Stochastic multicomponent reactive transport analysis of low quality drainage release from waste rock piles: controls of the spatial distribution of acid generating and neutralizing minerals

Abstract

In mining environmental applications, it is important to assess water quality from waste rock piles (WRPs) and estimate the likelihood of acid rock drainage (ARD) over time. The mineralogical heterogeneity of WRPs is a source of uncertainty in this assessment, undermining the reliability of traditional bulk indicators used in the industry. We focused in this work on the bulk neutralizing potential ratio (NPR), which is defined as the ratio of the content of non-acid-generating minerals (typically reactive carbonates such as calcite) to the content of potentially acid-generating minerals (typically sulfides such as pyrite). We used a streamtube-based Monte-Carlo method to show why and to what extent bulk NPR can be a poor indicator of ARD occurrence. We simulated ensembles of WRPs identical in their geometry and bulk NPR, which only differed in their initial distribution of the acid generating and acid neutralizing minerals that control NPR. All models simulated the same principal acid-producing, acid-neutralizing and secondary mineral forming processes. We show that small differences in the distribution of local NPR values or the number of flow paths that generate acidity strongly influence drainage pH. The results indicate that the likelihood of ARD (epitomized by the probability of occurrence of pH<4 in a mixing boundary) within the first 100 years can be as high as 75% for a NPR=2 and 40% for NPR=4. The latter is traditionally considered as a "universally safe" threshold to ensure non-acidic waters in practical applications. Our results suggest that new methods that explicitly account for mineralogical heterogeneity must be sought when computing effective (upscaled) NPR values at the scale of the piles.

Keywords: multicomponent reactive transport, mineralogical heterogeneity, stochastic analysis, acid rock drainage, waste rock piles, neutralizing potential ratio

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1. Introduction

In environmental mining assessments, one critical aspect to control is whether a waste rock pile (WRP) has a high or low effective neutralizing capacity, which reflects its overall (bulk) ability to buffer the acidity produced within the pile. Low effective neutralizing capacity can imply deleterious properties characteristic of acid rock drainage (ARD), e.g. pH<4 and high sulfate and metal concentrations in the pile's outflow. (e.g. INAP-GARD, 2014; Morin and Hutt, 1997; Parbhakar-Fox and Lottermoser, 2015; Price, 2009).

Bulk indicators are typically used in the industry to predict whether a WRP will possess a high or low effective neutralizing capacity. A widely-adopted and well-known indicator is the bulk neutralizing potential ratio (NPR), which is based on the acid-base accounting originally developed by Sobek et al. (1978). NPR is obtained from laboratory-based analysis of n_l

rock samples obtained from the site as

$$NPR = \frac{1}{n_l}\sum_{i=1}^{n_l}\frac{NP_i}{AP_i} \quad (1)$$

where NP is a measure of the total mass of minerals available in the sample to neutralize the acidity, typically carbonates, and is expressed as equivalent kg $CaCO_3$, and AP is a measure of total mass of acid producing minerals, typically sulfides, also expressed in equivalents kg of $CaCO_3$ (to be directly comparable with NP). Theoretically, $NPR > 1$ indicates that after complete reaction of the sample minerals the resulting solution will not be acidic, while $NPR < 1$ indicates that after complete reaction of the sample minerals the resulting solution will be acidic. Unfortunately, measuring $NPR > 1$ does not necessarily translate into a WRP with high effective neutralizing capacity. Indeed, ARD guidelines (e.g. Price, 2009) suggest that $NPR > 2$ would ensure a limited occurrence of acidic drainage from a pile, while $NPR > 4$ seems a well-established *universal* threshold to ensure no occurrence of acidic drainage. A value between $NPR = 1$ and $NPR = 4$ falls in the so-called "gray" or uncertain zone.

We highlight here some reasons to explain why laboratory-based bulk indicators such as the NPR are not always useful criteria to determine if drainage may become acidic at some point in the future. First, it shall be considered that WRPs are unsaturated and usually highly heterogeneous deposits (Eriksson and Destouni, 1997; Eriksson et al., 1997; Fala et al., 2013; Amos et al., 2014; Lahmira and Lefebvre, 2014; Lahmira et al., 2016) in which the formation and control of ARD depends on a large number of nonlinear, coupled physical, chemical and biological processes (e.g. Amos et al., 2009; Blowes et al., 2003; Lefebvre et al., 2001; Nicholson et al., 1990; Nordstrom, 2011; Pedretti et al., 2015; Lorca et al., 2016). Static chemical tests, such as the Sobek test, and small-scale kinetic tests, such as kinetic or humidity cells, do not properly account for all processes occurring under field conditions, and have been seen to significantly overestimate the reaction rates of weathering processes (e.g. Malmström et al., 2000).

As defined in (1), the bulk NPR can be seen as a crude homogenization based on a simple arithmetic averaging of NP and AP from samples collected from the site and analyzed in the laboratory. The bulk NPR does not account for the spatial variability of minerals within the WRPs, while the neutralizing capacity of WRPs may be controlled not only by the bulk amount of AP and NP minerals in the system, but also by their specific sequence along a flow path, as discussed for instance by Morin and Hutt (2000). Indeed, in geochemically heterogeneous systems, the water quality at the end of a flow path depends in part on the sequence of minerals encountered along the flow path (e.g. Palmer and Cherry, 1984). Thus, the spatial distribution of minerals in the piles, which are ubiquitously heterogeneous, may have an important control on pile drainage.

Since the exact distribution of the phases that contribute to NP and AP within WRPs is never known in practice, the prediction of ARD from WRPs becomes uncertain. Stochastic models handling this type of *epistemic* uncertainty (e.g. Tartakovsky and Winter, 2008) are not yet common for studies on WRPs. One reason is due to the intense computational burden required to solve for multidimensional multicomponent Eulerian-based reactive transport in heterogeneous WRPs (e.g. Demers et al., 2013; Fala et al., 2013; Lahmira and Lefebvre, 2014; Lahmira et al., 2016). Alternative computationally efficient methods, such as streamtube-based or Lagrangian models (e.g. Bellin et al., 1994; Finkel et al., 2002; Simmons et al., 1995; Thiele et al., 1996; Yabusaki et al., 1998), can be however adopted. For instance, Eriksson and Destouni (1997) used a Lagrangian approach to investigate the impact of preferential flow on a WRP in Sweden, previously analyzed by Strömberg and Banwart (1994). Malmström et al. (2004) used Lagrangian models for ARD formation and evolution in the context of mine tailings.

