

A Multicomponent Reactive Transport Modelling Toolbox for Prediction of Drainage Quality from Mine Waste Facilities

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Abstract

This study presents a new multiphase multicomponent mine-waste simulator, which is capable of capturing variably saturated water flow, multicomponent advective-dispersive transport both in aqueous and gaseous phase, and chemical reactions (solved with PHREEQC, utilizing PhreeqcRM module) including thermodynamic databases. We particularly emphasize on the Nernst-Planck and Maxwell-Stefan based formulations for the aqueous and gaseous transport, respectively, to explicitly resolve the multilevel process coupling, driven by solute/surface charge or gaseous pressure, across and within different phases. This framework radically goes beyond the state-of-the-art of classical mine-waste models, which exclusively rely on Fickian transport and capture only a subset of governing processes.

Keywords: Acid Rock Drainage, Nernst-Planck Equation, Maxwell-Stefan Equation, Reactive Transport Modelling, Lysimeter Experiment

Introduction

Management of mine wastes represents a key challenge in mining industry because uncontrolled disposal of such extractive materials, which typically have no value or even a negative value when they pose a threat to the environment, may result in liability for the operators with the risk of financial consequences and reputational damage (e.g. Blowes et al. 2014, Nordstrom et al. 2015). Of primary concern is the generation of acidity in the pore water, the release and mobilization of toxic metals and metalloids, and the subsequent leaching of contaminated drainage from these waste systems (e.g. Muniruzzaman et al. 2018a,b). Propagation and spreading of such mining-influenced acid rock drainage (ARD) in waterborne environments have the potential to severely contaminate ground- and surface water resources in the proximity of a mine site (e.g. Amos et al. 2015, Battistel et al. 2019). Despite the fact that the individual processes responsible for the generation/propagation of ARD is fairly well-known, the prediction of overall behavior in a mine-waste system

is challenging due to nonlinearity and multilevel coupling associated with these physiochemical mechanisms. Reactive transport models proved to be instrumental in describing such systems but most of the published mine-waste simulators mainly focus on the formulation based on Fick's law and consider only a subset of the key processes. In fact, to the best of our knowledge, a simulator rigorously capturing the simultaneous effects of the inherent inter- and intra-phase process coupling is still missing although processes such as gaseous movement due to compositional changes on pressure (e.g. van Berk and Wisotzky 1995) and/or electrostatic interactions induced by ionic charge or charged surfaces (e.g. Appelo and Wersin 2007, Rolle et al. 2013, Muniruzzaman et al. 2014) are extensively explored in the geochemical literature and their relevance on multicomponent transport is increasingly recognized.

In this work, we propose a new three-phase multicomponent reactive transport modeling toolbox taking into account the variably saturated water flow,

multicomponent advective-dispersive transport both in aqueous and gaseous phase, and geochemical reactions including thermodynamic databases. The modeling approach is based on the Nernst-Planck equation for aqueous species' transport, and Maxwell-Stefan formulation for gaseous transport to explicitly capture the species-species coupling due to solute/surface charge or gas phase pressure. The chemical reactions, including mineral dissolution/precipitation, are solved with PHREEQC (Parkhurst and Appelo 2013), utilizing PhreeqcRM (Parkhurst and Wissmeier 2015) module and taking advantage of the capabilities of coupling this geochemical simulator with the flow and transport code (e.g. Muniruzzaman and Rolle 2016, 2019, Sprocati et al. 2019). The proposed tool is applied to interpret a series of datasets collected in pilot-scale lysimeter setups packed with waste rocks from two different mine sites in Finland. These experiments involve extensive monitoring of lysimeter drainage compositions for a period of more than three years.

Modelling Approach

The water flow in partially saturated mine wastes is typically described by the Richards equation:

$$\frac{\partial \theta^w}{\partial t} - \nabla \cdot [\mathbf{K}(h)(\nabla h + \nabla z)] = Q_s \quad (1)$$

where θ^w is the water filled porosity, h is the pressure head, \mathbf{K} is the tensor for unsaturated hydraulic conductivity (which is a function of h and θ^w), Q_s is the source/sink term, and t is time.

