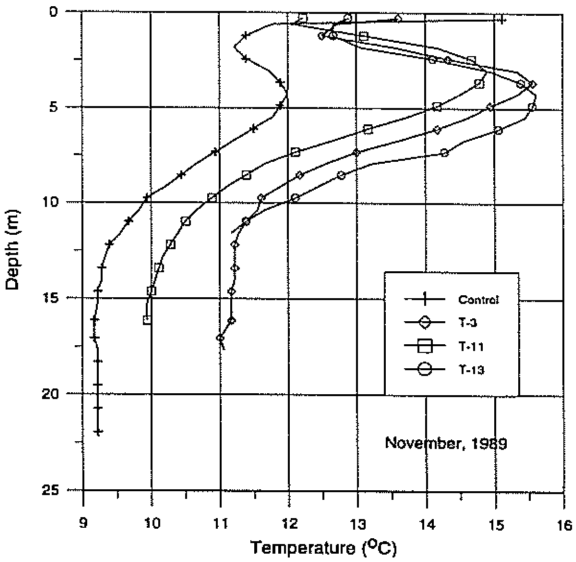

Figure 2. Temperatures in unsaturated spoil at mine 1, November, 1989. Control temperature was measured in a borehole in adjacent unmined area.

Air convection resulting from the temperature gradients induced by the exothermic pyrite-oxidation reactions is the dominant O_2 transport process at this mine (Guo and Parizek 1994). Thermal anomalies were detected in most deep boreholes during the study period. Spoil temperatures were 1-2°C higher than the background temperature measured in the control hole (Figure 2).

Mine 2. Diffusive-Transport Dominant

Mine 2 is a reclaimed surface mine on two adjoining hilltops (41°04′15″N, 79°26′45″W) in southern Clarion County (Cravotta et al. 1994a, b). During 1980-86, the lower Kittanning coal was mined. The lower Kittanning coal and a 1.2-m thick stratum of carbonaceous shale overlying the coal were pyritic, had total sulfur concentrations greater than 2.5 wt % and were laterally continuous across the mine. Spoil at this mine was friable shale with minor siltstone. Spoil fragments generally were less than 10 cm in diameter.

In 1991, a total of 12 clusters of two or more boreholes were drilled in spoil and underlying bedrock. Several clusters, or monitoring nests, included boreholes for ground-water sampling, pore-water sampling, and pore-gas sampling (Cravotta et al. 1994b). Lysimeters and gas-sampling ports were placed at depths of 1 to 1.5 m, 4 to 4.6 m, 7 to 7.6 m, and 10.7 to 11 m below the spoil surface to enable comparison of chemical concentrations in pore-water and pore-gas samples.

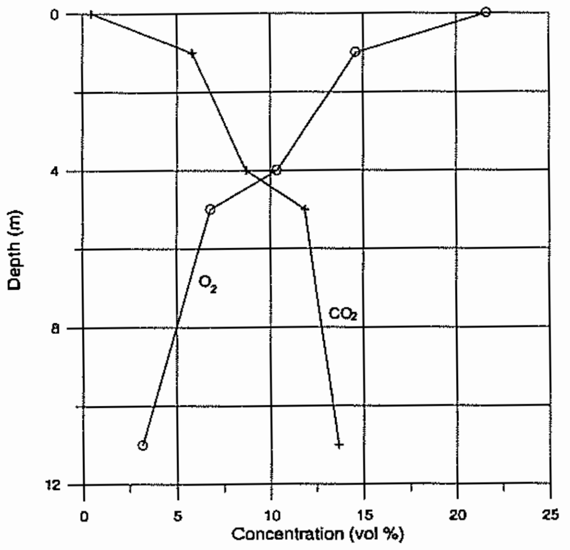

Figure 3. Mean concentrations of O_2 and CO_2 in pore-gas samples from a borehole (Nest 2) in unsaturated spoil at mine 2 in Clarion Co., PA February to December, 1992.