In this work we use a streamtube-based approach to develop a full Monte-Carlo analysis and quantify the role of the spatial distribution of minerals for a fixed bulk NPR on the formation of ARD in WRPs through time. Each streamtube is modeled using the multicomponent reactive transport code MIN3P (Mayer et al., 2002), which simulates the main acid-producing, acid-neutralizing and secondary mineral forming processes in unsaturated systems. The stochastic modeling allows explaining how, under the same bulk NPR, the spatial distribution of NP and AP phases affects the likelihood of water acidification in WRPs. We focus on those bulk NPR values that are traditionally considered in the gray zone (e.g. $NPR = 2$), as well as larger values ($NPR = 4, 10$) which are traditionally considered safe thresholds according to mine water guidelines (e.g. Price, 2009). Our purpose is to highlight and study the key difference between "local" and "bulk" NPR values, the first defined as the ratio of NP and AP in a lab-scale sample collected at a specific location of the pile, the second defined as the ratio of

NP and AP of all the minerals in the entire pile.

2. Problem statement

We create stochastic realizations of WRPs within which we simulate unsaturated flow and reactive transport. We use a simplified conceptual model (Figure 1) to study in detail the effects of the spatial distribution of NP and AP minerals in WRPs. The model is an idealization that contains the essential features that allow us to isolate the effects of the variability in local NPR values on the resulting drainage composition.

Each pile realization is conceptualized as a 2D profile 100 m long and 10 m high. One batter is located on the right side of the pile with a $\theta = 37°$ angle of repose, similar to the tipping phases (TP) and batters of real-world WRPs (e.g. Azam et al., 2007). Conceptually, a TP is similar to a geological depositional facies. Within each TP, the waste rock can be either characterized by similar mineralogical composition and abundance, assuming all rock in a TP is extracted from the same geological formation of the mine, or a more heterogeneous composition, due to natural geological heterogeneity of the rock formation, as well as internal segregation, layering and blending during pile construction (e.g. INAP-GARD, 2014).

We assume that the piles initially contain two reactive primary mineral phases, pyrite and calcite. Pyrite represents the most common sulfide mineral undergoing oxidation and generating acidity and provides a major source of AP. Calcite represents a carbonate mineral that buffers acidity and provides a major source of NP. Weathering of these two minerals can give rise to the formation of secondary mineral phases such as gypsum and ferrihydrite, providing solubility controls for Ca, SO_4 and Fe. Secondary minerals can form at any point and moment within the pile. Oxygen and carbon dioxide partial pressures remain in constant equilibrium with atmospheric conditions throughout the pile and for the entire simulation time, representing a well-ventilated system (e.g. Amos et al., 2009; Lefebvre et al., 2001). Sulfide oxidation is therefore not limited by the amount of oxygen, and similarly calcite dissolution is not affected by the accumulation of carbon dioxide within the pile (e.g. Lorca et al., 2016). Non-reactive minerals make up the bulk of the pile such that physical properties like porosity and permeability do not change in time as reactions occur. All these processes are accounted for in our simulations. The equations defining the geochemical system are reported as Supplementary Information (SI).

To isolate the effect of heterogeneous mineral distribution without the potentially complicated and non-trivial effects associated with different transport rates within the pile (e.g. Eriksson and Destouni, 1997), we assume hydraulic homogeneity in the WRPs. Unsaturated flow is driven by a wet-dry seasonal recharge rate which is applied uniformly across the crown and batter of the pile. The base of the pile is assumed to be impermeable, where pile drainage is collected to form a composite mixed drainage, as shown in Figure 1. Multiple observations made on WRPs suggest that the pile drainage is made up of well-defined sub-vertical flow paths, in some cases resulting in a preferential-like flow regime (e.g. Amos et al., 2014; Blackmore et al., 2014; Nichol et al., 2005; Peterson, 2014; Smith and Beckie, 2003). It is reasonable to expect that mixing of the multiple flow paths composing the system's drainage at the control plane dominates compared to local mixing occurring inside the piles along the flow paths or across the flow paths by transverse dispersion, as observed in saturated porous systems (e.g. Rahman et al., 2005).

Under these conditions, a stochastic streamtube (ST) modeling approach is a reasonable and computationally-efficient approximation for the simulation of multidimensional multicomponent reactive transport within heterogeneous WRPs under uncertainty. The stochastic analysis is based on the solution of Monte-Carlo simulations of ensembles of correlated random spatial fields or realizations and analysis of the statistics of the model outputs. Within each realization, the ST approach is used to solve for reactive transport, as conceptualized in Figure 1. Without lack of generality, it is assumed that flow occurs along vertical one-dimensional (1D) STs, whose hydraulic properties are fixed, as reported in the SI. While mixing occurs exclusively at the base of the pile, we note that in the ST approach the mixing layer does not necessarily need to be located at the base of the pile. It could also be located, for example, on top of a continuous capillary barrier within the piles, such as a traffic surface, giving rise to localized mixing of water and/or a lateral spring from the WRPs (e.g. Fala et al 2013).

3. Methodology

3.1. Generation of mineralogical random fields

We start by generating independent identically distributed (i.i.d.) random fields of volumetric fractions (ϕ) of pyrite and calcite. Each field has the same spatial statistics, including the same spatially averaged or bulk NPR, and represents a possible spatial map of NP and AP minerals within the pile. The volume fractions are adopted by MIN3P to define the amount of minerals in the model (SI) and can be related to wt% by simple conversion based on mineral densities and porosities.

To build random realizations of mineralogical assemblage, we utilize the Sequential Indicator Simulation (SIS) geostatistical algorithm (Emery, 2004; Goovaerts, 2000; Journel and Alabert, 1990; Soares, 1998) coded in SGEMS (Remy et al., 2009). For a specific mineral, each SIS simulation requires three variables: the spatially-averaged mineral volume fraction ($\overline{\phi}$), the variance (σ_ϕ^2) and the correlation function (C_ϕ). In all realizations we use an exponential covariance of the form

$$C_\phi(\theta_C) = \sigma_\phi^2 \exp\left(-\frac{d}{a(\theta_C)}\right) \quad (2)$$

where d is the distance between two points, θ_C is an angle oriented along one of the axes of the anisotropic covariance ellipsoid, and a is the range of the correlation along that direction. The ratio between $a(\theta_C)$ and the dimension of the domain along θ_C provides a measure of the continuity of the mineralogical content the direction θ_C.

We generate unconditioned 2D random fields of size 100 m × 10 m and a discretization of 1 m × 1 m (for a total number of cells n_c=1000 per field) replicating heterogeneous distributions of pyrite and calcite content in mineralogically heterogeneous WRPs. The grid resolution is assumed to be sufficient to capture the variability of the heterogeneity in the waste rock, and is similar to the one adopted in other studies involving numerical models of heterogeneous waste rocks (e.g. Lahmira and Lefebvre, 2014; Lahmira et al., 2016).