The governing equation for multicomponent aqueous and gaseous transport including Coulombic interactions, interphase mass-transfer, and geochemical reactions can be written as:

$$\frac{\partial(\theta^w c_i^w)}{\partial t} + \frac{\partial(\theta^g c_i^g)}{\partial t} + \nabla \cdot (\mathbf{q}^w c_i^w) + \nabla \cdot (\mathbf{q}^g c_i^g) - \nabla \cdot (\theta^w \mathbf{J}_i^w) - \nabla \cdot (\theta^g \mathbf{J}_i^g) = \sum_{r=1}^{N_r} v_{ir} R_r \quad (2)$$

where θ^g is the gas phase porosity, c_i^w and c_i^g are the aqueous and gaseous concentrations (which are connected via Henry's law: $c_i^g = H_1 c_i^w$ with H_1 being the dimensionless Henry's law coefficient), \mathbf{q}^w and \mathbf{q}^g are the specific discharge vectors in each phase, \mathbf{J}_i^w and \mathbf{J}_i^g are the vectors for diffusive/

dispersive fluxes, R_r is the reactive source/sink term, and v_{ir} is the stoichiometric coefficient. The most distinctive feature of the proposed modeling approach is associated to the explicit incorporation of intra- and interphase coupling, mainly caused by ionic/surface charge or gaseous pressure, between different aqueous and gaseous solutes. Instead of using Fick's law, which is a common practice in classic mine waste simulations, we adopt the Nernst-Planck equation (e.g. Appelo and Wersin 2007) for the movement of aqueous species, and the Maxwell-Stefan equation (e.g. Krishna and Wesselingh 1997) for the gaseous species' transport (fig. 1):

$$J_i^w = -D_i^w \left(\frac{\partial c_i^w}{\partial z} + c_i^w \frac{\partial \ln \gamma_i^w}{\partial z} + \frac{\zeta_i F}{RT} c_i^w \frac{\partial \varphi}{\partial z} \right) \quad (3)$$

$$- \sum_{j=1, j \neq i}^N \chi_j^g J_j^g - \chi_i^g J_i^g + \frac{J_i^g}{D_i^g} = - \left(\frac{\partial c_i^g}{\partial z} + \frac{M_i^g c_i^g g}{RT} \right) \quad (4)$$

where D_i^w is the hydrodynamic self-dispersion coefficient of species i (i.e. when ion i is electrostatically "liberated" from the other charged solutes in a multicomponent environment), γ_i^w is the activity coefficient, ζ_i is the charge number, F is Faraday's constant, R is ideal gas constant, T is the temperature, φ is the electrical potential (induced by the different mobility of dissolved charged species or by the external electric field), D_i^g and D_i^K denote, accordingly, the binary Maxwell-Stefan and Knudsen diffusion coefficients, g is the gravitational acceleration, χ_i^g is the mole fraction in the gas phase, and M_i^g is the molecular weight. The advection terms in both phases (Eq. 2) are described by the Darcy's law. This formulation certainly provides an improved representation of the multiphase solute transport processes compared to the Fickian based description, and allows capturing the interdependency between different gaseous and aqueous species' fluxes as well as the resultant coupled movement of the multicomponent solutes in the individual phases (e.g. Krishna and Wesselingh 1997, Muniruzzaman and Rolle 2015, 2017).

