Geochemical transport modelling of acid mine drainage within heterogeneous waste rock piles



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ABSTRACT

The geochemical evolution of acid mine drainage (AMD) within heterogeneous, unsaturated waste rock piles is numerically simulated using the reactive transport model POLYMIN (Molson et al., 2005). The conceptual model includes the processes of surface recharge, groundwater flow, oxygen diffusion, sulphide mineral oxidation, geochemical speciation and water-rock interactions. The physical system is based on stochastic distributions of grain size, hydraulic conductivity and sulphide mineral fraction. The numerical simulations show that sulphide mineral oxidation rates depend strongly on the grain size, sulphide fraction and moisture content distribution, causing large spatial variations in the composition of drainage water. The results have implications for pile construction methods, design of monitoring systems, and for predicting environmental impacts of acid mine drainage in complex mining environments.

RÉSUMÉ

L'évolution géochimique du drainage minier acide (DMA) dans des haldes à stériles est simulée avec le modèle POLYMIN (Molson et al., 2005). Le modèle conceptuel inclut les processus de recharge, d'écoulement, de diffusion de l'oxygène, d'oxydation des sulfures, et des réactions géochimiques. Le système physique se base sur des distributions stochastiques de la taille des grains, de la conductivité hydraulique et de la proportion des sulfures. Les simulations démontrent que les taux d'oxydation dépendent fortement de la taille des grains, la fraction des sulfures et la teneur en eau, ce qui produit des variations spatiales importantes dans la composition du DMA. Ces résultats sont utiles lors du design de haldes à stériles, de systèmes de suivi, et pour la prédiction des effets du DMA dans l'environnement.

1 INTRODUCTION

Acid mine drainage (AMD) from sulphidic waste rock piles continues to be a serious environmental concern in Canada and throughout the world (Aubertin et al. 2002; Price, 2003). While research is progressing rapidly into various treatment and cover systems, there are significant knowledge gaps on the generation and behaviour of AMD within heterogeneous, partially saturated waste rock piles.

The geochemical composition and discharge rate of AMD from a waste rock pile depends on a variety of factors including the local climatic conditions, mineralogical composition of the waste rock, as well as the depositional structure and hydraulic properties of the pile. Ptacek and Blowes (2003) provide data on the chemical composition of different mine drainage waters. The hydraulic properties are particularly critical as they control the degree of water saturation which affects flow behaviour and the diffusion rate of oxygen (Fala, 2008).

Numerical modelling has proven a useful tool for assessing conceptual models of AMD generation and evolution. Approaches vary in complexity from geochemical speciation models such as MINTEQ/A2 (Allison et al 1991) and PHREEQC (Parkhurst and Appelo, 1999) to multi-dimensional coupled flow and reactive transport models such as HydroGeosphere (Therrien and Sudicky, 1996), MIN3P (Mayer et al. 2002) and POLYMIN (Molson et al. 2006). Steefel & MacQuarrie (1996) provide an overview and comparison of different numerical solution approaches for reactive transport, and MacQuarrie and Mayer (2005) review the state of the art of reactive transport in fractured media.

In this paper, we apply the POLYMIN numerical model to simulate the geochemical evolution and advectivedispersive transport of AMD in waste rock piles exposed to surface recharge and oxygen diffusion. Two conceptual depositional structures are considered: a horizontally stratified pile, and an unstructured heterogeneous pile. The unsaturated flow systems for both conceptual models were obtained from the HYDRUS2D code (Simunek et al. 1999). In each case, kinetic sulphide mineral oxidation is simulated using the shrinking core model (Davis and Ritchie, 1986), constrained by the availability of oxygen at the grain surfaces.

2 SIMULATION APPROACH

Generation of acid mine drainage begins with the diffusion of oxygen into the reactive waste, where it is consumed by oxidation of sulphide minerals such as pyrite (FeS₂) and pyrrhotite (Fe_{1-x}S). For pyrite, the reaction can be expressed according to :

$$FeS_2 + 1/2H_2O + 15/4O_2 \implies Fe^{3+} + 2SO_4^{2-} + H^+$$
 (1)

The aqueous oxidation products are then transported by advection and hydrodynamic dispersion through the water

phase. For a partially saturated porous medium, transport is governed by :

$$\frac{\partial \left(\boldsymbol{\theta}_{w} \boldsymbol{C}_{k}\right)}{\partial t} = \frac{\partial}{\partial x_{i}} \left(\boldsymbol{\theta}_{w} \boldsymbol{D}_{ij} \frac{\partial \boldsymbol{C}_{k}}{\partial x_{j}}\right) - \frac{\partial \left(\boldsymbol{q}_{i} \boldsymbol{C}_{k}\right)}{\partial x_{i}} + \boldsymbol{R}_{k} \qquad (2)$$

where θ_w is the volumetric water content, C_k is the concentration of the k^{th} aqueous component in the pore water [ML³], q_i is the i^{th} component of the Darcy flux [LT¹] (which is derived from the HYDRUS2D flow model), D_{ij} is the dispersion coefficient tensor [L²T¹], R_k is a source/sink term from geochemical reactions [ML⁻³T¹], x_{ij} are the spatial coordinates (L), and *t* is time (T).

