

A Numerical Multi-Component Reactive Model for Pyrite Oxidation and Pollutant Transportation in a Pyritic, Carbonate-Rich Coal Waste Pile in Northern Iran

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Abstract A one-dimensional numerical finite volume model is presented to simulate pyrite oxidation and reactive transportation of the oxidation products in a pyritic, carbonate-rich, coal waste pile. The proposed model incorporates the shrinking core concept for describing pyrite oxidation, pyrite surface area reduction, oxygen diffusion, and transport of the oxidation products through the waste pile. The model governing equations were solved using the PHOENICS computational fluid dynamics model. The accuracy of the model was verified with field data. Pyrite oxidation was more intense at shallower depths where oxygen decreased almost linearly from the pile surface to an approximate depth of 2 m. The lowest pH, 3.5, was predicted at a depth of 0.5 m. The waste pile has high neutralisation potential due to buffering by carbonate minerals. The maximum concentration of SO_4^{2-} , 31.6 mol/m^3 , was predicted at an approximate depth of 4 m and to remain constant throughout the rest of waste profile. Simulation of a scenario with a cap shows that iron and sulphate was removed from the upper parts of the pile; their

peak concentrations shifted downward due to dilution. Oxygen source removal limited iron and sulphate production. These results will be useful for developing an appropriate remediation scheme.

Keywords Coal waste pile · Finite volume · Pyrite oxidation · Reactive transport model

Introduction

Coal extracted from the Zirab–Karmozd region of the Alborz Markazi coal field is washed in the Anjir Tangeh coal washing plant, in the city of Zirab, in northern Iran (Fig. 1) to raise the coal grade and remove impurities. Since 1989, this plant has produced and dumped more than 1.5 Mt of pyritic coal waste in a massive open-air pile at the plant site (Shahhosseini et al. 2012), where it undergoes rapid oxidation and produces acid mine drainage (AMD), degrading ground and surface waters (Atkins and Pooley 1982; Moncur et al. 2009; Doulati Ardejani et al. 2010). Prediction of pyrite oxidation and AMD generation together with transportation of the oxidation products are important factors to evaluate long-term environmental hazards and remediation costs.

Numerous numerical models have been developed by many researchers to describe sulphide oxidation in mine waste dumps and overburden mine spoils (Davis and Ritchie 1986; Davis et al. 1986; Gerke et al. 2001; Lefebvre and Gelinas 1995; Lefebvre et al. 2001; Molson et al. 2005), heap leaching (Bain et al. 2000; Cathles and Apps 1975; Pantelis and Ritchie 1991, 1992), mine tailings (Elberling et al. 1994; Walter et al. 1994; Wunderly et al. 1996) and open cut coal mines (Doulati Ardejani et al. 2004a; Jaynes et al. 1984a, b; Singh and Doulati Ardejani 2004).

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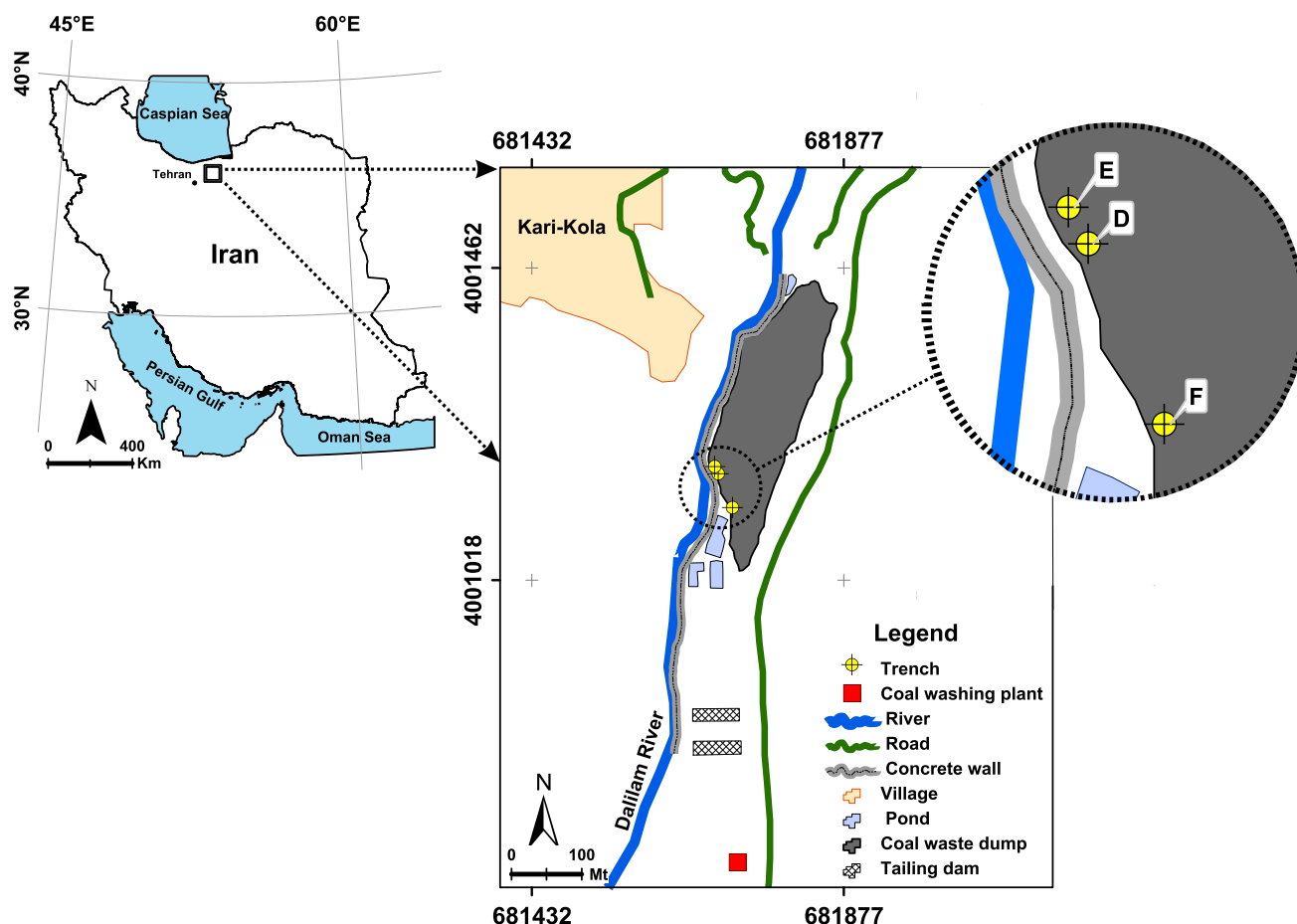


Fig. 1 Geographical location of the Anjir Tanghe coal waste pile, northern Iran

Lefebvre and Gelinas (1995) developed a model for the simulation of AMD generation in waste rock dumps. The model considers hydrology, gas and heat transfer, geochemistry, and mass transport; multi-component, multi-phase, and non-isothermal aspects are also important features.

