Modeling the effect of stratification on cemented layer formation in sulfide-bearing mine tailings

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Abstract

Reactive transport simulations have been applied to investigate possible effects of stratification on the potential of sulfide-bearing mine tailings to form protective cemented layers. The simulations are based on characteristic strata found at a German tailings site, including sulfide-enriched heavy mineral layers, mica-enriched silt layers, and homogeneously mixed layers. The simulated secondary phases (jarosite, gypsum, amorphous ferric arsenate, amorphous Fe hydroxide, alunite, amorphous silica, and kaolinite) are similar to those observed in the field. Using scanning electron microscope analyses of cemented layers, it has been observed that the pore area becomes disconnected if the porosity is decreased to values below 15%, which would indicate a strong decrease in permeability. Stratification was found to play a crucial role in cemented layer formation. Cemented layers are absent or insignificant in systems with a homogeneous distribution of Fe-bearing sulfides. They are extensively developed in systems with (a) an arsenopyrite-rich layer or (b) a mica-enriched layer situated immediately below an Fe-sulfide enriched layer. The modeling results have clearly demonstrated that the key processes operating in scenario (a) are very different from the key processes in scenario (b). In scenario (a), the oxidation of arsenopyrite is followed by the precipitation of amorphous ferric arsenate, which can be solely responsible for significant pore reduction. In scenario (b), the presence of a large amount of reactive aluminosilicates (e.g. biotite and Ca-bearing plagioclase) immediately below the Fe-sulfide rich layer appears to be crucial. Key processes are extensive formation of Acid Rock Drainage (ARD) followed by enhanced (pH-driven) weathering of aluminosilicates, resulting in the accumulation of secondary phases directly below the Fe-sulfide rich layer. In both scenarios, a cemented layer is formed that effectively retards the further downward movement of the oxidation front. The presented details on the role of stratification in the formation of cemented layers could be considered in the construction of mining heaps as a possible measure to stimulate natural attenuation.

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1. Introduction

Sulfide-bearing mine tailings are known for their potential to form ARD upon weathering. The oxidative dissolution of primary minerals and the precipitation of secondary phases have been studied in various detail at different tailings sites (e.g. Blowes et al., 1991; Dold and Fontboté, 2002; McGregor and Blowes, 2002; Gieré et al., 2003; Graupner et al., 2007; Moncur et al., 2005, 2009). In general, the ARD formation rate depends (a) on the amount, grain size (reactive surface area) and reactivity of residual Fe-bearing sulfide minerals (e.g. pyrite, arsenopyrite), (b) on the accessibility of O2, which transport rate is effectively reduced beneath a (local) water table due to the low solubility of O2 in water and (c) on the availability of phases that may buffer pH (e.g. carbonates, aluminosilicates, in particular biotite and Ca-bearing plagioclase, (Strömberg and Banwart, 1994)).

Various secondary phases have been reported from weathered sections of tailings dumps (e.g. gypsum, jarosite, Fe-(oxy)hydroxides, melanterite,rozenite, alunite, amorphous Fe-As phases, and amorphous Si-(Al) phases (see above references). Several studies have described a preferential precipitation in distinct layers, the so called cemented layers or hardpans (e.g. Blowes et al., 1991; Rammlmair, 1996, 2002; Rammlmair and Grissemann, 2000; Rammlmair et al., 2000, 2001; Jung et al., 2000, 2001; Dold and Fontboté, 2002; McGregor and Blowes, 2002; Gieré et al., 2003; Moncur et al., 2005, 2009; Gunsinger et al., 2006; Graupner et al., 2007; Romero et al., 2007). The porosity of such cemented layers may be significantly reduced (McGregor and Blowes, 2002; Moncur et al., 2005, 2009; Gunsinger et al., 2006; Graupner et al., 2007). Consequently, cemented layers may act as hydraulic barriers for transport of pore water and pore gases (Dold and Fontboté, 2002; McGregor and Blowes, 2002; Gieré et al., 2003; Gunsinger et al., 2006; Romero et al., 2007). Cemented layers have also been recognized for their potential to temporarily attenuate significant quantities of toxic compounds due to the amorphous or partially
crystalline nature of the frequent secondary phases (Rammlmair, 1996, 2002; McGregor and Blowes, 2002; Dold and Fontboté, 2002; Graupner et al., 2007; Romero et al., 2007).