Equation (2) is solved with the POLYMIN model using a Galerkin finite element discretization with linear triangular elements. The model was developed from a modified version of the MINTRAN code (Walter et al. 1994) which uses MINTEQA2 (Allison et al. 1991) for equilibrium geochemical speciation. Further details on the numerical scheme, and on the modified oxygen diffusion and sulphide oxidation modules are provided by Molson et al. (2005, 2006).

3 CONCEPTUAL WASTE ROCK MODEL AND PHYSICAL PARAMETERS

The conceptual model for the simulations is shown in Figure 1. The simulations are based on a transverse 2D cross-section through a symmetric waste rock pile; for convenience and computational efficiency, only the right-half symmetric section is simulated.

The 2D base case grid measures $45m \times 20m$ in the horizontal (x) and vertical (z) directions, respectively, and is resolved with a grid of 22,303 nodes and 44,005 triangular elements. The average grid spacing is 10 cm.

For the unsaturated flow systems, the left boundary is considered a symmetry divide (no-flow), a transient (seasonal) recharge condition is applied across the top (see Fala et al. 2008), and a free drainage condition is applied across the base. In the reactive transport simulations, a Cauchy mass-flux condition is applied across the top (using a recharge water composition from Molson et al. 2005), while all other boundaries are assumed zero-gradient Neumann conditions. A fixed oxygen concentration is applied at the pile surface and the system is assumed initially oxygen-free.

The waste rock is composed of a heterogeneous sand-sized material (SBL), characterized by Bussière (1999). In Conceptual Model 1, the primary physical parameters (saturated hydraulic conductivity, grain radius and sulphide mineral fraction) are horizontally correlated (λ_x =100m, λ_z =10m, σ =10m) while in Conceptual Model 2 these properties have a mixed horizontal and vertical correlation (λ_x =100m, λ_z =90m, σ =10m), hereinafter referred to as "mixed" or "unstructured" (Fala et al. 2008). The principal physical properties are provided in Table 1 while the major ion chemistry (which includes 12 aqueous components) is provided in Table 2.

Background mineralogy was assumed dominated by silicate minerals (95-99%vol.; represented by a single

pseudo-component of silica), 1-5% pyrite, and small amounts of calcite, siderite, gibbsite, and ferrihydrite (each < 0.1%). The system is assumed initially gypsum-free but gypsum is allowed to precipitate.

Two flow systems are analyzed for Conceptual Model 1: Case 1A uses a relatively high-recharge flow system (taken from the end of the annual cycle) while Case 1B uses a relatively low-recharge flow system from mid-year (summer). Case 2 (the unstructured pile) also uses the high-recharge flow system.

All transport simulations assume the flow system is at steady state which simplifies the interpretation of the transport system behaviour. The POLYMIN transport model is currently being extended to incorporate transient flow systems. Full details on the long-term flow systems and stochastic property distributions are provided by Fala (2008) and Fala et al. (2008).



Figure 1. Conceptual model for the heterogeneous waste rock pile simulations for Case 1A and 1B. Case 2 assumes a mixed (unstructured) heterogeneous system. Only the right half symmetric section is simulated.

Table	1.	Summary	of	major	system	variables	for	the
numer	ical	simulation	s.					

Parameter	Value
Porosity (θ)	0.30
Henry's constant (<i>H</i> ; c _{air} /c _{water})	33.2
Temperature	10.0 °C
Waste rock bulk density (ρ_b)	1836. kgm ⁻³
Oxygen diffusion coefficient through mineral grains (<i>D</i> ₂)	10 ⁻⁷ m ² yr ^{-1 (1)}
Dispersivities (α_L , α_T)	0.5 m, 0.05 m ⁽²⁾
Diffusion coefficient of chemical species in water (D_d)	0.005 m ² yr ⁻¹

(1) From Romano et al. (2003) and Wunderly et al. (1996) who used 1x10⁻⁷ to 3x10⁻⁷ m²/yr for tailings; and Gerke et al. (1998) who used 10⁻³ m²/yr for waste overburden.

