CONCEPTUAL AND NUMERICAL MODELS OF OXYGEN DIFFUSION, SULPHIDE OXIDATION AND ACID MINE DRAINAGE WITHIN DISCRETELY FRACTURED POROUS MEDIA

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ABSTRACT
The generation and transport of acid mine drainage (AMD) through discretely fractured porous media is simulated for two reactive mine waste systems. The first conceptual model is based on desiccated reactive paste tailings, such as those produced at the Bulyanhulu Mine, Tanzania, Africa. These tailings are deposited in successive layers as a thickened paste, which drain, consolidate and dry out by evaporation, leaving desiccation cracks on the order of several millimeters wide, up to 1 m deep (depending on layer thicknesses) and fracture spacing on the order of 0.2 - 2 m. The second conceptual model considers a deposit of reactive tailings overlying a fractured rock mass. Both modelling approaches consider oxygen diffusion, sulphide mineral oxidation, geochemical speciation and advective-dispersive transport within discretely fractured media. The paper addresses issues of time scales and AMD fluxes, assuming various fracture scenarios.

RÉSUMÉ
La génération et le transport des produits issus du drainage minier acide (DMA) dans un milieu poreux fracturé est modélisé pour deux systèmes comprenant des résidus miniers réactifs. Le premier modèle conceptuel est basé sur des résidus en pâte déposés en surface qui se sont asséchés, comme ceux produits au site de la mine Bulyanhulu en Tanzanie (Afrique). Ces rejets de concentré épaisse sont déposés en plusieurs couches qui se drainent, se consolident et s’assèchent par évaporation, ce qui laissé apparaître des fentes de retrait. Ces dernières ont une largeur de quelques millimètres, une profondeur pouvant atteindre environ 1 mètre (selon l’épaisseur des couches déposées) et un espacement variant entre 0,2 et 2 mètres. Le deuxième modèle présenté ici étudie le comportement de résidus miniers réactifs placés au-dessus d’un massif rocheux fissuré. Dans ces deux cas, les modèles incluent la diffusion de l’oxygène, l’oxydation des minéraux sulfureux, la spéciation géochimique, et le transport advectif et dispersif dans le milieu fracturé. Cet article s’attarde plus particulièrement aux effets du temps et aux flux de DMA, en supposant différentes conditions.

1. INTRODUCTION
Acid mine drainage (AMD) is generated from the oxidation of sulphide minerals within mine wastes and is usually characterized by low pH and high concentrations of sulphate, iron and heavy metals (Aubertin et al., 2002; Ptacek & Blowes, 2003). The environmental impact of AMD depends not only on the mineralogical and physical composition of the tailings, but also on the pathway of the AMD to receptors such as surface water or water supply wells.

Transport of AMD occurs first through the reactive source waste material. If not contained, it can then migrate through several possible paths including direct runoff to surface water, or through a permeable subsurface pathway, for example a porous aquifer, or through bedrock. Since pathways through bedrock often include flow through fractures, the behaviour of AMD through fracture networks can be an important consideration for determining environmental impacts. At a smaller scale, the tailings themselves can also be cracked or fractured as a result of drainage, consolidation and desiccation.

In this paper, we will address the issue of AMD generation and transport through two conceptual models of discretely fractured porous media. To date, research into AMD behaviour within fractured systems has been scarce. Understanding these and other AMD processes is important for improved mine waste management and is a critical concern of the Canadian mining industry (Aubertin et al., 2002).

2. MODELLING APPROACHES
A variety of groundwater flow and transport models exist for simulating acid mine drainage, but most do not consider discretely fractured systems. MacQuarrie and Mayer (2005) provide a thorough overview of recent developments in simulating reactive transport in fractured media. They identify important concepts and needs, and review various modelling approaches.