We formulate four different ensembles of simulations, each of which is characterized by a different bulk NPR value (0.5, 2, 4, 10) but identical coefficient of variance ($CV = \sqrt{\sigma_\phi^2}/\bar{\phi}$). We set CV=0.6, a value that maximizes the variability of mineral content in each realization without generating physically unrealistic negative ϕ values. We set ranges a_1=10 m along the major axis, parallel with the orientation of the waste rock tipping phases at an angle of $\theta_C = \theta = 37°$, and a_2=5 m along the perpendicular minor axis at an angle of $\theta_C = 127°$. At the scale of individual waste rock particles (grid blocks), we postulate an inverse correlation between the sulfide content and the carbonate content with an intermediate correlation coefficient $\rho = 0.5$. This selection is made to account for the expected lower sulfide content in carbonate-rich rocks (and vice-versa) with statistical uncertainty or noise.

An example of the random fields generated using this methodology and parameters is shown in Figure 2. It can be observed that the resulting spatial distributions are heterogeneous, with discrete zones having similar NPR values along the vertical direction. The vertical homogeneity is the result of using a_1 =10m, which generates a relatively continuity of the same mineral amount (i.e. same ϕ) along the TP dipping angle. This approach is representative for a single tip from haul trucks, where the load comes from one location in the mine. The lateral variability is the result of using a_2 = 5m, which is lower than the lateral extension of the pile (100m).

Using the same approach, we generate an ensemble of 100 random fields of pyrite and 100 for calcite for each bulk NPR value, each with a distinct spatial distribution of NP and AP minerals but same statistical distributions. The arbitrary number of simulations serves us to obtain a representative ensemble of results to evaluate the likelihood of low-quality drainage, as described in Section 4.2.

3.2. Reactive transport along each ST

For each realization of the ensemble, we simulate drainage chemistry over 1000 years along all individual STs in the pile. A succinct description of the flow and reactive transport model is provided here. Additional details about the model setup, boundary conditions as well as flow and transport parameters used in the analysis can be found in the SI.

Each realization consists of N_{ST}=100 STs, each of which was subdivided into cells of 1 m length, 1 m width, a cross sectional area A=1 m^2 and a volume of 1 m^3. The total pile discharge area at the pile base is 100 m^2. Below the crown the ST contains 10 cells, while below the batter the number of cells decreases as the pile thins towards the toe (as conceptualized in Figure 1). The number of STs is deemed adequate to evaluate the impact of geochemical heterogeneity on the long-term outflow geochemistry, while maximizing the efficiency of the model calculations. A sensitivity analysis reported in the SI confirms the adequacy of the selected vertical grid resolution against numerical dispersion, leaving the mineralogical distribution unchanged.

The saturated hydraulic conductivity and Van Genuchten unsaturated properties are homogeneous and isotropic at each point of the domain. The selected hydraulic parameters (SI) ensure that there is no surface ponding and that the outflow discharge rate from each ST (Q) is controlled by the recharge rates assigned at the top of each ST (q_r) and A. To simulate a wet-dry seasonality, each year a uniform daily recharge rate equivalent to q_r=1000 mm/y is applied for six months, followed by six months of q_r=0. Because q_r and A are constant in all STs, the maximum flow rate per ST is $Q = 3.17 \times 10^{-8}$ m^3/s during the wet season , while the minimum flow rates approach zero during the dry season. A prescribed concentration flux is defined at the surface, while a free-exit concentration boundary is set at the base. The recharge and initial pore-water composition within the pile have low solute concentrations, as reported in the SI.

To focus exclusively on the effect of the distribution of NP and AP minerals, we set homogeneous pyrite oxidation rates described by a simple zero-order kinetic model. This is a simplification of the actual nature of the process, which is actually better described by surface-area and pH-controlled mineral weathering rates (e.g. Park and Levenspiel, 1975), but not accounted for in this work for computational reasons. We set a representative effective rate coefficient of $k = 10^{-9}$ mol L^{-1}s^{-1}, which is in range of values found by Nicholson et al. (1990) using a shrinking core model. A sensitivity analysis (not reported) showed however that a different k does not substantially affect our conclusions. Geochemical calculations utilize a thermodynamic database derived from WATEQ4F (Ball and Nordstrom, 1991). We refer to Mayer et al. (2002) for details on the thermodynamic constants. The geochemical model accounts for all dissolved species associated with the components forming calcite, pyrite, water, oxygen and carbon dioxide. The principal secondary mineral phases defined by these elements are allowed to precipitate within a grid block when saturated. Calcite, gypsum and ferrihydrite are treated as in quasi-equilibrium conditions and allowed to precipitate and (re)dissolve.

3.3. Mixing

Mixing of waters at the base of the pile from the multiple STs is computed in two steps. The first step consists in the algebraic calculation of concentration of components (j) exfiltating from each streamtube (i) at the last day of each wet season (τ_l, where $l = 1, ..., 1000$ corresponds to each simulated year). A flux-averaged component concentration $T_F(j, \tau_l)$ is calculated as

$$T_F(j,\tau_l) = \sum_{i=1}^{N_{ST}} w(i) T_j(i,j,\tau_l) \qquad w(i) = \frac{Q_i(\tau_l)}{Q(\tau_l)} \tag{3}$$

For instance, $T_F(SO_4, \tau_1)$ is the mixed concentration of sulfate at the base of the pile at the last day of the first wet season; $T_F(SO_4, \tau_2)$ is the concentration at last day of the second wet season; and so on.

The second step uses MIN3P to calculate the geochemistry of the mixed basal drainage. Mixing calculations are performed under the assumption of equilibrium with atmospheric O_2 and CO_2 and no precipitating secondary minerals in the mixing boundary. The concentrations of the components, pH and alkalinity in the mixed waters are quantified and it is assumed that the resulting water discharged from from underneath the pile immediately after mixing. Alkalinity is calculated following the formulation of MINTEQ (Felmy et al., 1984).

The assumptions of no precipitating secondary minerals and a once-per-year mixing are made to increase the computational efficiency in light of the large number of simulations generated within the Monte Carlo framework. A sensitivity analysis, reported in the SI, reveals that mixing calculations performed on a daily basis and/or allowing secondary minerals (gypsum and ferrihydrite) to precipitate do not qualitatively affect the resulting model outputs and the conclusions of this work. It is noted that while mixing of components is computed once annually, flow and reactive transport along the STs are still computed continuously over the 1000 simulated years, with variable time steps spanning from 10^{-10} day to 1 day , utilizing the adaptive time stepping algorithm of MIN3P (Mayer and MacQuarrie, 2010).

4. Results & Analysis

4.1. Analysis of individual realizations

The results from two selected realizations (Figure 2) chosen from the ensemble with bulk NPR=2 are shown in Figure 3 .

The first key element to observe is that, in both realizations, the majority of the STs (gray lines) do not generate ARD. In realization 1 about 80% of the STs show low sulfate concentrations, with pH≈6.5 and elevated alkalinity. The remaining 20% of STs, however, display typical ARD-like conditions, with high sulfate concentrations and low pH, with minimum pH-values 2-3. Consistently, in these STs the alkalinity drops below zero (i.e. representing acidity) during the low pH stages. In realization 2, the number of ARD-like STs is about 10% of the total. This number is slightly lower than in realization 1 and graphically distinguishable in Figure 3 by the lower density of STs characterized by sulfate concentration peaks and low pH values.