The numerical model, PYROX (Wunderly et al. 1996), simulates one-dimensional oxygen diffusion and pyrite oxidation in the vadose zone of mine tailings. A shrinking-core model was used to simulate pyrite oxidation. The PYROX model is coupled with a two-dimensional finite element reactive transport model, MINTRAN, for contaminant transport and MINTEQA2 to solve the equilibrium geochemistry. The resulting model is called MINTOX. A two-step equilibrium approach has been used for the simulation.

Lefebvre et al. (2001) applied a numerical model for simulation of waste rock piles using the TOUGH/AMD code (Lefebvre 1994). The model incorporates air and water flow, pyrite oxidation, and transport of heat and sulphate. Their simulations were based on extensive site characterization data and indicated the control of gas

convection as a result of oxidation-induced thermal gradients. However, pH buffering by carbonates was not considered.

Mayer et al. (2002) developed a numerical finite volume model called MIN3P to simulate unsaturated flow and reactive mass transport considering with a general kinetic and global implicit formulation. MIN3P incorporates gas, aqueous, and solid phases, and includes surface and transport controlled reactions. The model uses the shrinking core concept to describe sulphide oxidation reaction.

Molson et al. (2005) presented a two-dimensional numerical finite element model to simulate layered, sulphide-bearing, unsaturated waste rock piles to show the effect of coupled processes on AMD generation. They used HYDRUS and POLYMIN models to simulate unsaturated flow and reactive transport, respectively. The simulations predicted low-pH AMD that was buffered by sequential mineral dissolution and precipitation reactions. The main goal of their study was to investigate the effect of internal structure and grain size on the generation and evolution of AMD.

However, very few numerical models have been developed to describe pyrite oxidation and leaching

processes acting within coal mine or coal washing spoils (Doulati Ardejani et al. 2008, 2010; Qiang et al. 2006). Qiang et al. (2006) developed a two-dimensional numerical finite element model for water flow and trace elements transport from coal mine spoil. In their study, the focus was mainly on the relationship between trace element concentrations and leaching times together with pH values of the medium. Again, pH buffering reactions by carbonate minerals was not considered.

Doulati Ardejani et al. (2008) applied the PHOENICS finite volume model (Spalding 1981) to simulate pyrite oxidation at the Alborz Sharghi coal washing waste pile near Shahrood, in northeast Iran. The transport of oxidation products was not considered. However, a time-lapse geo-electrical survey conducted downstream of the waste pile showed pollutant transport.

Doulati Ardejani et al. (2010) used a simple model (Elberling et al. 1994) based on the shrinking core concept to simulate pyrite oxidation in wastes produced by the coal washing operation at the Azad Shahr-Ramian region, Golestan province, in northeast Iran. Transport of the oxidation products and pH buffering reactions by carbonate minerals were not considered.

Existing codes for pyrite oxidation and reactive transport models mostly focus on waste rock dumps, open cut mines, and metal mine tailings. In addition, early simulations of wastes produced by coal mining and coal washing (Doulati Ardejani et al. 2008, 2010; Qiang et al. 2006) emphasised either physical or geochemical processes, with little effort to develop a numerical model for trace element transport from coal mine spoils. No multi-component reactive transport model has been specifically designed for coal waste piles produced by coal washing operations.

The main goal of the research was to develop a numerical finite volume model to simulate future pyrite oxidation and oxidation product transport within a specific coal waste pile and provide new data for future reclamation. The model incorporates oxygen diffusion, kinetically controlled pyrite oxidation, multi-component advection–dispersion transport, and pH buffering. To achieve this, a multi-purpose computational fluid dynamics (CFD) model called PHOENICS (Spalding 1981) was modified. The relevant settings and modifications for specific boundary conditions and all non-standard source or sink terms incorporated in the model-governing equations were carried out by creating a PHOENICS input file (Q1) and applying extra coding in FORTRAN in the GROUND subroutine. Field measurements were used as a basis of comparison to the model outputs.

Field Measurements

Twenty-five 1 kg coal samples were taken in 0.5 m intervals from three trenches (D, E, F) excavated in the waste

pile (Fig. 1). The vertical sampling was performed from the pile surface to a depth of 3.8, 4, and 3 m in D, E, and F trenches respectively.

To prepare paste samples, 100 mL of distilled water were added to a 200 g sample. Hence, the water to soil ratio (W/S) was maintained at approximately 1/2 for paste measurements. The sample was then mixed with a spatula until a homogeneous paste readily slipping from the spatula was produced.

The pH values of the paste samples were measured using an ORION 420A pH-metre. To measure pH, the electrode of the instrument was inserted into the slurry and after swirling slightly, the paste pH was measured until a constant value was obtained. The EC of each sample was measured in the same manner. The concentrations of SO_4^{2-} and other major anions of the paste samples were determined using a Pal-intest-Photometer 7,000 in the water laboratory of the Semnan Science and Technology Park, Iran.

The $\leq 75 \mu\text{m}$ sample fractions were pulverised in an agate mill. About 20 g of each sample was systematically taken as a representative sample. The concentrations of 54 elements, including iron, were determined by inductively coupled plasma mass spectrometer (ICP-MS) by ACME Analytical Laboratories Ltd, Canada. Total reduced inorganic pyrite was determined using a method presented by the ASTM (Gladfelter and Dickerhoof 1976; Shahhoseiny et al. 2012). The analytical results are given in Shahhoseiny et al. (2012); our model input data were taken from this reference.