Ground-water samples from the spoil at mine 2 were highly mineralized, with concentrations of sulfate that exceeded 400 mg/L (Lescinsky et al. 1993). Despite this evidence of pyrite oxidation, overall ground-water quality was alkaline because of neutralization by carbonate minerals (mainly siderite) in the saturated zone (Cravotta et al. 1994b). Locally in the unsaturated zone, however, shallow pore water sampled within or near pyritic zones was acidic and had high concentrations of sulfate. For example, in December 1992, pore water sampled from a depth of 4.6 m in the northern part of the mine (nest N2) had pH of 4.0 and concentrations of sulfate, dissolved iron, and dissolved manganese of 5,000, 1.3, and 260 mg/L, respectively.

Data for pore-gas compositions at mine 2 indicate that Po_2 decreases from 21 vol % at the land surface to less than 2 vol % at 10.7 m below the surface, with corresponding increases of Pco_2 with depth (Figure 3). The increase of Pco_2 with depth resulted from the dissolution of carbonate minerals. Because the pore water in spoil is extremely mineralized and dissolved anions are dominated by sulfate, oxidation of organic matter is not considered to be an important control of O_2 and CO_2 at the mine. Cravotta et al. (1994b) concluded that pyrite oxidation rates at mine 2 were controlled by rates of O_2 diffusion and not the amount of pyrite, because concentrations of O_2 declined rapidly at shallow depths in the spoil, independent of pyrite concentrations.

Model Description

A two-dimensional numerical model was developed to investigate the distribution, transport, and reaction of O_2 in unsaturated mine spoil. This model simulates coupled heat transfer and gas flow, dispersive-advective oxygen transport, steady-state ground-water flow, and pyrite oxidation reactions (Guo 1993).

Coupled heat transfer and gas flow in mine spoil are described by the following set of equations:

$$\frac{\partial}{\partial t}(\phi_s \rho_s C_s T + \phi_l \rho_l C_l T + \phi_g \rho_g C_g T) =$$

$$\nabla \cdot (\kappa \nabla T) - \nabla \cdot (\rho_g C_g \vec{v}_g T) - \nabla \cdot (\rho_l C_l \vec{v}_l T) + SS_{energy} \tag{1}$$

$$\phi_g \frac{\partial}{\partial t}(\rho_g) = -\nabla \cdot (\rho_g \vec{v}_g) \tag{2}$$

$$\vec{v}_g = -\frac{k}{\mu_g}(\nabla P + \rho_g \vec{g}) \tag{3}$$

Equation 1 describes heat transfer through solid, liquid and gas phases in spoil; equation 2 represents gas flow through porous medium; and equation 3 is the Darcy law, which links equations 1 and 2. In these equations, ρ is the density $[ML^{-3}]$; *C*, the heat capacity $[JM^{-1}K^{-1}]$; ϕ, the volume fraction [dimensionless]; T, temperature [K]; κ, the thermal conductivity of spoil [$JL^{-1}K^{-1}T^{-1}$]; t, time [T]; SS_{energy}, the energy generation and/or consumption rates [$JT^{-1}L^{-3}$] which includes the energy released from pyrite oxidation reactions and the energy transfer due to phase changes; $\vec{v}$, the flow velocity of fluid [LT^{-1}]; g, the gravitational constant [LT^{-2}]; P, the air pressure [$ML^{-1}T^{-2}$]; k, the air permeability [L^2]; and μ, the viscosity of gas [$ML^{-1}T^{-1}$]. Subscripts s, l, and g represent solid, water and gas phases respectively.

To simplify the problem so that it can be solved numerically, several assumptions are made: (1) local thermal equilibrium between all the phases is present at all points, because the temperature difference between the phases generally disappears quickly; (2) thermal conductivity is treated as a constant because the range of temperature changes is relatively small; (3) radiation is negligible; (4) thermal dispersion is insignificant; (5) Darcy's law is valid for gas flow of relatively low velocity, as considered in this study; (6) physical properties of water and solid are constant; (7) gas density is independent of its component composition; (8) air is in equilibrium with pore water and obeys the ideal gas law; and (9) water is assumed to be saturated with respect to the local Po_2 in pore gas in accordance with Henry's law.