The number of acidic STs in the realization strongly affects the composition of the basal mixed drainage in each simulation. In realization 1, the mixed drainage shows pH<4 over extended periods of time (about 100-150 years since the beginning of the simulations), dropping to lows of pH≈4, which corresponds to lows in alkalinity and a peak in sulfate concentrations. After 150-200 years, the pile rapidly recovers to circumneutral values, while sulfate concentrations tend to gradually decrease towards a stable value. In realization 2, at the initial stages the composite drainage is characterized by generally higher alkalinity (i.e. less acidity) than in realization 1, with less pronounced peaks of sulfate and pH>4 for most of the simulation time.

Over short and intermediate time scales (<300 years), the spatial configuration of mineral abundances seems to have an important control on basal drainage chemistry. Indeed, there are pronounced differences in the composite drainage of the two realizations which can be uniquely related to the different number of acidic STs, and are thus ascribable exclusively to mineralogical heterogeneity. While the majority of ST drainage waters show circumneutral pH in the simulations, some STs can reach acidities much higher than the maximum alkalinities in neutral STs. The solubility of carbonates limits the alkalinity of carbonate-saturated water to hundreds of mg/L, whereas sulfide oxidation has no mineral solubility control and acidities can reach thousands of mg/L. Thus, the higher acidities of the acidic STs dominate the basal drainage chemistry despite being a minority of the total STs.

These first observations explain why it can be difficult to predict the actual neutralizing capacity of WRPs in presence of mineralogical heterogeneity. Just a small subset of STs releasing ARD was seen to be responsible for the acidification of the entire drainage collected from the base. Moreover, the fact that the majority of STs is circumneutral is not a sufficient condition to ensure that the resulting mixed drainage will be circumneutral.

For upscaling purposes, it is possible that the same results would equally hold if mixing accounts only for those streamtubes that more actively contribute to basal discharge and solute loadings. Here, we can find some analogies between the effect of the spatial distribution of minerals on the resulting mixed drainage and the effect of flow heterogeneity documented by Eriksson et al. (1997). They concluded that because of flow by-passing and preferential flow, only 55%-70% of the pile's rock effectively contributed to the loadings from the WRP. Thus, the effect of flow channeling by Eriksson et al. (1997) results in a fraction of the waste rocks that actually contribute to the pile's overall behavior observed at a control section. We note however that the combined effect of mineral and flow heterogeneities is not yet well understood and requires further investigation.

Over the long term (>300 years), the total sulfate concentrations become comparable in the two piles and the pH tends to approach circumneutral values. This occurs because at long time scales the pyrite is almost entirely oxidized in the two piles and sulfate release is only associated with gypsum dissolution. Gypsum precipitates and accumulates in most streamtubes in both realizations during the active phase of sulfide oxidation and redissolves later on, therefore yielding a relatively homogeneous release of

SO_4. In real WRPs, several more minerals can exist in the piles, including slower-reacting aluminosilicates, which can provide pH buffering over time scales longer than carbonates. While the behavior of real WRPs will thus differ somewhat from our results, our conclusions about the effect of mineral distribution on composite outflow chemistry at short and intermediate time scales (<300 years) will not. Indeed, the variability in outflow chemistry between realizations here is fundamentally driven by the different distribution of minerals, and any changes in geochemical assumptions should affect all realizations in approximately the same way.

4.2. Monte-Carlo simulations

From each realization, a unique mixed drainage chemistry time series is produced using MIN3P and the approach described in Section 3.3. One time series reflects only possible random outcome from the ensemble of results belonging to a specific NPR value. In the following, we examine the likelihood or probability of occurrence of a particular value of mixed-drainage pH at given times by analyzing the statistics from the ensemble of results from each bulk NPR.

We first analyze the ensemble results for the case with bulk NPR=2. In Figure 4, the histograms represent the frequency of the mixed-drainage pH from the individual realizations. In the plots the y-axis scale is limited to a density of 0.25 in all panels to emphasize the difference among the different cases. The red lines represent the empirical cumulative density function, which can be interpreted as the probability (P) that the mixed drainage pH falls below a certain value. Using P, we can define a likelihood of occurrence

(L) as

$$L = P(\text{pH} < \text{pH}^*) \tag{4}$$

which is the proportion of scenarios in which the mixed-drainage pH is below a threshold of compliance pH*. As a working assumption, we describe the results based on pH* <4.

Figure 4 shows that as the piles evolve geochemically over time, the relative frequency of specific pH values in the composite drainage changes. The results highlight that bulk NPR =2 is rarely a sufficient condition to expect neutralized drainage from WRPs within short and intermediate time scales. For instance, after 25 years in the majority of simulations the composite drainage shows pH≈3-4, while it only remains circumneutral in a limited subset of the simulations. At 25 years, the probability curve suggests that the likelihood of pH < 4 is L ≈90%, i.e. 90 out of 100 realizations with bulk NPR=2 yield a composite drainage with pH<4. The likelihood of not exceeding the selected pH*=4 is still 75% after one century since the placement of the WRPs. The likelihood drops to lower values after 150 years, where it stabilizes around L=30%, and remains almost identical, even after 300 years. Results not plotted here suggest that likelihood drops to very low values (L <5%) for very large time scales (1000 years).

The histograms and cumulative distributions for bulk NPR scenarios are shown in Figure 5, including the guidelines-recommended $NPR = 4$ (Price, 2009). In addition to the line representing the selected threshold pH*=4, we plot the lines corresponding to L=50% and L=5%. For NPR=0.5, the likelihood of water acidification increases compared with the case NPR=2. This result is not surprising and in line with the expected behavior of a WRP with a lower calcite-to-pyrite ratio and thus with a lower probability of pH buffering.

Surprisingly, for NPR=4 we found that the likelihood is still $L \approx$70% at 50 years and $L \approx$40% at 100 years. After 150 years the number of simulations with pH<4 drops, with $L \approx$15%. We thus found that NPR=4 is not a reliable threshold to ensure good quality drainage water from a WRP with similar characteristics as those simulated in this work, questioning the validity of NPR=4 as a *universal* indicator to predict poorly acidified drainage exfiltrating waste rock piles.

A higher NPR than 4 is needed to ensure low likelihood of water not exceeding the threshold pH*. For instance, the results for NPR=10 show it to be a much safer criterion than NPR=4, although we did not carry out simulations for intermediate NPR values that may provide similar results.

Summary & Conclusion

We present and discuss the results from a stochastic modeling approach where we study the effects of heterogeneous mineral distributions on the likelihood of acid drainage from WRPs for different bulk NPR values. To allow a more direct interpretation of our results, we adopt some simplifications compared to real sites, such as homogeneous flow conditions and no control of silicate weathering on the long term. Gas transport is not rate-limited in our simulations.