To determine the maximum depth from the surface of the waste pile wherein oxygen can be transported by diffusion, the in situ mole fraction of oxygen was measured at various depths within the pore space of the waste. The oxygen measurements were made before the trenches were excavated using a portable oxygen indicator (Model XP-204, Eijkelpkamp Company, the Netherlands). The measurement depths and locations corresponded to those depths in which the solid samples were subsequently removed for geochemical analysis. Supplemental Table 1 (supplemental files accompany the on-line version of this paper, which can be downloaded for free by all subscribers) gives the measured oxygen mole fractions each location.

Conceptual Model of the Coal Waste Pile

Figure 2 shows a conceptual model that qualitatively illustrates the physical and chemical processes occurring in an unsaturated coal waste pile. The top surface is exposed to atmospheric concentrations of oxygen and to rainfall and evaporation; water can drain freely from the bottom of the pile. A vertical waste profile, 20 m in height, was used for the one-dimensional simulations.

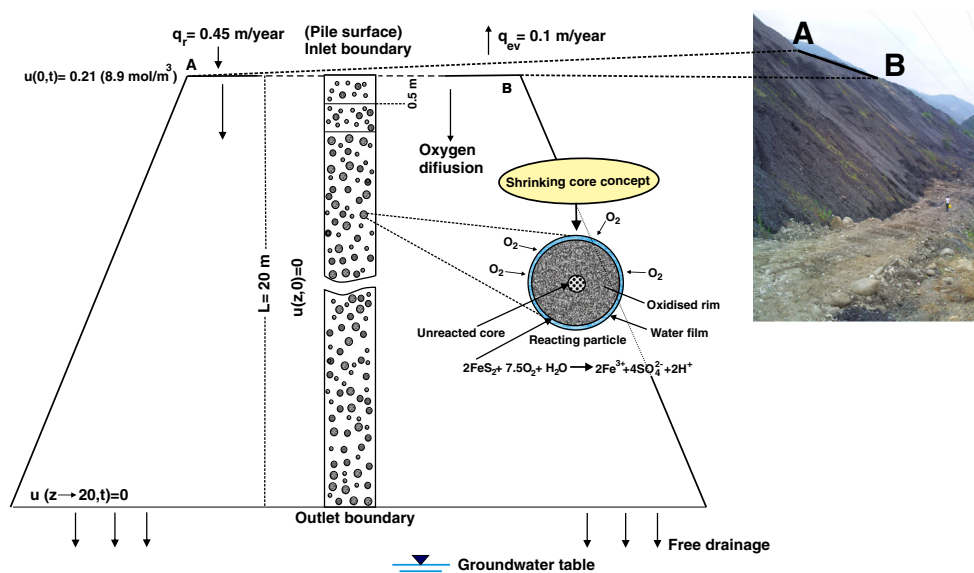


Fig. 2 Boundary and initial conditions specified for oxygen diffusion model

The waste pile system is assumed to be homogeneous and to consist of spherical, uniformly-sized particles containing a homogeneous distribution of pyrite. This situation contrasts with metal mine tailings, where pyrite grains are mostly free (Lefebvre et al. 2001). Oxygen is assumed to be the only oxidant, ignoring the role that iron-oxidizing bacteria and ferric iron play in pyrite oxidation. Oxygen diffuses from zones of greater oxygen concentration to zones of less oxygen concentration through the air-filled pore space and a water film that surrounds the particles. Pyrite oxidation proceeds from the surface of waste particles. As pyrite near the surface is depleted, the oxygen must penetrate within the waste particles to reach fresh pyrite. Oxidation products are leached from the shrinking particles and transported from the waste materials. The chemical oxidation of Fe^{2+} consumes O_2 and H^+ , and produces Fe^{3+} . A reaction between aqueous H^+ and the waste matrix can occur, consuming H^+ from the waste solution and increasing the pH (Jaynes et al. 1984a). The oxidation products are transported by recharge water from the waste materials, considering both advection and dispersion.

The conceptual model described above also assumes that: water flow is modelled under steady state conditions; porosity and permeability of the wastes are not affected by pile consolidation or by mineral precipitation or dissolution reactions (Molson et al. 2005); pyrite oxidation is governed by the shrinking core concept; evaporation does not affect the geochemistry of the pile, and; waste deposition is much faster than the bulk oxidation rate of the pile.

In this work, such assumptions are necessary, as the main goal is to simulate future pyrite oxidation and AMD

generation processes within the coal waste pile, so that we can reduce the contaminant production rate and minimise the pollution load on the receiving environment.

Mathematical Equations

Pyrite Oxidation Model

A well-known shrinking core approach (Elberling et al. 1994; Levenspiel 1972) was used to describe the pyrite oxidation process within the coal wastes particles, assuming that the waste particles were spherical and of uniform size, surrounded by a water film, and have a homogeneous distribution of pyrite.

$$\frac{d\text{FeS}_2}{dt} = -KSu^n \quad (1)$$

where K = a kinetics constant of FeS_2 consumption; u = gaseous concentration of oxygen in the wastes pore space, and; S = pyrite surface area per unit volume of particle. This reaction core model uses only oxygen as the pyrite oxidant, thus making a direct connection between gaseous oxygen concentration and the oxidation kinetics (Elberling et al. 1994; Levenspiel 1972. In Eq. (1), n is assumed to be one at low oxygen concentrations. This equation is a first-order kinetics model with respect to oxygen.

Surface area per unit volume of particle (S) may be obtained as follows (Elberling et al. 1994):

$$S_t = S_{t-1} - K\Delta t/\rho \quad (2)$$

where ρ = molar density of pyrite; S_{t-1} = pyrite surface area per unit volume of particle at previous time step, and;