Rather than consisting of a single uniform body, tailings dumps are usually composed of multiple layers and/or lenses of sediment that differ in grain size and/or mineralogical content (Graupner et al., 2007). Stratification is inherent to sedimentation, as the heavier particles settle before the lighter particles. This may directly influence the ARD formation rate by inducing the formation of local water tables at the finer grained layers. Stratification may also promote the formation of cemented layers, which may further decrease the permeability of the involved layers. Thermodynamically, cemented layer formation is favored at geochemical interfaces characterized by sudden changes in geochemical parameters (pH, Eh, availability of specific ions, e.g. K⁺). Stratification may supply these interfaces.

A possible relationship between intensely stratified tailings and extensive cementation has been discussed by Dold and Fontboté (2002) and Graupner et al. (2007). Graupner et al. (2007) investigated a tailings dam containing multiple thin layers or lenses (often at mm-scale) predominantly composed of “heavy minerals” like barite, arsenopyrite and arsenian pyrite, as well as of their weathering products. Other layers or lenses spatially related to the aforementioned ones consist of very fine-grained material enriched in micas (e.g. biotite, chlorite). The effects of stratification on the development of geochemical interfaces and subsequent geochemical reactions is well-known from artificial settings such as reactive barriers or self-repairing liners (e.g. Wait et al., 2002; Conca et al., 2002; Rowland, 2002; Morrison et al., 2002).

Although the individual processes of mineral dissolution, mineral precipitation, and mass transport resulting in the formation of protective cemented layers are well understood, their spatial interaction and temporal progress are still unclear in large part. For example, it remains unclear why the significance of cemented layer formation differs from site to site and from location to location. The application of reactive-transport modeling will shed some light on the complicated processes occurring at geochemical interfaces in the heaped sediment. Furthermore, it provides the basis for an estimation of spatial and temporal aspects and is, therefore, indispensable to forecast developments over a longer period in the future.

In this study, possible effects of stratification on the potential of sulfide-bearing mine tailings to form protective cemented layers have been investigated systematically by reactive transport modeling. The simulations are based on characteristic strata found at a German tailings site, showing the effects of homogeneous sediment versus heterogeneous mineral distributions (e.g. the presence of Fe sulfide-enriched heavy mineral layers and/or mica-enriched silt layers).

2. Materials and methods

2.1. Site description and tailings mineralogy

The reference site is the Muenzbachtal tailings impoundment within the poly-metallic sulfide mine district Freiberg, Saxony, Germany, which contains low-sulfide low-carbonate tailings. The site is ~320 m wide, has a maximum height of ~30 m and an almost flat plateau which covers an area of ~60,000 m² (Fig. 1). Tailings were deposited from 1955 to 1968 and were almost exclusively derived from the processing plant of the “Grube Beilhille” mine in Halsbruecke, which produced Pb–Zn concentrate using ore from the hydrothermal “Halsbruecker”-, “Ludwig”-, and “Drei Prinzen-Spat” ore veins.

Multiple cemented layers have been observed at the eastern rim of this site, which shows a very complex stratification, revealing variations in particle size and mineralogy (Graupner et al., 2007). Two characteristic vertical field profiles from the eastern rim of the site have been considered for this study (Fig. 1): (1) field profile C (length ~1 m), which is characterized by mm thick heavy mineral-rich layers with originally high concentrations of arsenopyrite (FeAsS), pyrite (FeS₂) and barite (BaSO₄), interbedded within layers of medium-grained sand and (2) profile D (length 1.5 m), which is in parts characterized by a strong alternation of Fe sulfide-rich layers and very fine grained mica-rich layers. A detailed geochemical and mineralogical analysis of these profiles is given in Graupner et al. (2007).

Widespread ore minerals in the central sub-district of the Freiberg mining district are sphalerite (ZnS), galena (PbS), arsenopyrite, pyrite and chalcopyrite (CuFeS₂) (Scheinert et al., 2009). Main gangue minerals, intergrown with the ores, were quartz, ferric oxides, and carbonates (Seifert and Sandmann, 2006). The wall rock consisted predominantly of gray paragneiss from the gneiss dome of Freiberg (Baumann et al., 2000). Typical mineral constituents are ~30 vol.% of quartz, ~32 vol.% of plagioclase, ~12 vol.% of K-feldspar, ~8 vol.% of muscovite and ~14 vol.% of biotite (Tichomirowa, 2001).

In the oxidized zone of the Muenzbachtal tailings impoundment, Graupner et al. (2007) found pyrite (partly arsenian pyrite), arsenopyrite, sphalerite (mostly Fe-rich), galena, mica, feldspar, quartz, barite and fluorite (CaF₂). In the weathered tailings, Graupner et al. (2007) reported gypsum (CaSO₄•2H₂O), Fe(III)-oxyhydroxides, Fe(III)-oxy-sulfates (i.e. jarosite ([KFe₃(SO₄)₂(OH)₆])), amorphous silica (SiO₂), Si–Fe-rich and Fe–As-rich gels, alunite (KAl₃(SO₄)₂(OH)₆), native S and clay minerals (i.e. kaolinite (Al₂Si₂O₅(OH)₄), illite–smectite).