We use a cell-centered finite difference method (FD) to numerically solve the water flow (Eq. 1) into variably saturated mine waste systems. In this step, a backward Euler scheme was adopted for the temporal integration,

and the system of equations is solved with the Thomas algorithm in connection with Piccard iteration. In contrast, the multiphase multicomponent reactive transport is solved with the finite volume method (FVM) by adopting a sequential non-iterative operator splitting scheme to decouple the transport and reaction calculations. The latter is handled with the geochemical solver PHREEQC as a reaction engine (e.g. Rolle et al. 2018, Muniruzzaman and Rolle 2019). The coupled system of equations describing the advective-dispersive transport within aqueous and gaseous phases (Eq. 2 to 4) is solved with the direct matrix solver UMFPAK and by utilizing a Piccard iterative scheme. After the computation of flow and transport in a time step, the concentrations are passed to PHREEQC, utilizing PhreeqcRM module, to perform all the geochemical calculations including mineral dissolution/precipitation (e.g. Sprocati et al. 2019, Muniruzzaman et al. 2020). A series of averaging approaches at the numerical cell interfaces, flux computation methods (upwind, central and TVD), time integration schemes (implicit Euler and Crank-Nicolson), and time varying boundary conditions are employed to provide enhanced flexibility and numerical rigor. The entire toolbox is implemented in MATLAB, and further details regarding the implementation steps, numerical solution strategies, and the benchmarking of the different features are presented in a recent study (Muniruzzaman et al. 2020).

Lysimeter Experiments

To demonstrate the capability of the modeling toolbox, we simulate two datasets collected within pilot-scale lysimeter experiments involving different types of waste rocks. The experimental setup is equipped with two cubic lysimeters with dimensions of $1\text{ m} \times 1\text{ m} \times 1\text{ m}$ (fig. 2). The lysimeters were installed, by following the guidelines of MEND, at the premises of Geological Survey of Finland (Kuopio, Finland), and were subjected to outdoor atmospheric conditions. The first lysimeter was packed with the mica schist waste rock samples from the Hitura nickel mine site (northern Ostrobothnia, Finland), whereas the second setup was packed with the olivine pyroxenite containing waste rocks from the Kevitsa nickel-copper mine site (Sondankylä, Finnish Lapland). These waste rocks have distinct properties with a relatively higher sulfide content (2.3%: with 0.86% pyrrhotite, 0.5% pyrite, 0.1% pentlandite and 0.1% chalcopyrite) and no observable carbonate minerals for the Hitura materials but a considerably lower sulfide content ($<0.29\%$: 0.09% pyrrhotite, 0.02% pentlandite, 0.03% pyrite and 0.01% chalcopyrite) and a minor fraction of carbonate minerals (1.3%: with 0.23% calcite, 1.01% dolomite and 0.05% magnesite) for the Kevitsa materials.

The experiments were initiated as the rainwater flushed through the waste rocks within the lysimeters. The drainage samples were periodically collected at the bottom of the setup for a duration of more than three

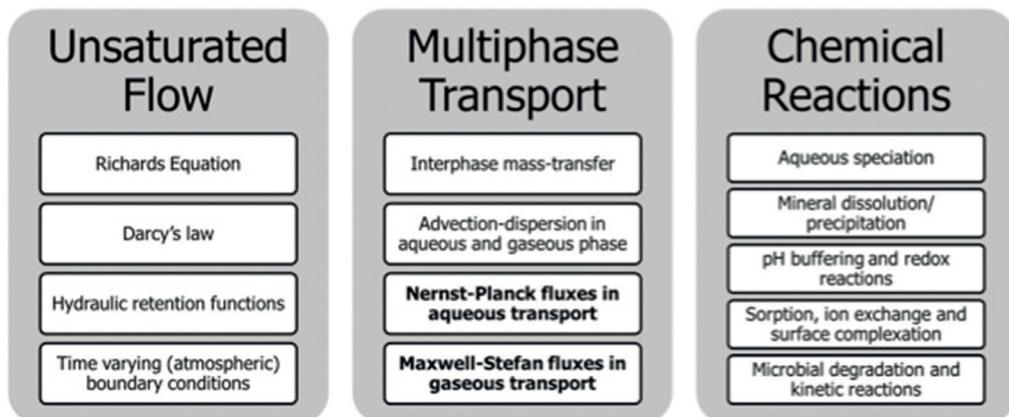


Figure 1 Schematic of the multiphase multicomponent reactive transport modeling toolbox.