Generation of acid mine drainage begins with the diffusion of oxygen into the reactive waste, where it is consumed by oxidation of sulphide minerals. For pyrite, the reaction can be expressed according to:

$$\text{FeS}_2 + \frac{1}{2}\text{H}_2\text{O} + \frac{15}{4}\text{O}_2 \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + \text{H}^+$$  \hspace{1cm} (1)
The aqueous oxidation products are then transported by advection and dispersion through the water phase. For a saturated porous medium, transport is governed by:

\[
\frac{\partial \theta_{\text{w}} C_i}{\partial t} - \frac{\partial}{\partial x_i} \left( \theta_{\text{w}} D^i \frac{\partial C_i}{\partial x_i} \right) - \frac{\partial}{\partial x_i} \left( q_i C_i \right) + R_k = 0 \tag{2}
\]

where \(C_i\) is the concentration of the \(k\)th component in the pore water \([\text{ML}^{-3}\text{T}^{-1}]\), \(\theta_{\text{w}}\) is the water filled porosity, \(q_i\) is the \(i\)th component of the Darcy flux \([\text{LT}^{-1}]\), \(D^i\) is the dispersion coefficient tensor \([\text{LT}^{-1}]\), \(R_k\) is a source/sink term resulting from geochemical reactions \([\text{ML}^{-3}\text{T}^{-1}]\), \(x_i\) are the spatial coordinates (L), and \(t\) is time (T).

The corresponding governing equation for mass transport within a 1D fracture can be written as (Yang, 2006):

\[
\frac{\partial C'}{\partial t} + \frac{\partial (\nabla C')}{\partial x_i} - \frac{\partial}{\partial x_i} \left( D^i \frac{\partial C'}{\partial x_i} \right) - \frac{D^i}{b} \left[ \frac{\partial C}{\partial z} \right]_{z=b} = 0 \tag{3}
\]

where \(C'\) is the concentration in the fracture, \(C\) is the concentration in the porous matrix, \(\nabla_i\) are the flow velocities in the fractures \([\text{LT}^{-1}]\), \(D^i\) is the dispersion coefficient and \(b\) is the half-fracture aperture (L). The last term on the left hand side of (2) represents the mass loss from the fracture to the adjacent porous matrix.

Several fracture flow and transport models have been developed over the past decade, including for example, those by Molson & Frind (1994), Therrien & Sudicky (1996), Yang (2006) and Brouyère (2006). The modelling approaches generally vary in terms of processes considered, dimensionality, numerical solution method and to whether fractures are incorporated as part of a dual-continuum medium or as discrete features within a porous matrix.

One of the more advanced models for simulating flow and transport through porous and discretely fractured porous media is FRAC3DVS (Therrien & Sudicky, 1996). This code has recently been adapted to handle inclined fractures (Graf and Therrien, 2005), and can simulate some types of reactive systems (Ghogomu and Therrien, 2000); however it has not yet been applied to simulate pyrite oxidation and acid mine drainage systems.

In addition to new models for fracture flow and transport, advances are also being made for simulating reactive mass transport in heterogeneous porous media. One of the most advanced models in this category is MIN3P (Mayer et al., 2002) which is a fully coupled simulator for variably saturated flow and multi-component transport with generalized kinetic and/or equilibrium controlled chemical reactions. Applications of this model include a study of environmental impacts caused by closure of a former uranium mine (Bain et al. 2001). MIN3P is currently limited, however, to unfractured porous media. Other models such as TOUGHREACT (Xu et al., 2006) can also handle complex acid mine drainage systems, however fractures are represented using a multiple interacting continua approach; discrete fractures are not considered. Mayer et al. (2003) provide a review of these and other modelling approaches for AMD problems. Most of these models are by their nature, very complex and require significant computational resources.

In the current paper, we will use two somewhat more simplified approaches for simulating AMD in fractured systems. The first approach uses the flow model HYDRUS-2D (Simunek et al., 1999) and the transport model POLYMIN (Molson et al., 2005), with the fractures discretized directly using the finite element mesh, while the second approach uses a coupled version of the HEATFLOW/MINTRAN models (Molson et al. 1992; Walter et al., 1994) for simulating kinetic sulphide oxidation and geochemical speciation with discrete fracture elements embedded directly into the porous media mesh.