We account for the mineral content (volumetric fractions) as the effective property controlling the variability of drainage quality exfiltrating the piles. We do not explicitly correlate mineralogical reactivity and particle size, for instance assigning a higher reaction rates to smaller size. Instead, we assume that a high-content mineral zone means both higher amount of NP or AP mineral and a higher reactivity for the minerals present in the zones. For instance, it can be seen as a zone enriched in minerals with high surface areas. Vice-versa, a low content mineral zone contains with a lower fraction of NP or AP minerals with a lower reactivity.

We show that, for the conceptual model developed in this analysis, WRPs with bulk NPR=2 generate drainage pH<4 after 100 years with a probability of about 75%. Unexpectedly, after 100 years this probability is still about 40% when bulk NPR=4. In other terms, two out of five WRPs with bulk NPR=4 are expected to generate poor-quality pH<4 drainage after 100 years. This aspect should be take into account by decision makers, as NPR=4 is generally considered a safe criterion when operating WRPs (Price, 2009).

The Monte-Carlo result is explained considering the results from individual realizations from the ensemble. In two geostatistical simulations having bulk $NPR \approx 2$ we observe that the composite drainage can give rise to either acidic or circumneutral drainage because of a limited subset of streamtubes (flow paths) discharging at a mixing plane and undegoing acidic conditions. For upscaling purposes, the impact of mineralogical heterogeneity can be seen as qualitative similar to the behavior of hydraulic heterogeneity and preferential flow described by Eriksson and Destouni (1997). Only a subset of stramtubes effectively contribute to the pile-average composition of the exfiltrating drainage, depending on concentration loadings and acidity/alkalinity. These results suggest one possible way towards a correct upscaling of the effective neutralizing capacity of mineralogically heterogeneous waste rock piles.

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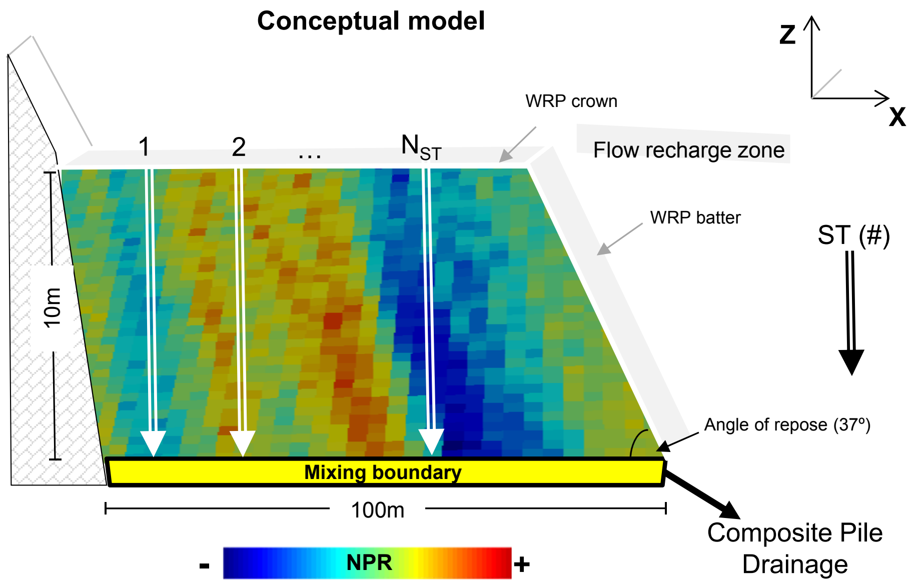

Figure 1: Conceptual model of the problem analyzed in this work. From the recharge zones (crown and batter), water infiltrates into the pile forming multiple hydraulically-homogeneous streamtubes (STs). Each ST intercepts a random sequence of minerals, and in turn a random sequence of NPR zones. For a specific realization, the composition of the resulting WRP drainage depends on the flux-averaged concentration of each ST being collected at the control plane (mixing boundary at base of the pile). The composition of each ST at the control plane, and in turn of the composite drainage, depends on the specific sequence of minerals encountered in each realization.

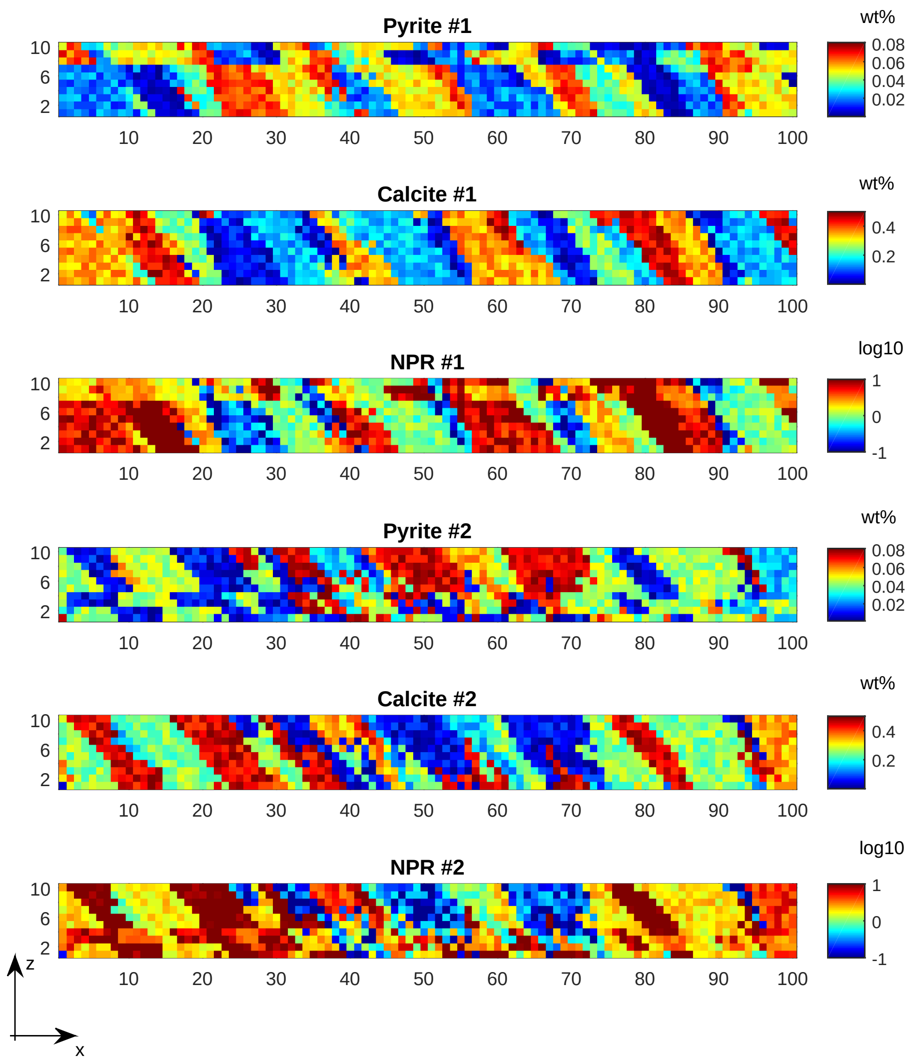

Figure 2: Two example realizations or maps of initial mineral distributions. The average dip along the major axis is parallel with the angle of repose of the waste rock ($\theta = 37^{\circ}$).