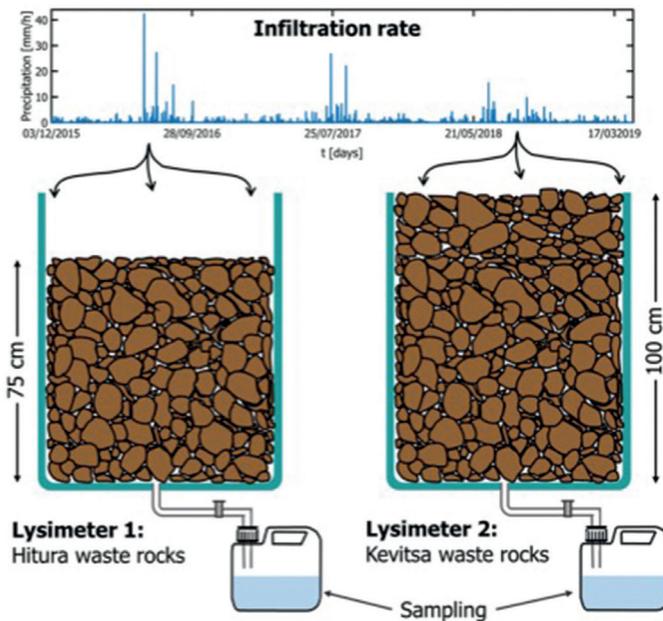


Figure 2 Schematic diagram of the lysimeter experiments.

years (fig. 2). The composition of the effluent samples was measured with ICP-MS, ICP-OES, and ion chromatography (Labtium Oy, Kuopio), whereas the waste rocks' mineralogy was measured with a field emission electron microscope (FE-SEM, JEOL JSM 7100F Schottky with EDS X-Max 80 mm²). As both lysimeters were located at the outdoor environment, we mimic the natural conditions in the simulations by employing a temporally variable water infiltration rate proportional to the observed hourly precipitation rates (Finnish Meteorological Institute, fig. 2, top panel) at the top boundary and a free drainage boundary at the bottom.

Results and Discussion

This section summarizes the results obtained from the lysimeter experiments along with the reactive transport simulations performed

with the proposed approach. Fig. 3 shows a comparison between the measured (markers) and simulated (lines) drainage concentration profiles for both lysimeters. The simulations include advection-dispersion in the water phase, coupled diffusion of gaseous species (O₂, N₂ and CO₂), kinetic dissolution of sulfide, carbonate and a range of silicate minerals (biotite and tremolite in the first lysimeter; and talc, chlorite and serpentinite in the second one), and precipitation of the secondary minerals (Fe(OH)₃, gypsum, jarosite and gibbsite). It is evident that the waste rocks from Hitura mine site lead to a characteristic composition of acid rock drainage as reflected in the low pH (about 4.3) and elevated sulfate concentrations (up to 3000 mg/L) in the effluent (fig. 3a-b). Such behavior is certainly driven by the lower carbon to sulfur ratio (=0.22) of the material,

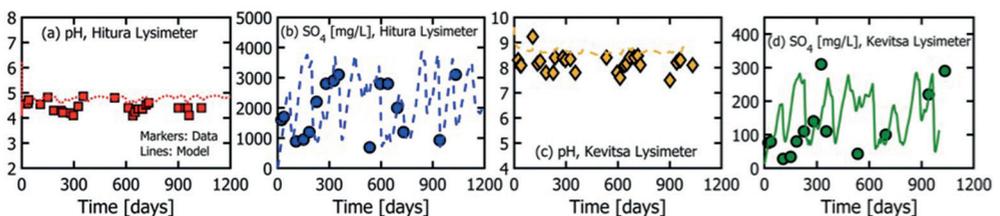


Figure 3 Evolution of the drainage chemistry as a function of time in different experiments.