Δt = simulation time step (s). Equation (2) can be rearranged in the following form:

$$\frac{S_t - S_{t-1}}{\Delta t} = -K/\rho \quad (3)$$

which reduces to:

$$\frac{\partial S}{\partial t} = -K/\rho \quad (4)$$

Oxygen Transport Model

Pyrite is oxidised in the waste pile primarily by oxygen where the oxygen can move through the air-filled pore space in the coal waste materials dominantly by a gaseous diffusion mechanism. The partial differential equation governing oxygen movement through the pore space of the waste, comprising the volumetric oxygen consumption terms by pyrite oxidation and chemical oxidation of ferrous iron, wherein air-filled porosity is assumed to be constant over time, can be expressed as follows (modified from Doulati Ardejani et al. 2004a; Elberling et al. 1994; Jaynes et al. 1984a):

$$\phi_a \frac{\partial u}{\partial t} = D_e \frac{n^2 u}{nz^2} - K_{O_2} u - b \phi_w [Fe^{2+}] u \left(\frac{K_1}{[H^+]^2} + K_2 \right) \quad (5)$$

where D_e = effective diffusion coefficient of oxygen within the pore space of the pile (m^2/s); ϕ_a = air-filled porosity of the waste; z = vertical coordinate (m); ϕ_w = water-filled porosity of the waste; t = time (s); b = stoichiometric ratio of Fe^{2+} consumption to oxygen consumption; K_{O_2} = first order rate constant for the oxygen consumption in pyrite-oxygen reaction (1/s); K_1 and K_2 = Kinetics constants of ferrous iron oxidation, and; $[Fe^{2+}]$ and $[H^+]$ = concentrations of Fe^{2+} and H^+ (mol/m^3).

Equations (1, 4, and 5) define a simplistic model for describing pyrite oxidation process of a waste pile. Appropriate transport models can now be presented to simulate leaching process of the oxidation products through the waste materials. They are given below.

Fe^{2+} Transport Model

Where oxygen is available, Fe^{2+} produced by pyrite oxidation can react with oxygen and be converted to Fe^{3+} . The partial differential equation for Fe^{2+} transport incorporating both physical processes (advection and dispersion) and mathematical expressions describing the kinetics of the chemical reactions can be expressed as follows (Jaynes et al. 1984a):

$$\phi \frac{\partial [Fe^{2+}]}{\partial t} = D \frac{\partial^2 [Fe^{2+}]}{\partial z^2} - q_z \frac{\partial [Fe^{2+}]}{\partial z} + b' K S u - b'' \phi_w [Fe^{2+}] u \left(\frac{K_1}{[H^+]^2} + K_2 \right) \quad (6)$$

where ϕ = porosity of the flow medium; q_z = component of the pore fluid specific discharge (m/s); b' = the stoichiometric ratio of pyrite consumption to ferrous iron production (1.0), and; b'' = the stoichiometric ratio of ferrous iron consumption to H^+ ions consumption (1.0). Pyrite oxidation by oxygen produces ferrous iron (source term in Eq. 6) and the Fe^{2+} -oxygen reaction consumes ferrous iron (sink term in Eq. 6).

Sulfate Transport Model

The amount of sulphate produced by pyrite oxidation remains constant even though the H^+ released by pyrite oxidation is completely neutralised by alkaline materials in the spoils. The sulphate ions released by the pyrite oxidation reaction is transported through the spoil materials by surface recharge. Sulphate transport, incorporating both physical processes and chemical reactions, can be expressed by the following equation (Rubin and James 1973):

$$\phi \frac{\partial [SO_4^{2-}]}{\partial t} = D \frac{\partial^2 [SO_4^{2-}]}{\partial z^2} - q_z \frac{\partial [SO_4^{2-}]}{\partial z} + \beta K S u \quad (7)$$

where β = the stoichiometric ratio of pyrite consumption to sulphate production (0.5).

H^+ Transport Model

Hydrogen ions released by pyrite oxidation decrease solution pH. Some H^+ ions are consumed by the oxidation of Fe^{2+} to Fe^{3+} in the zones where oxygen is available. In addition, H^+ released by pyrite oxidation may be neutralised by carbonates or transformed into weaker acids by reactions with the spoil materials (Rogowski et al. 1977). As the pH rises above 6–6.3, bicarbonate is produced (Blowes et al. 1994). Therefore, H^+ neutralisation processes must be included in the model.

A simple empirical expression was presented by Jaynes et al. (1984a) to account for H^+ neutralisation reactions taking place in coal mine spoils:

$$\frac{H^+}{H_{Gen}^+} = \{1.0 - \text{EXP}(G_A - \text{pH})\} \quad (8)$$

where H^+ = the actual increase of hydrogen ion in solution (mol/m^3); H_{Gen}^+ = H^+ generated by pyrite oxidation (mol/m^3), and; G_A = an empirical constant that defines the buffer system. This expression was used by Doulati Ardejani et al. (2004a) to address long-term pyrite oxidation and pollutants leaching from coal mine spoils, and in the present work.

Rearranging Eq. (8) yields H^+ consumption per cubic metre of waste materials per unit time:

Table 1 Parameters used for modelling

Model characteristic/unit	Quantity	References
Model length (m)	20	
Effective diffusion coefficient (m ² /s)	Variable (2×10^{-9} – 7×10^{-9})	
Pyrite fraction (%)	(1.07–1.35)	
Density of pyrite (kg/m ³)	5,900	Elberling et al. (1994)
Particle diameter containing pyrite (m)	0.002–0.004	
First-order rate constant for oxygen (molO ₂ m ⁻² s ⁻¹)	1.0×10^{-9}	Modified from Elberling et al. (1994)
First-order rate constant for pyrite (molFeS ₂ m ⁻² s ⁻¹)	4.0×10^{-10}	Elberling et al. (1994)
Kinetics constants of ferrous iron oxidation	$K_1 = 1.3 \times 10^{-10}$ (mol ² /(m ³) ² s) $K_2 = 1.7 \times 10^{-9}$ s ⁻¹	Singer and Stumm (1970)
Simulation time (years)	22 Years	
Simulation type (time dependence)	Transient	
Number of iterations	1,000	
Time steps	264	
Cell numbers	80	
Size of each control volume (m)	Variable with a ratio of 1.7	
Average annual precipitation (m/year)	0.45	Shahhoseiny et al. (2012)
Average annual evaporation (m/year)	0.10	Shahhoseiny et al. (2012)
Spoil porosity	0.25	
Water filled porosity	0.15	
Air filled porosity	0.1	
Infiltration rate (m/s)	7.4×10^{-9} – 1.0×10^{-8}	
Empirical constant for defining the buffer system	5.0	
Dispersivity (m)	0.5–1	Molson et al. (2005)
Diffusion coefficient of dissolved chemical species (m ² /s)	1.5×10^{-10}	Molson et al. (2005)

$$\frac{\partial H^+}{\partial t} = -\frac{H_{Gen}^+}{\Delta t} \exp(G_A - pH) \quad (9)$$

where Δt = the simulation time step (s). The H^+ governing transport equation, incorporating its source and sink terms, is given below:

$$\begin{aligned} \phi \frac{\partial [H^+]}{\partial t} = & D \frac{\partial^2 [H^+]}{\partial z^2} - q_z \frac{\partial [H^+]}{\partial z} + \gamma K Su \\ & - \phi_w [Fe^{2+}] u \left(\frac{K_1}{[H^+]^2} + K_2 \right) \\ & - \frac{H_{Gen}^+}{\Delta t} \exp(G_A - pH) \end{aligned} \quad (10)$$

where γ = stoichiometric ratio of pyrite consumption to H^+ ion production (0.5).