(2) Based on system scale; see, for example, Gerke et al. (1998), and Schulze-Makuch (2005)

Water content is determined by the flow solution and controls the effective oxygen diffusion coefficient D_e , which is calculated using the Aachib et al. (2004) model based on an oxygen diffusion coefficient in air of $D_a = 1.8 \times 10^{-5} \text{ m}^2/\text{s}$, and that in water of $D_w = 2.1 \times 10^{-9} \text{ m}^2/\text{s}$ (Fredlund and Rahardjo, 1993).

Execution times for a 12-component, 20-year simulation using a Pentium IV, 3.3Ghz machine were on the order of 48 hours.

Component	Background mol/L	Recharge Conc. mol/L
Ca ²⁺	9.8e-03	2.0e-05
Mg ²⁺	2.2e-03	2.0e-05
Na ⁺	1.1e-03	7.0e-05
K ⁺	5.0e-04	5.0e-06
Cl	5.0e-04	2.0e-05
CO3 ²⁻	1.7e-06	2.0e-05
SO4 ²⁻	1.1e-02	7.4-05
Mn ²⁺	1.6e-04	1.0e-06
H ₄ SiO ₄	1.9e-03	1.0e-08
Fe ²⁺	1.7e-05	2.2e-16
Fe ³⁺	2.8e-16	1.0e-08
Al ³⁺	4.7e-13	1.0e-10
рН	7.0	7.0

Table 2. Background and recharge concentrations

4 CONCEPTUAL MODEL 1: HORIZONTALLY STRATIFIED WASTE ROCK PILE

The spatially-correlated distributions of selected physical parameters (grain radii and sulphide fraction) for Conceptual Models 1A and 1B are shown in Figure 2. The input parameters were generated to be strongly correlated in the horizontal direction, with the grain radii varying from 0.1 mm to 1 mm and the sulphide fraction varying from 1 to 5%. In this example, an inverse correlation was assumed between the grain radius and the sulphide mineral fraction. Other correlations are also possible and are currently being analysed.

The steady state moisture content, velocity field and selected flow lines for Model 1A (high recharge) are also provided in Figure 2. The simulated moisture content distribution varies from about 0.01 to 0.1 and also shows a strong horizontal correlation. The flow field is predominantly downward, but shows significant local deviations which are caused by the material stratification.

Selected results for the reactive transport simulation of Case 1A are provided in Figure 3, showing oxygen, pH, sulphate and Fe(II) after 20 years. Although the water content is highly variable, it is relatively low (<10%) thus the effective oxygen diffusion rate is governed primarily by the higher diffusion rate through the air phase. As a result, the oxygen concentrations in the air phase are relatively uniformly dispersed, showing no clear influence from the moisture content distribution.

By 20 years, the oxygen concentrations have reached a steady state distribution, decreasing from the fixed atmospheric concentration at the pile surface (0.26 mg/L) to about 0.14 mg/L in the interior. Diffusion from the outer surface is thus balanced by oxygen consumption in the interior of the waste rock pile.



Figure 2. Case 1A: Grain radii, sulphide fraction, water content and velocity field.



Figure 3. Case 1A: Simulated oxygen (in air phase), pH, sulphate and iron after 20 years.

After 20 years, the pH remains buffered at about 2.8 throughout a large part of this pile. Where the sulphide oxidation rate is high and the buffering minerals have been depleted, the pH drops to about 2.5. Most of the acidity originates from the surface of the waste rock pile and propagates downward with the flow system. Low-pH sources are created at the pile surface in localized areas where oxygen concentrations and the sulphide fraction are high and where the grain radii are small which provides a large reactive surface area.

In other areas, three relatively less acidic zones (pH of 4-5) can be seen where the sulphide minerals have not been as extensively oxidized due to larger grain diameters (and thus a lower surface area per volume) and lower sulphide content. Sulphate and iron concentrations can be correlated to the pH distribution, with high concentrations coinciding with the low pH zones, and with lower concentrations within the three relatively less active flow zones of more neutral pH.

As the pH drops due to sulphide mineral oxidation, the carbonate buffer minerals become depleted. This is most clearly seen in the calcite distribution of Figure 4 which shows the progressive depletion of calcite from 1-4 years. At early time (<2 years), the calcite depletion zones appear to advance horizontally inward from the outer surface, and follow the zones of higher sulphide fraction and smaller grain size. This pattern suggests that dissolution is controlled at early time (>2 years) the influence of the low-pH preferential flow zones can be seen as the calcite depletion zones extend downwards following the low-pH drainage water.



Figure 4. Case 1A: Simulated calcite concentrations at 1, 2 and 4 years, showing calcite dissolution due to acidic mine drainage.