Transport of O_2 by dispersion-advection is mathematically described as:

$$\phi_g \frac{\partial C}{\partial t} = \nabla \cdot ([D']\nabla C) - \nabla \cdot (\vec{v}_g C) - \nabla \cdot (\vec{v}_l C) + SS_{oxygen} \qquad (4)$$

where C is the concentration of O_2 in air [ML^{-3}]; [D'] is the dispersion coefficient tensor [L^2T^{-1}]; SS_{oxygen} is the source/sink terms including all the O_2 consumed in a unit time inside a block [$MT^{-1}L^{-3}$].

Factors affecting the rate of pyrite oxidation have been expressed numerically by previous investigators using a variety of approaches, of which the shrinking core model is perhaps the most popular one used to simulate pyrite oxidation (Harries 1969; Roman et al. 1974; Madsen et al. 1975; Cathles and Apps 1975; Jaynes et al. 1984a, b). In an unreacted-core model, as used in this study, oxidation proceeds as a narrow front moving into the solid particle and solid reactant concentration remains constant inside the unreacted cores. All the pyrite is assumed to be oxidized in the ash zone outside the unreacted core. Mathematical expressions for these reaction-control mechanisms and for different particle geometry were given by Levenspiel (1972).

Combining of surface-reaction rate and reacted layer diffusion controls gives the reaction rate of a particle containing pyrite:

$$\frac{dN}{dt} = \frac{-1}{\frac{1}{3}\tau_1 N^{-\frac{2}{3}} + 2\tau_2 (N^{-\frac{1}{3}} - 1)} \qquad (5)$$

where N is the amount of unreacted pyrite in mole fraction. τ_1 and τ_2 are the time [T] for complete reaction of a particle under surface reaction control and diffusion through ash layer control. Two sets of equations, as defined above, are used to represent the rate of pyrite oxidation by dissolved O_2 and Fe^{3+}, respectively.

Equation 5 defines the reaction rate under non-biological conditions. However, pyrite oxidation can be greatly accelerated by the iron-oxidizing bacterium, *Thiobacillus ferrooxidans* (Singer and Stumm 1970). Increases in pyrite oxidation rates because of biological catalysis are reported to vary from 10 to 50 times (Lorenz and Tarpley, 1963) to 10^6 times (Singer and Stumm, 1970). A simple relation, similar to that given by Jaynes et al. (1984a) is modified and used in this model to account for the activity of iron-oxidizing bacteria.

The mathematical model, described above, was solved using the Newton-Raphson method in a fully-coupled, implicit way based on the block-centered finite difference scheme. Detailed discussion of this model, its numerical procedure, model calibration and testing were presented by Guo (1993).

Results and Discussion

Numerical simulations were performed to evaluate relative effects of advection and diffusion of O_2 in spoil that could cause differences in the spatial distribution of Po_2 at mines 1 and mine 2. One simulation (Test 1) considered effects from both advection and diffusion, and a second test (Test 2) simulated effects from diffusion only, by setting the air permeability to zero. Both tests simulated conditions for 10 years since reclamation and used a generalized geometric configuration (Figure 4). For these tests, 15 cells within the interior of the spoil were simulated to contain 10 wt % pyrite (= 5.3 wt % sulfur), and surrounding cells did not contain any pyrite. This distribution of pyrite represents the selective placement of high-sulfur content overburden into compacted layers above the water table in the backfill. The geometry, initial conditions, and boundary conditions, which were held constant for the tests, are shown in Figure 4. The parameters specified are listed in Table 1.

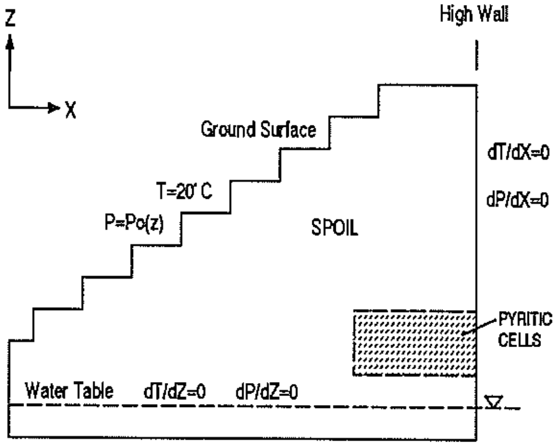

Figure 4. Boundary and initial conditions for numerical simulations. Shaded cells contain 10 wt % pyrite (= 5.3 wt % sulfur) initially; surrounding cells do not contain any pyrite.