Fe³⁺ Transport Model

Fe³⁺ is produced by Fe²⁺ oxidation in the coal waste pile. In the absence of iron-oxidising bacteria, ferrous iron oxidation to ferric iron is normally slow at low pH (Singer and Stumm 1970). Fe³⁺ moves downward through the waste by advection (surface recharge) and dispersion. The

governing transport equation for ferric iron can be expressed by:

$$\begin{aligned} \phi \frac{\partial [Fe^{3+}]}{\partial t} = & D \frac{\partial^2 [Fe^{3+}]}{\partial z^2} - q_z \frac{\partial [Fe^{3+}]}{\partial z} \\ & + \eta \phi_w [Fe^{2+}] u \left(\frac{K_1}{[H^+]^2} + K_2 \right) \end{aligned} \quad (11)$$

where η = the stoichiometric ratio of ferrous iron consumption to ferric iron production (1.0).

Modelling Tool and Model Input Data

A numerical simulation was carried out to represent pyrite oxidation and oxidation products transportation within the Anjir Tangeh waste pile. PHOENICS software developed by Spalding (1981) was modified to solve model-governing mathematical equations described in this paper by applying a finite volume discretisation technique. PHOENICS is a general-purpose CFD software that can be used for simulation of fluid flow, heat transfer, and mass transfer. The partial differential equation solved by PHOENICS has the following general form (Spalding 1981):

Table 2 Source and background concentrations of chemical species used for simulation

Chemical species	Source concentration	Background concentration
FeS ₂ (%)	–	(1.07–1.35)
Mole fraction (O ₂) (mol/m ³)	0.21	0
Fe ²⁺	0	0
SO ₄ ^{2–}	20	20
H ⁺	0.01	0.005
Fe ³⁺	10 ^{–15}	10 ^{–8}
pH	5	8

$$\frac{\partial}{\partial t}(r_i \rho_i \phi_i) + \frac{\partial}{\partial x_j} \left(r_i \rho_i u_{ji} \phi_i - r_i \Gamma_{\phi i} \frac{\partial \phi_i}{\partial x_j} \right) = r_i S_{\phi i} \quad (12)$$

where ϕ_i = any of the dependent variables of phase i ; t = time; r_i = volume fraction of phase i ; ρ_i = PHOENICS-term for density of phase i ; u_j = velocity component in the x_j direction; $\Gamma_{\phi i}$ = diffusive exchange coefficient for ϕ in phase i , and; $S_{\phi i}$ = source rate of ϕ_i . The general term $S_{\phi i}$ in Eq. (12) can include all sources and sinks terms related to chemical reactions due to pyrite oxidation and AMD generation. In the case of a single-phase problem, the volume fraction, r_i , can be omitted; therefore Eq. (12) reduces to:

$$\frac{\partial}{\partial t}(\rho \phi) + \frac{\partial}{\partial x_j} \left(\rho u_j \phi - \Gamma_{\phi} \frac{\partial \phi}{\partial x_j} \right) = S_{\phi} \quad (13)$$

In the present case, ρ is set equal to 1.0.

The model equations include terms that are not incorporated in the PHOENICS general equation (Eq. 13), and therefore they must be implemented in PHOENICS by introducing the appropriate setting for each term in the Q1 file and applying extra FORTRAN coding in a user-accessible subroutine called GROUND (see more in Doulati Ardejani et al. 2004a). This allows PHOENICS to simulate pyrite oxidation and reactive transportation of the oxidation products in a pyrite-bearing, carbonate-rich coal waste pile.

Table 1 gives the model input data. Table 2 gives the influx chemistry, the background history of the oxidation products, and their hydrodynamic dispersion. A waste profile with a depth of 20 m was divided into 80 non-uniform size control volumes with a size ratio of 1.7.

One initial and two boundary conditions were specified for the oxygen transport model. The surface of the waste pile was initially indicated as a first-type boundary condition with the oxygen concentration in the atmosphere, 0.21 mol fraction (8.9 mol/m³). A zero-gradient boundary condition was assigned at the base of the waste column. It was further considered that no oxygen (initial condition) primarily exists within the waste profile (Fig. 2).

Specifying these initial and boundary conditions allows Eq. (5) to be solved numerically.

The gaseous concentration of oxygen within the pore space of the waste is related to its concentration in the liquid phase using Henry's law and the gas law (Lefebvre and Gelinas 1995; Wunderly et al. 1996):

$$C = \gamma u \quad (14)$$

where C = oxygen concentration in the aqueous phase; u = oxygen concentration within the waste pore space, and; γ = conversion factor between the oxygen concentrations in the gas and liquid phases.

For transport of the dissolved aqueous species, a surface recharge of 0.45 m/year and an average annual evaporation of 0.1 m/year were specified at the top surface of the pile. The unsaturated vertical flow system was assumed to be steady state with a constant water content of 0.25. According to Molson et al. (2005), the assumption of steady state flow in an unsaturated coal waste pile is most limiting, since transient events may significantly change the internal moisture distribution.

The velocity field and water content were introduced into the transport model by activating the advection term in the PHOENICS-governing equation for each chemical component and identifying the term $-q_x \partial C_i / \partial t$ as an additional source/sink term. C_i is the concentration of i th species in multi-component reactive transport model.

A fixed concentration boundary condition was assigned at the top surface of the pile. An initial boundary condition was specified to describe the distribution of the dissolved species within the water in the spoil profile. A zero-concentration gradient condition was finally allocated at the outlet boundary of the waste profile.