The discrete fracture version of the HEATFLOW model was first presented by Molson & Frind (1994), and has since been applied to simulate temperature-dependent geochemical reactive systems (Molson et al., 1994) and density-dependent hydrothermal systems (Yang et al., 1996). It has most recently been adapted for coupled thermal/brine transport in large scale fractured geologic media by Yang (2006). The MINTRAN model uses the geochemical speciation code MINTEQ/A2 (Allison et al., 1991) and was modified and applied by Gerke et al. (1998) to simulate AMD and transport through reactive overburden mine waste. In both approaches, kinetic sulphide mineral oxidation is simulated using the shrinking core model which assumes oxygen diffusion (at a rate \(D_o\)) and sulphide oxidation occur within an outer oxidized rim of spherical particles (Levenspiel 1972; Davis and Ritchie 1987). Thus, as oxidation continues, the unoxidized core radius and reaction rate decrease. The sequential non-iteration approach (SNIA; see Steefel and MacQuarrie, 1996) is used to couple the physical transport domain with the chemical domain.

The primary limitations of the approaches adopted here are: the systems are 2D, the geochemical reactions (speciation, dissolution, precipitation) are equilibrium controlled (except for oxidation which is kinetic), flow is steady state, density effects are not considered, the fractures are open with constant fracture apertures and there is no infilling due to mineral precipitation or widening due to dissolution.

3. CONCEPTUAL MODEL 1

3.1 Overview

Development of the first conceptual model was motivated by the paste tailings at the Bulyanhulu gold mine, Tanzania, Africa (Figure 1). The Bulyanhulu tailings contain up to 80% silicates, 1-12% pyrite and 5% carbonates (calcite, dolomite ankerite); they are deposited...
as a thickened paste slurry in sequential layers up to 1m thick (Theron et al., 2005; Martin et al., 2006). Consolidation, drainage and evaporation cause desiccation cracks to develop at the tailings surface, with apertures up to 2-3 cm, and with fracture spacing on the order of 20-200 cm. Open and dry fracture surfaces are exposed to atmospheric concentrations of oxygen; however, the effect of this enhanced oxygen availability on oxygen fluxes into the partially saturated tailings and on internal oxidation rates remains uncertain. Tailings consolidation and development of the desiccation cracks themselves are being addressed in other studies and will not be considered here.

This conceptual model is considered most representative of the final, exposed tailings layer, as the deeper layers are usually covered within about 30 days, thus limiting oxygen availability.

In this preliminary approach, the flow system is assumed at steady state, under fully drained conditions. The model is designed primarily as a basis for further study which would include coupling of the geochemical processes with consolidation, transient flow and desiccation. Adapting the approach to handle kinetic geochemical speciation will be a further objective.

The reactive transport simulations were made assuming the tailings are of uniform grain size ($d_{50} = 0.023$ mm, from laboratory data) with a porosity of 0.4 and a bulk density of 1680 kg/m$^3$. The mineralogy is assumed dominated by silicates, with 10%(vol.) pyrite as well as some minor calcite and secondary gibbsite and gypsum. Ferrihydrite and jarosite are not present initially but are allowed to precipitate. A similar geochemical conceptual model was applied to interpret AMD from laboratory tailings columns by Jurjovec et al. (2002).

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Longitudinal and transverse dispersivities are 0.1m and 0.01m, respectively, with a diffusion coefficient for all dissolved species of 1.4$\times$10$^{-5}$ m$^2$/d. The bulk oxygen diffusion coefficient is dependent on the water content (after Millington & Quirk, 1961; see also Ritchie, 2003). A uniform temperature of 25ºC is assumed. Two examples will be shown which use different oxygen diffusion coefficients through the oxidized rim of the grains ($D_2$): in Case A, $D_2 = 10^{-8}$ m$^2$/d and in Case B, $D_2 = 10^{-9}$ m$^2$/d.
3.3 Simulation Results

The simulated moisture distribution (assumed identical for Case A and B) shows the water content ranging from about 0.05 (12% saturation) at the top to about 0.20 (50% saturation) at the base of the 2m-thick layer. The fractures are assumed to remain water-free.