2.2. Additional analyses

In addition to the samples and data described in Graupner et al. (2007), analytical results were used from a large volume sample (~300 L) of tailings material from an essentially oxidized zone of the dump (Fig. 1: location F). The sample is composed of fine sand and subordinate silt and comes from the margin of the central slimes area of the tailings impoundment. This material was thoroughly homogenized using a sample splitter and a subsample was subjected to X-ray fluorescence (XRF), analysis of total C and total S (LECO), and particle-size analysis. For particle-size analysis, an automatic particle-size analyzer (<63 μm fraction; Micrometrics SediGraph 5100), based on X-ray scattering was used.

Cemented parts of a neighboring tailings dump (Davidschacht-Halde, Freiberg, Germany) were analyzed to investigate pore size and geometry, in order to quantify the critical porosity at which
the pore area becomes disconnected, which would indicate a strong decrease in permeability. Thereto, thin sections from a “gel-rich” and a “gel-poor” cemented layer have been investigated. In the “gel-rich” cemented layer, over 50% of the secondary phases were characterized as amorphous, whereas in the “gel-poor” cemented layer formation (0.15–0.90 m), node length was 0.02 m. At greater depths, node length was gradually increased to 0.20 m. The upper boundary was defined as a constant field boundary (1.015 bar, water-saturated, anoxic) at a hypothetical depth of 4 m, which is sufficient for not influencing the main zone of cemented layer formation. The initial pore water was defined as pH-neutral, O2-saturated, and in equilibrium with gypsum and kaolinite. The simulated run time was 40 a, which approximately represents the time span between the end of deposition at the study site and the time the investigations were started on site. On the basis of the chosen boundary conditions, which imply a continuous light rainfall, the formation of hardpans at the capillary fringe due to precipitation as a result of evaporation processes is not possible.

Geochemical speciation calculations were based on the EQ3/6 database (Wolery, 1992) that was included in the TOUGHREACT model. The database was modified with respect to solubility constants of various primary and secondary phases (see Table 2). Furthermore, equilibrium constants for As(III) and As(V) species were included from Langmuir et al. (2006). The FLOTRAN thermodynamic database was adjusted in order to create an identical database as used for TOUGHREACT. The simulations described here include ion strengths up to ~0.1 M, so that the extended Debye–Hückel algorithm could be used to calculate activity coefficients. The TOUGHREACT model, however, contains Debye–Hückel parameters optimized for NaCl (Xu et al., 2004), and a comparison of activity coefficients calculated with TOUGHREACT and FLOTRAN has shown that in 0.06 M Ca–SO4-dominated solutions, significant differences occur, in particular for di- and trivalent ions. This discrepancy was circumvented by using activities instead of concentrations to describe initial and boundary water compositions.

The interaction of O2 with the aqueous solution is assumed to be at equilibrium. Aqueous complexation reactions are also assumed at equilibrium, even though some aqueous redox pairs may not be at equilibrium. The (oxidative) dissolution of the primary minerals is considered to be rate-controlling. Rate

---

### Table 1

Properties of bulk tailings material.