Modelling Results

Oxygen Diffusion Model Calibration

Initially, a simulation was run to calibrate the oxygen diffusion model. The modelling results were compared with the results obtained applying an analytical solution (Doulati Ardejani et al. 2010; Reddi and Inyang 2000). In this simulation, three different effective diffusion coefficients (1×10^{-9} , 1×10^{-8} , and 1×10^{-7} m²/s) were taken into consideration for oxygen movement through the pile wastes. A reasonable agreement can be seen between numerical results and analytical solutions (supplemental Fig. 1).

Transport Model Calibration

The capability of the PHOENICS model that was modified in this manuscript has been well calibrated and verified by

analytical solutions (Doulati Ardejani et al. 2004b), previously developed numerical models (Agah et al. 2013; Doulati Ardejani 2003; Doulati Ardejani et al. 2004b), lab experiments (Doulati Ardejani et al. 2012; Seifpanahi Shabani et al. 2011), and field data (Singh and Doulati Ardejani 2004) for reactive transport models.

Model Predictions

After specifying appropriate initial and boundary conditions, models describing pyrite oxidation (Eq. 1), reduction in pyrite surface area (Eq. 4), and oxygen transport (Eq. 5), together with the multi-component reactive transport models of the oxidation products (Eqs. 6, 7, 10, 11) were simultaneously solved using PHOENICS.

An initial condition was assigned for the pyrite oxidation model to explain the initial distribution of the pyrite within the waste throughout the waste profile. The initial and boundary conditions for oxygen transport and oxidation products models have been described above. The model was run for a simulated 22 years, the approximate age of the Anjir Tangeh waste pile at the time of the investigation and characterisation (2010).

Figure 3 compares the field and the simulated oxygen mole fraction and the amount of pyrite remaining in the waste particles versus depth after 22 years of pyrite oxidation. There is good agreement between the model predictions and the field measurements.

Gaseous diffusion can provide oxygen to oxidation sites. The oxygen concentration is greatest at the pile surface. Figure 3 (top) shows that the oxidation process consumes oxygen in the surface layers of the waste profile and creates steep gradients, so that oxygen decreased linearly from the waste surface to a depth of about 1 m. Below this depth, oxygen gradually decreased to the reaction front, where it reached zero at an approximate depth of 2.5 m. However, the field data show almost a linear reduction of oxygen from the spoil surface to the reaction front at an approximate depth of 1.8 m, yielding a relative error of about 11 %.

The bottom part of Fig. 3 shows the fraction of pyrite remaining. The field-measured pyrite remaining fraction (Shahhoseiny et al. 2012) in the waste particles observed in the upper 4 m of the waste pile from three sampling locations (E, D, and F) were compared with the simulated results. The numerical model predicted the fraction of pyrite remaining over the entire waste profile. There is a sharp decrease in the fraction of pyrite oxidised in the upper layers of the pile in the top 1 m, where the oxygen mole fraction decreased rapidly. At a depth between 1 and 3 m, the fraction of pyrite oxidised gradually decreased, as oxygen decreased. Below 3 m, no oxygen is available to

oxidise pyrite; hence, pyrite oxidation totally ceased and a large potential for AMD production remains. As observed by Shahhoseiny et al. (2012), pyrite oxidation is more extreme in profile F than profiles D and E because oxygen can diffuse more easily through the coarse-grained pyritic waste particles in profile F.

Figure 4 shows the simulated Fe^{2+} concentration as a function of waste pile depth. The results are given for different simulation times of 5, 7, 10, and 22 years after pyrite oxidation commenced. In the top 0.5 m, where oxygen concentration is highest, Fe^{2+} concentrations increased linearly. Between 0.5 and 3 m, the rate of Fe^{2+} concentration increase gradually slowed, due to conversion of some Fe^{2+} to Fe^{3+} and dilution. At depths below 3 m, where no oxygen is available to oxidise pyrite, the Fe^{2+}

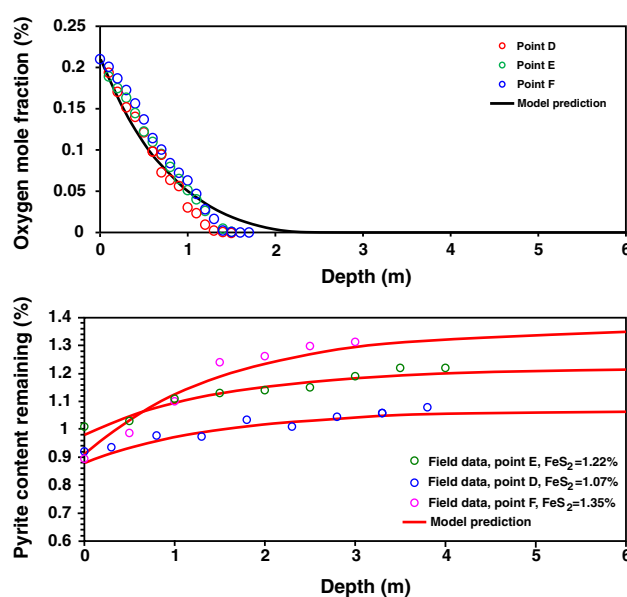


Fig. 3 Comparison of the field measurements (Shahhoseiny et al. 2012) and simulated conditions in the Anjir Tangeh waste pile: *top* oxygen mole fraction for an effective diffusion of $5.0 \times 10^{-9} \text{ m}^2/\text{s}$; *below* fraction of pyrite remaining in the waste particles (initial pyrite content varied between 1.07 and 1.35 %)

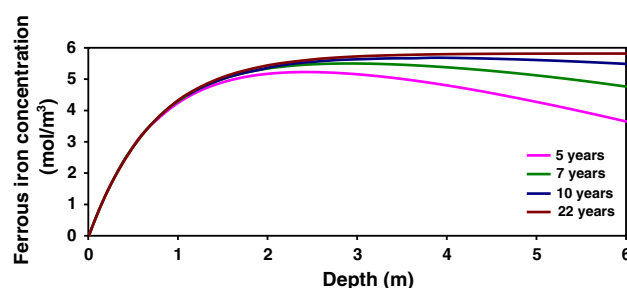


Fig. 4 Model predictions for ferrous iron concentration versus depth given for different simulation times

concentration decreased steadily after 5 years of simulation. As time progressed (from 5 to 22 years), the peak concentration of Fe^{2+} shifted to deeper depths due to the transport process. An increase in simulation time resulted in lower gradients.