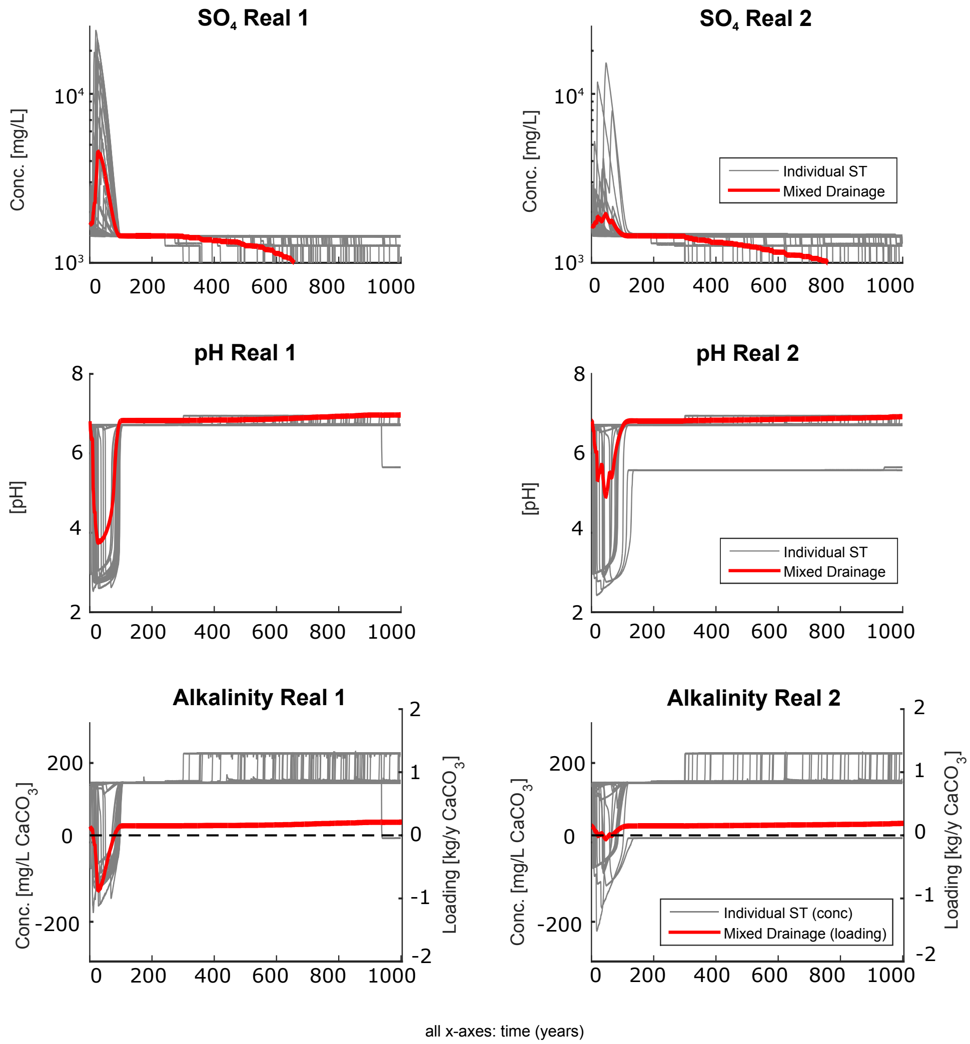

Figure 3: Analysis of two individual realizations with bulk NPR=2. The geometry, flow field, bulk properties and boundary conditions are identical in both realizations. They differ only in the organization of primary minerals (calcite and pyrite) within the piles, which generates a heterogeneous distribution of local NPR values. The dotted lines highlights zero alkalinity. The red line indicated the mixing values calculated using MIN3P (see Section 3.3).

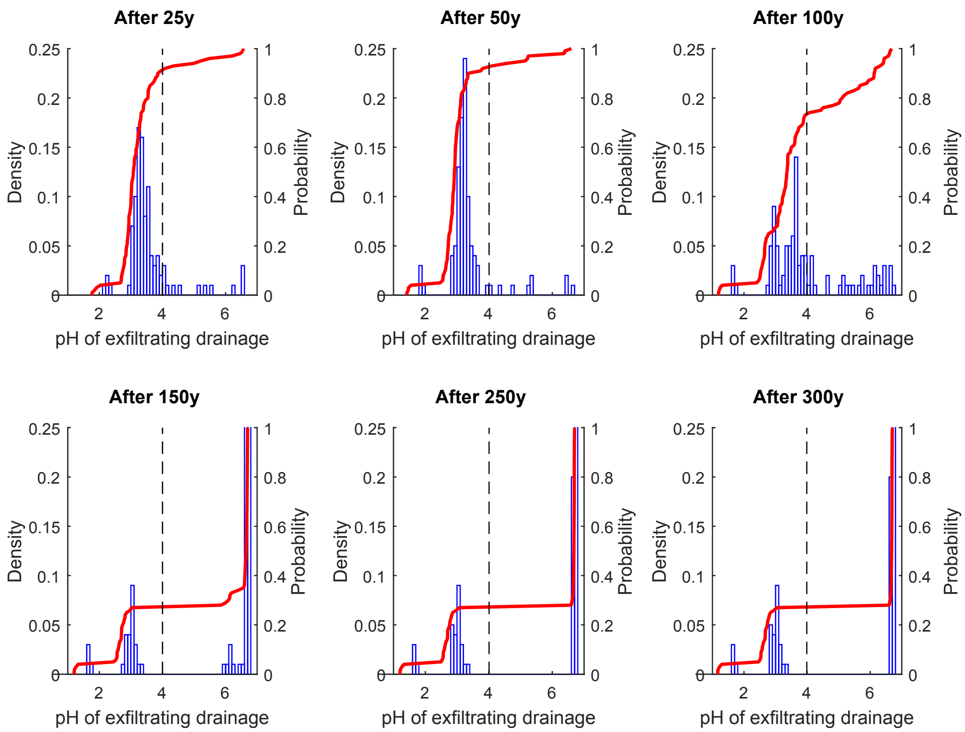

Figure 4: Ensemble results of the mixed-drainage pH from the scenarios with bulk NPR =2 at different times. The vertical dotted line emphasizes pH=4, an arbitrary value selected to estimate the likelihood (L) of the piles to generate low-quality drainage.