For Test 1 where advection is the dominant transport mode, the fraction of pyrite oxidized after 10 years was much greater than that for Test 2 where diffusion is the dominant transport mode (Table 2). This difference in oxidation rate implies that temperature-driven air circulation (Figure 5), induced by pyrite oxidation, is significant and may exacerbate AMD formation because substantial O_2 is available for acid-forming oxidation reactions in mine spoil.

Thermal anomalies at depth as a result of pyrite oxidation are indicated by both simulated temperature profiles (Figure 6) and observed temperature profiles (Figure 2). Thermal anomalies in pyritic waste materials have also been reported (Bennett et al. 1989; Fielder 1989; Alpers and Nordstrom 1991). Higher temperatures are achieved in the more oxygenated environment, simulated by Test 1, because of greater pyrite oxidation and corresponding amounts of heat generation than for Test 2. Higher peak temperatures for simulations than for field observations are an artifact of concentrating pyritic material into one zone, rather than dispersing it throughout the spoil.

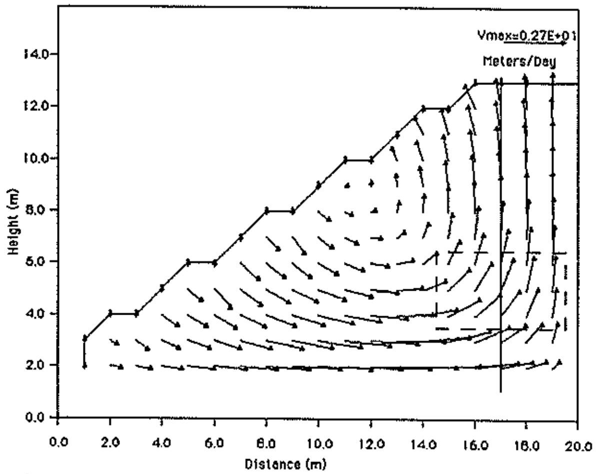

Figure 5. Simulated convective air-flow pattern in spoil 10 years after reclamation (Test 1). Vertical line marks the position of temperature and Po_2 profiles shown in Figures 6-9.

Table 1. Parameters used in numerical simulations.

Bulk density	1650 kg/m^3
Porosity	0.35
Infiltration rate	426.7 mm/yr
Thermal conductivity	2.0 W/m-K
Heat capacity	
Solid	760.0 J/kg-K
Water	4187.0 J/kg-K
Air	1000.0 J/kg-K
Air permeability	0 to 1×10^{-8} m^2
Tortuosity	0.6
Water content	15% by volume
Diffusion coefficient of oxygen in air	1.78×10^{-5} m^2/sec
Longitudinal dispersivity	10.0 m
Transverse dispersivity	1.0 m
Particle size	0.1 cm (radius)
Surface reaction constant	2.5×10^{-5} cm/sec
Diffusion coefficient in reacted zones	1.5×10^{-6} cm^2/sec

Table 2. Summary of Results of Test 1 and Test 2.

Test Number	Test 1	Test 2
Features	Dispersion-Advection	Diffusion Only
Tmax (°C)	27.814	23.006
P_{O_2} min (%)	17.79	4.10
Reacted Pyrite (%)	30.56	12.90

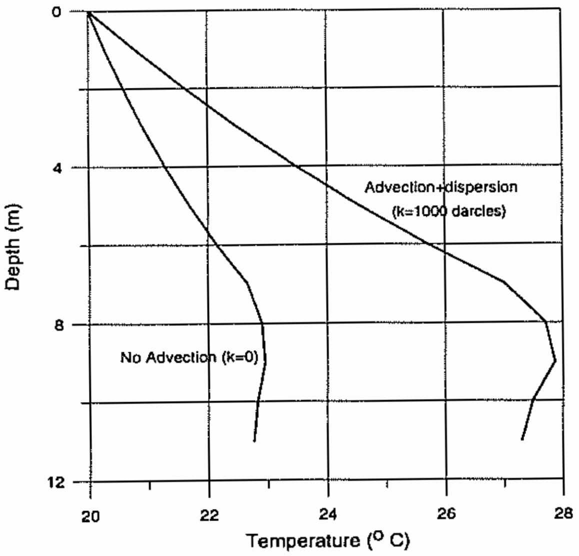

Figure 6. Simulated temperature profiles in unsaturated spoil 10 years after reclamation.