Figure 5 shows the model predictions for pH versus depth over a 22 year time period, with and without neutralization. After 22 years, the pH dropped to about 3.5 in the top 0.5 m, where the oxygen reacts with pyrite and H^+ ions are released. It increased at a steady rate from 3.5 to 6.9 between 0.5 and 9 m (not shown in Fig. 5) and then increased at a more gradual rate, from 6.9 to 7.5, between 9 and 11.5 m. Below 11.5 m, it remained constant. Acid neutralisation by carbonates is responsible for the relatively high pH values (Shahhoseiny et al. 2012). The pH of the Dalilam River downstream of the waste pile (Fig. 1) ranges between 7.91 and 8.18, while the pH of drainages originating from the pile ranges from 7.16 to 7.85. Net alkalinity ranges between 125.8 and 328.9 mg/L, as CaCO_3 (Shahhoseini et al. 2013). These confirm the model predictions.

If neutralization is not considered, pH drops to about 2.25 at 0.5 m and continues to decrease gradually from 2.25 to about 2 between 0.5 and 1.7 m. Below 1.7 m, it

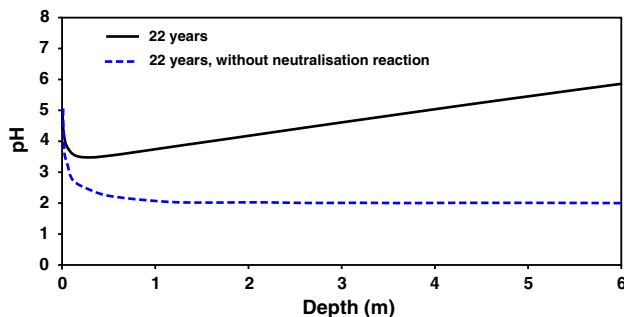


Fig. 5 Model predictions for pH versus depth over 22-year time period with and without neutralization reaction

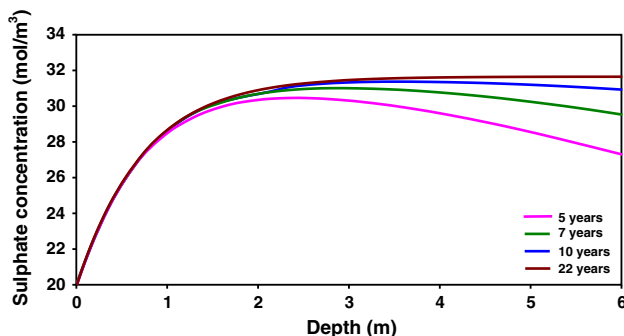


Fig. 6 Model predictions for sulphate concentration versus depth given for different simulation times

remains constant. This simulation is important for predicting what could occur in the waste pile when no pH buffering minerals remain to react with the AMD.

Figure 6 shows the simulated concentration of sulphate in mol/m^3 versus waste pile depth after 22 years. The sulphate concentration increased linearly from 20 to about 26 mol/m^3 down to a depth of 0.5 m after 22 years, and then increased gradually to about 31 mol/m^3 at a depth of 2.5 m. At depths below 2.5 m, the sulphate concentrations decreased steadily after 5 years of simulation. As time progressed (from 5 to 22 years), the peak concentration of sulphate shifted deeper due to the transport process. Increased simulation times resulted in lower gradients.

A sensitivity analysis was conducted to gain insight into how oxygen transport is affected by system parameters. The simulation results showed that the concentration of oxygen is most sensitive to the effective diffusion coefficient. Smaller diffusion values caused steeper gradients and oxygen decreased linearly from the pile surface to the reaction front. An increase in the effective diffusion coefficient increased oxygen concentrations at shallower depths. The results also showed that as simulation time increased, oxygen diffused to deeper layers, increasing the rate of pyrite oxidation at those depths.

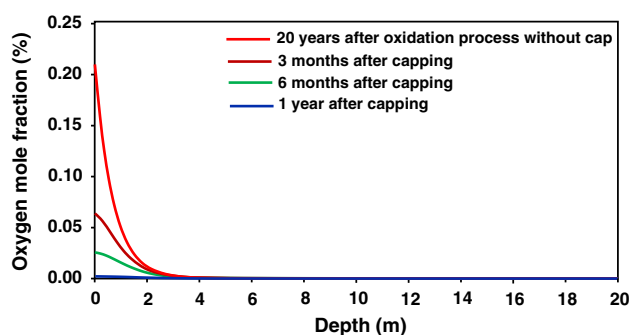
Supplemental Fig. 2 shows the simulated oxygen mole fraction versus the waste pile depth after 22 years of pyrite oxidation for four effective diffusion coefficients, ranging from a very low value ($1 \times 10^{-10} \text{ m}^2/\text{s}$) to a high value representing well-drained waste conditions ($1 \times 10^{-7} \text{ m}^2/\text{s}$). Under the low diffusion coefficient value ($1 \times 10^{-10} \text{ m}^2/\text{s}$), oxygen diffused less than 1 m in 22 years compared with the well-drained waste condition where the oxygen penetrated about 11 m over the same time period.

Supplemental Fig. 3 shows the sensitivity of the pyrite oxidation rate (illustrated as fraction of pyrite remaining) to oxygen penetration. The effective diffusion coefficients ranged between 1×10^{-10} and $1 \times 10^{-7} \text{ m}^2/\text{s}$. This indicates that the overall pyrite oxidation rate is highly dependent on the effective diffusion coefficient. Increasing the effective diffusion coefficient significantly increased the amount of pyrite oxidation.