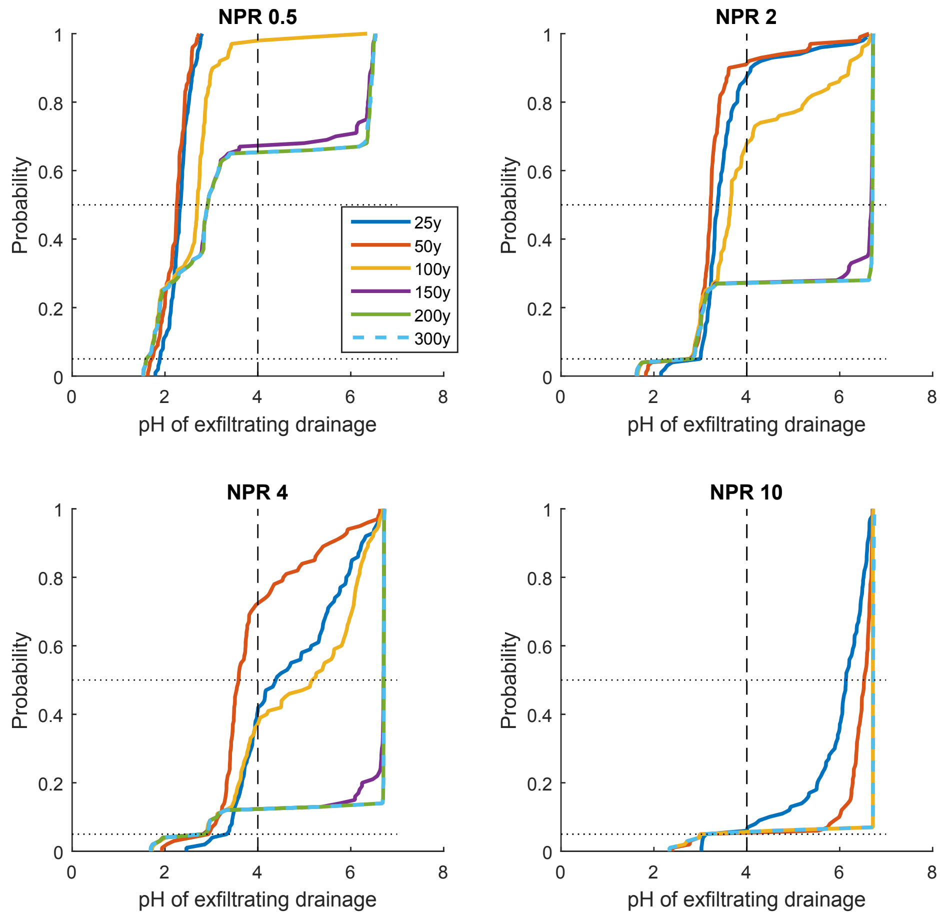

Figure 5: Comparison of ensemble results from different bulk NPR values, at different times. All panels show the pH of the mixed drainage from 100 random simulations. In each individual simulation, pH is calculated using the mixing approach described in Section 3.3.

References

Amos, R.T., Blowes, D.W., Bailey, B.L., Sego, D.C., Smith, L., Ritchie, A.I.M., 2014. Waste-rock hydrogeology and geochemistry. Applied Geochemistry doi:10.1016/j.apgeochem.2014.06.020.

Amos, R.T., Blowes, D.W., Smith, L., Sego, D.C., 2009. Measurement of Wind-Induced Pressure Gradients in a Waste Rock Pile. Vadose Zone Journal 8, 953. doi:10.2136/vzj2009.0002.

Azam, S., Wilson, G., Herasymuik, G., Nichol, C., Barbour, L., 2007. Hydrogeological behaviour of an unsaturated waste rock pile: a case study at the Golden Sunlight Mine, Montana, USA. Bulletin Of Engineering Geology And The Environment 66, 259–268.

Ball, J., Nordstrom, D., 1991. WATEQ4F – User's manual with revised thermodynamic data base and test cases for calculating speciation of major, trace and redox elements in natural waters. USGS Numbered Series 90-129.

Bellin, A., Rubin, Y., Rinaldo, A., 1994. Eulerian-Lagrangian approach for modeling of flow and transport in heterogeneous geological formations. Water Resources Research 30, 2913–2924. doi:10.1029/94WR01489.

Blackmore, S., Smith, L., Ulrich Mayer, K., Beckie, R.D., 2014. Comparison of unsaturated flow and solute transport through waste rock at two experimental scales using temporal moments and numerical modeling. Journal of Contaminant Hydrology 171, 49–65. doi:10.1016/j.jconhyd.2014.10.009.

Blowes, D., Ptacek, C., Jambor, J., Weisener, C., 2003. The Geochemistry of Acid Mine Drainage, in: Treatise on Geochemistry. Elsevier, pp. 149–204.

Demers, I., Molson, J., Bussire, B., Laflamme, D., 2013. Numerical modeling of contaminated neutral drainage from a waste-rock field test cell. Applied Geochemistry 33, 346–356. doi:10.1016/j.apgeochem.2013.02.025.

Emery, X., 2004. Properties and limitations of sequential indicator simulation. Stochastic Environmental Research and Risk Assessment 18, 414–424. doi:10.1007/s00477-004-0213-5.

Eriksson, N., Destouni, G., 1997. Combined effects of dissolution kinetics, secondary mineral precipitation, and preferential flow on copper leaching from mining waste rock. Water Resources Research 33, 471–483.

Eriksson, N., Gupta, A., Destouni, G., 1997. Comparative analysis of laboratory and field tracer tests for investigating preferential flow and transport in mining waste rock. Journal of Hydrology 194, 143–163. doi:10.1016/S0022-1694(96)03209-X.

Fala, O., Molson, J., Aubertin, M., Dawood, I., Bussire, B., Chapuis, R.P., 2013. A numerical modelling approach to assess long-term unsaturated flow and geochemical transport in a waste rock pile. International Journal of Mining, Reclamation and Environment 27, 38–55. doi:10.1080/17480930.2011.644473.

Felmy, A., Girvin, D., Jenne, E., 1984. MINTEQ–a Computer Program for Calculating Aqueous Geochemical Equilibria.

Finkel, M., Liedl, R., Teutsch, G., 2002. Modelling Reactive Transport of Organic Solutes in Groundwater with a Lagrangian Streamtube Approach, in: (DFG), D.F. (Ed.), Geochemical Processes. Wiley-VCH Verlag GmbH & Co. KGaA, pp. 115–134.

Goovaerts, P., 2000. Geostatistical approaches for incorporating elevation into the spatial interpolation of rainfall. Journal of Hydrology 228, 113–129. doi:10.1016/S0022-1694(00)00144-X.

INAP-GARD, 2014. GARD (Global Acid Rock Drainage) Guide The International Network for Acid Prevention (INAP). URL: http://www.gardguide.com/.

Journel, A.G., Alabert, F.G., 1990. New Method for Reservoir Mapping. Journal of Petroleum Technology 42, 212–218. doi:10.2118/18324-PA.