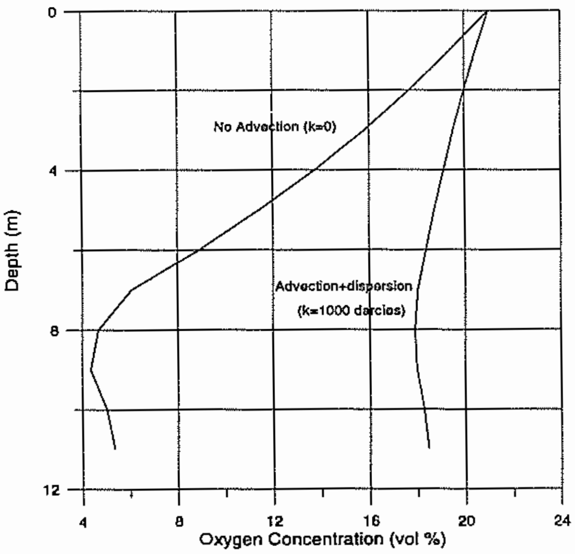

Figure 7. Simulated Po_2 profiles in unsaturated spoil 10 years after reclamation.

Uneven temperatures in mine spoil cause air convection in spoil (Figure 5). If the air flows from the land surface, where Po_2 is high, it brings O_2 into the subsurface. As air convection develops, a greater amount of O_2 is transported into mine spoil and greater rates of pyrite oxidation result, causing a perpetuation of the oxidation cycle. Consequently the temperature will be higher and convective flow is enhanced. However, the system is also controlled by the temperature, because once the temperature reaches about 55°C, bacterial catalysis slows or stops (Cathles 1979) and then the system reaches an equilibrium thermal condition and reaction rate.

Simulated Po_2 profiles for Tests 1 and 2 (Figure 7) are comparable with observed Po_2 profiles for mines 1 and 2, respectively (Figures 1 and 3). The simulated Po_2 profiles indicate that Po_2 remains relatively high throughout the spoil if advective transport takes place, but Po_2 decreases with depth if only diffusive transport takes place.

Results of Test 1 indicate that high Po_2 is attained in spoil when temperature-driven air flow is generated by the heat released from pyrite oxidation. In Test 2 for the simulation of only diffusive transport, Po_2 decreases exponentially from 21 vol % at the land surface to about 4 vol % at 9 m. Once the Po_2 declines to such a low level, the rates of acid-generating reactions are reduced. Results of laboratory experiments indicate the rate of pyrite oxidation reactions decreases when Po_2 is lower than vol 8% (Pugh et al. 1984) to as low as vol 1% (Hammack and Watzlaf 1990). This might be the situation observed in mine 2, where spoil is predominantly shale. The Po_2 remains low while most pore-water samples indicate negligible changes in concentrations of sulfate and iron with increasing depth below about 5 m (Cravotta et al. 1994b). Shale tends to disaggregate and become compacted, and hence shaly spoil (as in mine 2) has relatively low air permeability. In contrast, sandstone spoil (as in mine 1) tends to be very coarse and poorly compacted, which causes it to have higher air permeabilities. Neutralization by calcareous minerals may also contribute to the lower rate of AMD generation in deep spoil at mine 2 than that at mine 1.

If other conditions remain constant (Table 1), the air permeability of spoil is the determining factor for the occurrence of air convection.