Supplemental Fig. 4 shows the simulated sulphate concentrations versus waste pile depth for four different effective diffusion coefficients. Simulation time was 22 years. Relatively small amounts of sulphate was produced when the effective diffusion coefficient of oxygen transport was $1 \times 10^{-10} \text{ m}^2/\text{s}$. Sulphate reached 22 mol/m^3 at a depth of 1 m when the effective diffusion coefficient was increased from 1.0×10^{-10} to $1.0 \times 10^{-9} \text{ m}^2/\text{s}$. The concentrations of sulphate reached about 32.6 mol/m^3 (at a depth of 2 m) and 87.1 mol/m^3 (at a depth of 8 m)

Table 3 Source and background concentrations used for simulation, scenario with cap

Chemical species	Source concentration	Background concentration
FeS ₂ (%)	—	Simulation results over a 22 year period of pyrite oxidation process used as initial chemistry
Mole fraction (O ₂)	—	
Infiltration rate (m/s) (mol/m ³)	0	
Fe ²⁺	—	
SO ₄ ²⁻	—	
H ⁺	—	
Fe ³⁺	—	
pH	—	

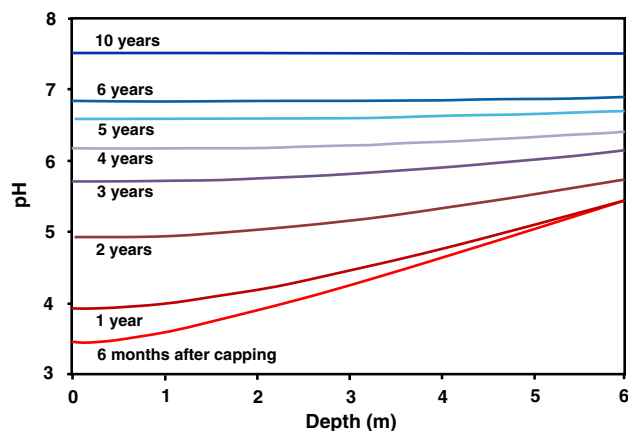
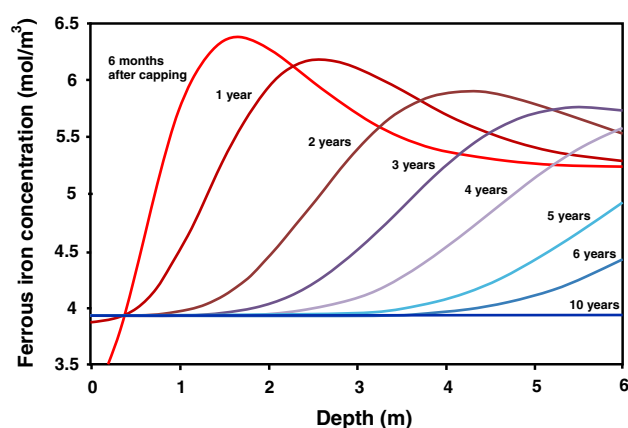
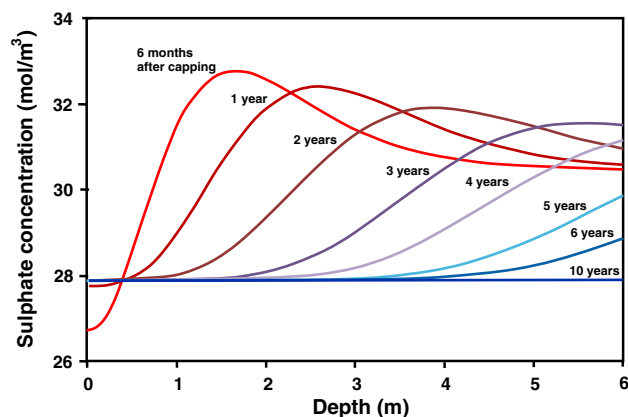
**Fig. 7** Simulated oxygen mole fraction as a function of depth presented over 1-year period of capping process

when the effective diffusion coefficients were increased, respectively, to 1.0×10^{-8} and 1.0×10^{-7} m²/s.

Model Prediction of Scenario with Reclamation

In this section, an additional simulation scenario is presented to gain insight into how pyrite oxidation products in the waste pile could be affected if a cap is used to limit oxygen diffusion and surface recharge infiltration. Modeling this scenario could be part of an effective remediation program, and can be used to provide insight into the cost/benefit of various cap designs. Table 3 gives the source and background concentrations of the chemical constituents used for this scenario.

Figure 7 indicates the simulation results for oxygen mole fraction versus depth. The model prediction for oxygen transport after 22 years of oxidation was used as an initial condition. Oxygen was almost zero in the waste 1 year after capping. Figure 8 shows the pH distribution in the waste profile after 10 years of capping. The pH increased from 3.5 to 7.5 due to pH neutralization and

**Fig. 8** pH as a function of the pile depth presented over a 10 year period of capping process**Fig. 9** Ferrous iron concentration versus pile depth presented over a 10 year period of capping process**Fig. 10** Sulphate concentration versus pile depth presented over a 10 year period of capping process

dilution by diffusion. Figures 9 and 10 show the evolution of ferrous iron and sulphate concentrations, respectively, 10 years after capping. As time progressed, iron and

sulphate was removed from the upper parts of the pile and their peak concentrations shifted to deeper depths due to diffusion. Removing the oxygen definitely limited iron and sulphate production.

Conclusions

Pyrite oxidation, AMD generation, and subsequent release of oxidation products in a pyritic, carbonate-rich, coal waste pile were simulated by developing a multi-component reactive transport model. The governing equations of the model were numerically solved using PHOENICS software. The simulation resulted in a minimum pH of 3.5 at a depth of 0.5 and maximum concentrations of sulphate of about 31.6 mol/m^3 and Fe^{2+} of about 5.8 mol/m^3 at an approximate depth of 4 m after 22 years. The oxygen diffused about 2 m over this time period. The pyrite oxidation process sharply decreased in the upper metre of the waste pile, as the oxygen mole fraction rapidly decreased. The concentration of sulphate reached about 87.1 mol/m^3 at a depth of 8 m when the effective diffusion coefficient was increased to $1.0 \times 10^{-7} \text{ m}^2/\text{s}$. Model prediction of a reclamation scenario with a cap shows that reducing oxygen diffusion through the pile wastes is critical in reducing future pyrite oxidation and subsequent AMD generation. Therefore, to limit AMD, an impermeable layer must be designed to cap the waste pile using non-weathered and high quality natural clays or a poly-synthetic plastic material. This will limit oxygen diffusion and surface recharge infiltration through the pore space of the pile wastes and virtually stop pyrite oxidation. The simulated results have provided insight into the processes controlling pollution generation and provided useful information for developing an appropriate site remediation strategy.

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