In the simulation of Case A (Figure 3), the oxygen diffusion profile after 36 days shows distinct diffusion halos surrounding each open fracture but only limited downward advancement of the oxygen front due to oxygen consumption during oxidation of the pyrite. The oxygen profile is essentially at a quasi-steady state, having been attained within a few days and remaining fairly constant for the 36-day simulation.

Figure 3. Numerical simulation of acid mine drainage from a fractured tailings deposit; Case A: $D_2 = 10^{-8}$ m$^2$/d; water content at steady state, oxygen, pH, sulphate concentration and unoxidized core radius at 36 days.

Figure 4. Numerical simulation of Case A; concentrations of selected minerals at 36 days.

Figure 5. Numerical simulation of acid mine drainage from a fractured tailings deposit; Case B: $D_2 = 10^{-9}$ m$^2$/d; oxygen, pH, sulphate and unoxidized core radius at 36 days.
As the pyrite is oxidized, the pH decreases to a low of about 2.3, and sulphate concentrations increase to about 40 g/L. Note that the lowest pH occurs along the margins of each fracture and in a zone about 20 cm down from the top surface. At ground surface, the pH has begun to recover slightly as the unoxidized core radius of the particles decreases and the reaction rate slows down. The model also simulated calcite dissolution, siderite precipitation at the leading edge of the calcite dissolution zone, gibbsite dissolution and ferrihydrite precipitation (Figure 4).

In Case B (Figure 5), in which the oxygen diffusion coefficient into the unoxidized rim ($D_2$) is reduced by a factor of 10, the oxygen front has advanced significantly further into the tailings. The minimum pH is somewhat higher at 3.1, and the maximum sulphate concentration is only 7 g/L. Although the pH in Case B has not dropped as low as in Case A, the low pH front in Case B, delimited by pH < 7, appears further advanced. With the lower $D_2$ value of Case B, less oxygen is consumed near the top of the tailings, allowing the oxygen front to advance further and causing increased oxidation deeper in the pile, thus lowering the pH in these deeper zones of Case B relative to Case A.

These results have provided a preliminary idea of the possible behaviour of desiccated tailings, however further insights will require comparisons with field data and more advanced conceptual models coupled to consolidation.

4. CONCEPTUAL MODEL 2

4.1 Overview

The second conceptual model considers a layer of reactive tailings overlying a fractured host rock (Figure 6). This situation may occur, for example, with above ground or open pit disposal or as in-mine waste disposal (as paste backfill) where the host rock is naturally or artificially fractured (e.g. mine-blast-induced). The tailings saturation is assumed constant while the underlying fractured rock mass is assumed saturated. A uniform background temperature of 10°C is assumed.

4.2 Simulation Approach

The system is considered in the 2D vertical plane, with a random fracture network for the base case (Case 2a) as shown in Figure 6. The domain measures 20 m × 5 m and is resolved using a grid of 100 × 50 deformable rectangular elements in the horizontal and vertical dimensions, respectively (the model is 3D but we will use here a single element in the transverse direction).

The intact rock matrix porosity is 0.1 and the hydraulic conductivity is $1.0 \times 10^{-9}$ m/s. The porosity and conductivity of the non-fractured porous buffer layer between the tailings and rock are 0.35 and $1.0 \times 10^{-9}$ m/s, respectively. The longitudinal and transverse hydrodynamic dispersivities are 1.0 and 0.01 m, respectively.

The simulation includes 15 aqueous components: Ca, Mg, Na, K, Cl, CO$_3$, SO$_4$, Mn, H$_2$SiO$_4$, Fe(II), Fe(III), Al, Cr, Pb, and H. These components are initially at equilibrium with the background host rock which is composed of 10 minerals, including about 60% silicates, with some calcite, siderite, ferrihydrite, gypsum and gibbsite.

The fracture network, generated using the NETWORK model (Molson, 2006) has log-normally distributed apertures with a mean aperture of 500 µm. A steady surface infiltration rate of 250 mm/yr is applied across the top boundary, and the right face is assigned a fixed head of 5.0 m, giving an average horizontal gradient of 0.00025 with flow from left to right. The left boundary and base are assumed impermeable. A thin non-reactive buffer layer was placed in the model below the tailings to allow recharge to naturally distribute into the fractures.