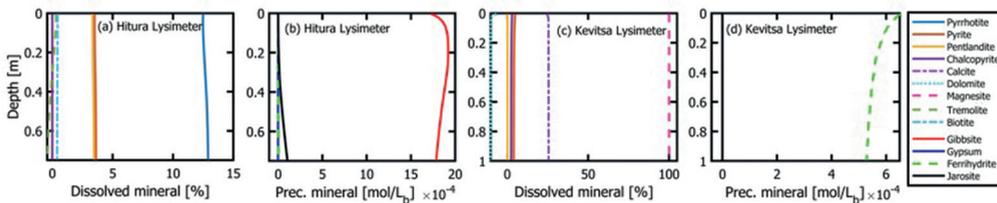


Figure 4 Dissolved/precipitated mineral contents after 1200 days of simulation in different lysimeters.

and indicates ongoing oxidation of the sulfide minerals (fig. 4).

The situation is different in the second lysimeter, where the effluents show basic pH values (>8) due to the presence of the considerable extent of carbonate minerals ($C/S=1.29$) and the subsequent buffering of the acidity. The released sulfate concentrations are also more than an order of magnitude lower compared to the observed values in the first lysimeter (fig. 3b,d). Due to the variation in the atmospheric infiltration rates and the subsequent complex sequence of weathering within waste rocks, a very dynamic pattern is evident in all breakthrough curves shown in fig. 3. However, the model could reproduce very well most of these complex dynamic trends and the concentration ranges in the different breakthrough curves.

The observed behavior in the effluent breakthrough curves is also supported by the acid base accounting (ABA) test, which showed a neutralization potential ratio (NPR) of 0.2 (indicative of potentially acid generating material) for the Hitura waste rocks and 7.4 (indicative of non-acid generating material) for the Kevitsa waste rocks. Dissolution of silicates and the precipitation of secondary minerals can also exert further controls on the buffering of pore water pH and the release and attenuation of the major ions (Ca, Mg and K, results not shown). In fact, the drainage from the Hitura waste rocks show a characteristic pH range (4.3), which is known to be controlled by gibbsite buffering reactions (Dold 2017). The smaller depletion of different minerals at the end of the experiments indicates a rather long lifecycle for the weathering processes in these wastes.

Conclusions

In this study, we have presented a new multiphase multicomponent reactive

transport modeling toolbox specifically tailored for mine waste simulations and capable of taking into account the coupled water-gas movement and a wide range of geochemical reactions in homogeneous and heterogeneous unsaturated porous media. The most unique feature of the proposed approach includes the Nernst-Planck and Maxwell-Stefan based description of the multicomponent solute fluxes, which allows capturing the species-species interactions due to ionic/surface charge and/or gas phase pressure. To demonstrate the capability of the modeling toolbox, we have also presented a series of long-term pilot-scale lysimeter experiments involving mine waste rocks from two different mine sites in Finland. In these experiments, the dynamic evolution of the lysimeter drainage composition was monitored for more than three years in all setups and the potential for a particular waste rock to generate acidic drainage was evaluated. The simulation results reveal that the proposed approach allows us to accurately describe the complex behavior within waste rock systems and to reproduce the experimental observations along with the dynamic trends. Such outcomes verify that the presented toolbox can be effectively used in mine waste applications such as drainage quality prediction from waste dumps (waste rocks or tailings), robust risk analysis in environmental impact assessment, interpretation of lysimeter tests, humidity cell tests or column studies, long-term prediction in a decommissioned pile, early predictions in proposed piles, evaluation of effective remediation options, and design of cover structures. The current formulation provides particular advantages over the classic mine waste or subsurface codes when the specific objective is to capture the involved mechanisms from a process-based

approach. Besides the application examples presented in this study, the proposed tool is also applicable to other complex mine waste settings (e.g. real field-scale piles or sophisticated laboratory experiments) or even generic vadose zone studies (e.g. landfills, biocovers or multiphase transport). Further developments are also envisioned to incorporate non-isothermal heat transport processes, freeze-thaw cycle, coupling between porous media flow and atmospheric free flow, and electrokinetic transport mechanisms, which have implications both in the ARD simulations in Nordic conditions or in engineered remediation.

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