Lahmira, B., Lefebvre, R., 2014. Numerical modelling of transfer processes in a waste rock pile undergoing the temporal evolution of its heterogeneous material properties. International Journal of Mining, Reclamation and Environment 0, 1–22. doi:10.1080/17480930.2014.889362.

Lahmira, B., Lefebvre, R., Aubertin, M., Bussire, B., 2016. Effect of heterogeneity and anisotropy related to the construction method on transfer processes in waste rock piles. Journal of Contaminant Hydrology 184, 35–49. doi:10.1016/j.jconhyd.2015.12.002.

Lefebvre, R., Hockley, D., Smolensky, J., Lamontagne, A., 2001. Multiphase transfer processes in waste rock piles producing acid mine drainage: 2.

Applications of numerical simulation. Journal of Contaminant Hydrology 52, 165–186. doi:10.1016/S0169-7722(01)00157-7.

Lorca, M.E., Mayer, K.U., Pedretti, D., Smith, L., Beckie, R.D., 2016. Spatial and Temporal Fluctuations of Pore-Gas Composition in Sulfidic Mine Waste Rock. Vadose Zone Journal 15. doi:10.2136/vzj2016.05.0039.

Malmström, M.E., Destouni, G., Banwart, S.A., Str¨mberg, B.H.E., 2000. Resolving the Scale-Dependence of Mineral Weathering Rates. Environmental Science & Technology 34, 1375–1378. doi:10.1021/es990682u.

Malmström, M.E., Destouni, G., Martinet, P., 2004. Modeling Expected Solute Concentration in Randomly Heterogeneous Flow Systems with Multicomponent Reactions. Environmental Science & Technology 38, 2673–2679. doi:10.1021/es030029d.

Mayer, K.U., Frind, E.O., Blowes, D.W., 2002. Multicomponent reactive transport modeling in variably saturated porous media using a generalized formulation for kinetically controlled reactions. Water Resources Research 38, 13–1–13–21. doi:10.1029/2001WR000862.

Mayer, K.U., MacQuarrie, K.T.B., 2010. Solutions of the MoMaS reactive transport benchmark with MIN3P - model formulation and simulation results. Computational Geosciences 14, 405-419.

Morin, K.A., Hutt, N., 1994. An empirical technique for predicting the chemistry of water seeping from mine-rock piles., in: Proceedings of the Third International Conference on the Abatement of Acidic Drainage, Pittsburgh, Pennsylvania, USA.

Morin, K.A., Hutt, N., 1997. Environmental geochemistry of minesite drainage: practical theory and case studies. MDAG Pub.

Morin, K.A., Hutt, N., 2000. Discrete-zone mixing of net-acid-neutralizing and net-acid-generating rock: Avoiding the argument over appropriate ratios.

Nichol, C., Smith, L., Beckie, R., 2005. Field-scale experiments of unsaturated flow and solute transport in a heterogeneous porous medium. Water Resources Research 41, W05018. doi:10.1029/2004WR003035.

Nicholson, R., Gillham, R.W., Reardon, E.J., 1990. Pyrite oxidation in carbonate-buffered solution: 2. Rate control by oxide coatings. Geochimica et Cosmochimica Acta 54, 395–402. doi:10.1016/0016-7037(90)90328-I.

Nordstrom, D.K., 2011. Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters. Applied Geochemistry 26, 1777–1791. doi:10.1016/j.apgeochem.2011.06.002.

Palmer, C.D., Cherry, J.A., 1984. Geochemical evolution of groundwater in sequences of sedimentary rocks. Journal of Hydrology 75, 27–65. doi:10.1016/0022-1694(84)90045-3.

Parbhakar-Fox, A., Lottermoser, B.G., 2015. A critical review of acid rock drainage prediction methods and practices. Minerals Engineering 82, 107–124. doi:10.1016/j.mineng.2015.03.015.

Park, J.Y., Levenspiel, O., 1975. The crackling core model for the reaction of solid particles. Chemical Engineering Science 30, 1207–1214. doi:10.1016/0009-2509(75)85041-X.

Pedretti, D., Lassin, A., Beckie, R.D., 2015. Analysis of the potential impact of capillarity on long-term geochemical processes in sulphidic waste-rock dumps. Applied Geochemistry 62, 75–83. doi:10.1016/j.apgeochem.2015.03.017.

Peterson, H.E., 2014. Unsaturated hydrology, evaporation, and geochemistry of neutral and acid rock drainage in highly heterogeneous mine waste rock at the Antamina Mine, Peru .

Price, W., 2009. Prediction manual for drainage chemistry from sulphidic geologic materials.

Rahman, M.A., Jose, S.C., Nowak, W., Cirpka, O.A., 2005. Experiments on vertical transverse mixing in a large-scale heterogeneous model aquifer. Journal of Contaminant Hydrology 80, 130–148. doi:10.1016/j.jconhyd.2005.06.010.

Remy, N., Boucher, A., Wu, J., 2009. Applied Geostatistics with SGeMS. A User's Guide. New york cambridge university press. ed.

Simmons, C.S., Ginn, T.R., Wood, B.D., 1995. Stochastic-Convective Transport with Nonlinear Reaction: Mathematical Framework. Water Resources Research 31, 2675–2688. doi:10.1029/95WR02178.

Smith, J., Beckie, R., 2003. Hydrologic and geochemical transport processes in mine waste rock, in: Jambor, J., Blowes, D., Ritchie, A. (Eds.), Environmental aspects of mine wastes. Mineralogical Association of Canada, Ottawa. Short course series, pp. 51–72.

Soares, A., 1998. Sequential Indicator Simulation with Correction for Local Probabilities. Mathematical Geology 30, 761–765. doi:10.1023/A:1022451504120.

Sobek, A.A., Schuller, W.A., Freeman, J.R., Agency, E.P., 1978. Field and laboratory methods applicable to overburdens and minesoils.

Strömberg, B., Banwart, S., 1994. Kinetic modelling of geochemical processes at the Aitik mining waste rock site in northern Sweden. Applied Geochemistry 9, 583–595. doi:10.1016/0883-2927(94)90020-5.

Tartakovsky, D.M., Winter, C.L., 2008. Uncertain future of hydrogeology. ASCE J. 394 Hydrologic Engrg. 13, 37–39.

Thiele, M., Batycky, R., Blunt, M., Orr, F., 1996. Simulating Flow in Heterogeneous Systems Using Streamtubes and Streamlines. SPE Reservoir Engineering 11, 5–12. doi:10.2118/27834-PA.

Yabusaki, S.B., Steefel, C.I., Wood, B.D., 1998. Multidimensional, multicomponent, subsurface reactive transport in nonuniform velocity fields: code verification using an advective reactive streamtube approach. Journal of Contaminant Hydrology 30, 299–331. doi:10.1016/S0169-7722(97)00050-8.