The tailings AMD source term was generated using the PYROX model (Wunderly et al. 1996), assuming a sulphide mineral volume fraction of 10%, a diffusion coefficient into the oxidized shell of $D_2 = 1.0 \times 10^{-9}$ m$^2$/d a uniform water content of 10%, a grain size of 0.1 mm, a bulk density of 1680 kg/m$^3$ and a porosity of 0.3. The tailings source extends over one-half of the upper model surface.

Two fracture networks are considered: Case 2a with a relatively sparse network, and Case 2b with a denser network. The model was run for 600 days with variable time steps increasing from 0.1 to 2 days. Simulation times were about 4 hours on a Pentium III, 2 GHz machine.

4.3 Simulation Results

The results for selected components after a 600 day simulation clearly show the effect of the fracture network (Figure 7). After 600 days, the minimum pH is about 4.3, and a zone of pH < 5 extends throughout the tailings and porous buffer zone. The acidic pH front (pH < 7) has advanced into the fracture network, reaching the bottom of the rock unit, and extending about 4 m downgradient of the source edge. Since the pH is buffered by the carbonate minerals of the fractured host rock, it advances at a relatively slow rate.
The oxidation product of sulphate, in comparison, is relatively unretarded and migrates further into the fracture network. Although some sulphate is removed by gypsum precipitation (not shown) the effect is not significant in this case and sulphate migrates almost as far as the chloride conservative tracer (not shown).

Iron, also an oxidation product of pyrite oxidation, is more retarded since a significant amount is precipitated as siderite (and some as ferrihydrite), at the advance of the calcite dissolution front. Under these saturated, oxygen-poor conditions within the rock, most of the iron remains in its reduced form Fe(II).

Finally, the infiltration of low pH AMD water creates a calcite dissolution front below the source and extending into the fracture network. The limit of the depletion zone, within which calcite has been completely dissolved, can be correlated to the low pH impacted area. Although calcite is dissolved here, the simulation approach assumes the fracture apertures are not affected. This is a reasonable assumption in this case since calcite forms less than 2% of the rock volume.

In Case 2b (Figure 8), a similar behaviour is observed. However, with the denser fracture network, the oxidation products disperse more widely and hence do not advance as deep or downgradient as in Case 2a. The AMD component plumes are almost behaving as if within an equivalent homogeneous porous medium.

In all simulations, the width of the calcite depletion zone along each discrete fracture is well constrained by the small grid size. Although most alteration in reality would occur along the fracture walls, diffusion of dissolved components into the matrix can also occur which could widen the alteration zone. The results show that artificial dispersion has been well controlled and the reaction fronts have remained sharp.

5. CONCLUSIONS
The preliminary results shown here suggest that in principle, the adopted numerical approaches function well, with open fractures either resolved by the mesh...
The primary limitation is the assumption of geochemical equilibrium with the discrete fracture approach (model 2). Higher groundwater velocities through the fractures will likely prevent attainment of equilibrium in the field, especially with respect to silicate minerals, and will therefore require a kinetic rate approach for more realistic geochemical behaviour.

The advantage of a mixed kinetic oxidation and equilibrium geochemical approach is that kinetic rates (which are often unknown or highly uncertain) are not required, and execution times are much faster, thereby allowing much finer spatial resolution. This is critical, especially for reactive transport in fracture networks, since the behaviour of a geochemical system depends on the degree of mixing of the aqueous components. Finer grids allow smaller, more realistic dispersions while limiting numerical dispersion.

The HEATFLOW/MINTRAN Model in Case 2 can also include thermal transport and feedback of mineral precipitation and dissolution on fracture apertures; this will be the focus of further work.

The simulations presented here are not meant to represent specific cases, but rather to illustrate how somewhat similar systems may behave.

6. ACKNOWLEDGEMENTS

This research was financially supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) and by the partners of the Industrial NSERC Polytechnique-UQAT Chair in Environment and Mine Wastes Management (www.polymtl.ca/enviro-geremi).

7. REFERENCES


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