In Model 1B, with a lower recharge rate (but with identical grain size and sulphide fraction distributions), the simulated water content values are lower, with peak values of only about 6% (Figure 5). The flow system again shows mostly downward flow, but with some preferential flow focussing along the horizontal stratifications.

With a lower water content in this case, oxygen advances slightly further into the waste rock pile relative to Case A (Figure 6). After 20 years, the steady state minimum oxygen concentration at the pile core is therefore relatively higher at 0.17 mg/L. In addition, the pH is relatively lower everywhere within the pile, while the sulphate and iron concentrations have significantly increased. The aqueous components again follow the flow field, producing concentration distributions clearly different from Model 1A.



Figure 5. Case 1B (lower recharge): Water content and flow system (the grain radii and sulphide fractions in Case 1B are identical to those in Case 1A).

5 CONCEPTUAL MODEL 2: MIXED CORRELATION WASTE ROCK PILE

The grain radius, sulphide fraction, water content and flow system for the mixed correlation model are provided in Figure 7. In this case, there is no clear horizontal stratification. However, the grain size is generally coarser towards the base and toe of the pile.

Although the water content variability is similar to Case 1A (but without horizontal structure), the rate of oxygen consumption is clearly higher since the minimum steady state oxygen concentration has decreased to about 0.08 mg/L (Figure 8). This trend of higher oxygen consumption in Model 2 is likely due to the combination of smaller grain size (which increases the reactive surface

area) and higher sulphide mineral fractions toward the core of the waste rock pile.

In this mixed (unstructured) case, the pH has decreased even further compared to the structured Models 1A and 1B, and the concentrations of sulphate and iron, especially in the left half of the domain, are significantly higher. These trends are consistent with the higher oxygen consumption rate which coincides with the zone of smaller grain size and higher sulphide mineral fraction.

As the low pH drainage water percolates through the pile, calcite is gradually dissolved, becoming completely depleted from the left half of the pile within 4 years (Figure 9).



Figure 6. Case 1B (lower recharge): Simulated oxygen, pH, sulphate and iron after 20 years.



Figure 7. Case 2 (unstructured waste rock pile): Grain radii, sulphide fraction, water content and velocity field.

6 DISCUSSION & CONCLUSIONS

Sulphide mineral oxidation and generation of acid mine drainage within heterogeneous and reactive waste rock piles are complex processes which depend on the spatial distribution of the physical, geochemical and hydraulic properties.

While the rate of oxygen diffusion through an unsaturated waste rock pile depends on the moisture distribution, at relatively low water contents the effect of water content on oxygen diffusion appears relatively weak. In these cases, the rate of oxygen advance into the waste rock pile, and thus the oxygen concentrations, appear more sensitive to the oxygen consumption rate due to sulphide oxidation, which is governed primarily by the grain size distribution (through the reactive surface area) as well as the sulphide mineral fraction. In the cases studied here, which assumed an inverse correlation between the grain size and the sulphide fraction, the effects of these parameters are compounded since both a small radius and high sulphide fraction increase the degree of oxidation. For specific case studies, the correlation between grain size and the sulphide fraction (whether positive, negative or absent) should be quantified.

The influence of water content is expected to be more important at higher water contents and in systems with positive or no correlation between grain size and sulphide content.



Figure 8. Case 2 (unstructured waste rock pile): Simulated oxygen, pH, sulphate and iron after 20 years.



Figure 9. Case 2 : Simulated calcite concentrations at 1, 2 and 4 years, showing calcite dissolution due to acidic mine drainage.

The simulations have shown that drainage from structured waste rock piles with horizontal stratification may be less acidic relative to poorly structured piles (i.e. without strong horizontal stratification). This appears partly the result of the tendency in the unstructured pile considered here towards higher sulphide content and smaller grain radii near the outer pile surface toward the top of the pile, which promotes sulphide oxidation. In the horizontally structured case, the zones of high sulphide fraction and low grain radii are distributed more deeply within the pile, delaying the rate of oxidation.

While the lower recharge rate scenario in the horizontally structured waste rock pile (Model 1B) produced somewhat lower pH values relative to the higher recharge case (Model 1A), the volumetric discharge was also less. Drainage from the unstructured case (Model 2) was the most acidic, and since this case also has a higher recharge rate, the unstructured waste rock pile represents the worst case scenario of the three simulations.

Work is currently in progress to compare these types of conceptual simulations with observed field data, including water content derived from geophysical resistivity profiles (e.g. Chouteau et al. 2006).

The results have shown the utility of reactive transport modelling for assessing the influence of pile structure on the generation and fate of acid mine drainage. Further work is underway to include transient flow and to quantify and compare mass and acidic flux rates.

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