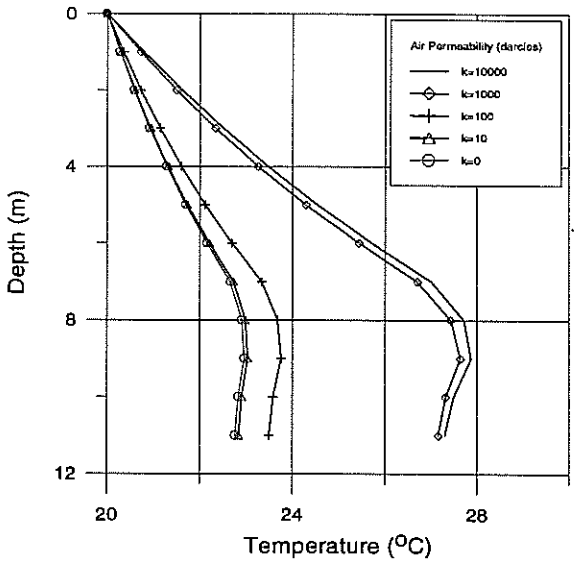

Figure 8. Simulated temperature profiles for different values of air permeability (k) 10 years after reclamation.

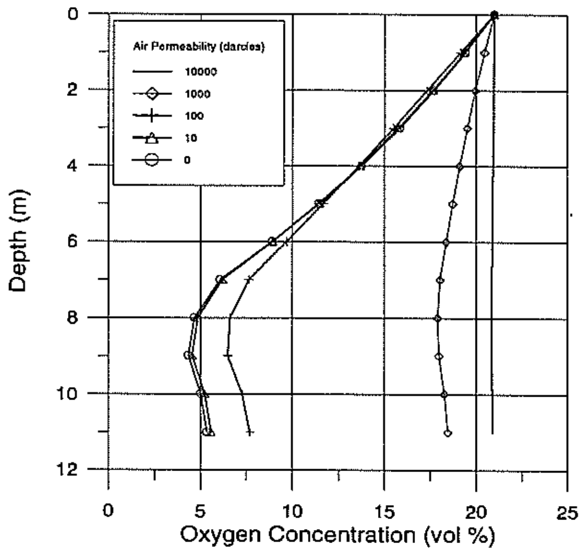

Figure 9. Simulated Po_2 profiles for different values of air permeability (k) 10 years after reclamation.

A series of numerical simulations was made in which only the air permeability was varied from 0 to 10^{-8} m^2. The temperature and Po_2 distributions predicted by these tests are shown in Figures 8 and 9, respectively. It is apparent that diffusion will be the dominant transport process when the air permeability is less than 10^{-10} m^2 (approximately 100 darcies), which is typical for soils. Pantelis and Ritchie (1992) also found that the oxidation rate in a heap with an air permeability of 10^{-10} m^2 is not much faster than that in which diffusion is the only gas transport process, but when the permeability is increased to 10^{-9} m^2, the oxidation rate is substantially faster.

Conclusions

Results of the numerical simulations indicate that differences in the distribution and transport of O_2 in coal-mine spoil can be explained by differences in the air permeability of spoil. Advective transport becomes significant if the air permeability of spoil is greater than 10^{-9} m^2, which is expected for blocky sandstone spoil. In the advective-dominant system, thermally-induced convective air flow, as a consequence of the exothermic oxidation of pyrite, supplies the O_2 to maintain high Po_2 within the deep unsaturated zone. Po_2 changes little with depth if advective transport of O_2 dominates, as at mine 1. In contrast, Po_2 decreases greatly with depth if diffusive transport of O_2 dominates, as in mine 2. Diffusive transport becomes significant if the air permeability of spoil is less than 10^{-10} m^2, which is expected for shaly spoil.

The numerical simulations, combined with field observations of the chemistry of pore-gas and pore-water samples, indicate that unsaturated-zone permeability is a critical variable affecting O_2 flux is spoil and the extent of pyrite oxidation. If the O_2 supply is not restricted, AMD formation can be severe. Thus, engineering practices to reduce O_2 transport into spoil may help to control the formation of AMD. Air permeability and O_2 supply in spoil can be reduced by covering the land surface with a low-permeability layer or by eliminating air-filled voids by compaction or filling with water. Field measurement of unsaturated-zone permeability, temperature, and pore-gas and water chemistry would be helpful for evaluation of the effectiveness of these practices.

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