<table>
<thead>
<tr>
<th>Component</th>
<th>Units</th>
<th>300 L sample</th>
<th>Historical data</th>
<th>Tailings dam</th>
<th>Freiberger gneiss</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>wt.%</td>
<td>53.87</td>
<td>66.32</td>
<td>60.9</td>
<td></td>
</tr>
<tr>
<td>TiO2</td>
<td>wt.%</td>
<td>0.46</td>
<td>0.33</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Al2O3</td>
<td>wt.%</td>
<td>10.71</td>
<td>9.32</td>
<td>15.2</td>
<td></td>
</tr>
<tr>
<td>Fe2O3</td>
<td>wt.%</td>
<td>5.12</td>
<td>2.53</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>MoO</td>
<td>wt.%</td>
<td>0.03</td>
<td>0.02</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>wt.%</td>
<td>1.2</td>
<td>0.71</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>wt.%</td>
<td>6.36</td>
<td>5.53</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Na2O</td>
<td>wt.%</td>
<td>0.81</td>
<td>0.58</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>K2O</td>
<td></td>
<td>2.85</td>
<td>2.18</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>P2O5</td>
<td>wt.%</td>
<td>0.11</td>
<td>0.08</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>wt.%</td>
<td>≥0.16</td>
<td>≥0.16</td>
<td>≥0.16</td>
<td></td>
</tr>
<tr>
<td>(SO4)2</td>
<td>wt.%</td>
<td>≥5.7</td>
<td>≥3.3</td>
<td>≥0.5</td>
<td></td>
</tr>
<tr>
<td>LOI</td>
<td>wt.%</td>
<td>7.38</td>
<td>6.57</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Sum</td>
<td>wt.%</td>
<td>92.94</td>
<td>95.76</td>
<td>96.60</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>ppm</td>
<td>≥400</td>
<td>≥470</td>
<td>≤10</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>ppm</td>
<td>1056</td>
<td>375</td>
<td>240</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>ppm</td>
<td>641</td>
<td>618</td>
<td>&lt;100</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>ppm</td>
<td>381</td>
<td>615</td>
<td>&lt;100</td>
<td></td>
</tr>
<tr>
<td>CO2-tot</td>
<td>wt.%</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO4-tot</td>
<td>wt.%</td>
<td>9.17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfide-S</td>
<td>wt.%</td>
<td>0.22–1.4</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay (&lt;2 μm)</td>
<td>wt.%</td>
<td>3.4</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silt (2–63 μm)</td>
<td>wt.%</td>
<td>65.0</td>
<td>28.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sand (63–2000 μm)</td>
<td>wt.%</td>
<td>31.6</td>
<td>70.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

a Data from ACD-report (1993).
b Sample L1/2, 171–176 cm depth, data taken from Graupner et al. (2007).
c Scheinert et al. (2009).
d Sulfid-content is between 0.22% (measured in a neighboring profile (Graupner et al., 2007) and 1.4% (estimated as the difference between LECO-SO3 and XRF-SO3).
expressions are discussed in Section 3.3. Because the precipitation of secondary phases was considered to be fast in comparison to the dissolution of the primary minerals, the formation of secondary minerals occurred effectively at conditions close to local equilibrium. FLOTRAN was additionally used to simulate As and Zn sorption to ferrilithprite. Thereto, surface complexation constants for sorption of Zn, As, Ca and SO$_4$ to amorphous Fe hydroxide, as well as site densities of amorphous Fe hydroxide were taken from Dzombak and Morel (1990).

The transport of O$_2$ gas in shallow sediments mainly occurs as a diffusion process (Xu et al., 2001). Therefore, the calculations were simplified by choosing the TOUGHREACT module that assumes a passive gas phase. The calculations with FLOTRAN, which included both gas convection and diffusion, confirmed that diffusion is the most significant transport mechanism for O$_2$ gas here. Effective diffusion coefficients ($D_{eff}$) for species in phase $p$ (gas or liquid phase) were calculated as a function of porosity ($\phi$), tortuosity ($\tau$), and saturation ($S_p$) according to Eqs. (1) and (2) in TOUGHREACT (Pruess et al., 1999), and according to Eqs. (3)–(5) in FLOTRAN (Lichtner et al., 2004; Lichtner, 2007). Eq. (2) represents the tortuosity–porosity relationship proposed by Millington and Quirk (1961). A standard diffusion coefficient ($D_p^0$) for aqueous
Accordingly, the different strata were described as "sandy loam" different texture classes (Carsel and Parrish, 1988; Brown, 2003). Simulations (e.g. scenario HOM, see Table 4) were based on the observed soil texture and published values for permeability due to changes in porosity were initially modeled with the simplified cubic law (Eq.(6), e.g. Xu et al., 2004), which refers to initial parameter values. These parameter settings result in approximately similar $D_s^{\text{diff}}$ coefficients as calculated by Eqs. (1) and (2) in TOUGHREACT.

$$D_s^{\text{diff}} = \phi \cdot \tau_0 \cdot D_s^0$$

$$\tau_0 = \phi^2 \cdot S_{\text{up}}$$

(1)

(2)

In FLOTRAN, the tortuosity for the liquid phase (Eq. (3)) was set to 0.20, which was optimized for the dominant texture in the simulations (e.g. scenario HOM, see Table 4). However, different $D_i^0$ will be calculated by TOUGHREACT and FLOTRAN for regions with different $S_i$ (e.g. in the mica-enriched silt loam regions). Parameters $\text{EXPS}$ (Eq. (4)), and $\tau_i$ and $n$ (Eq. (5)) were set to 2.33, 0.75 and 0.33, respectively. Subscript $i$ refers to initial parameter values. These parameter settings result in approximately similar $D_s^{\text{diff}}$ coefficients as calculated by Eqs. (1) and (2) in TOUGHREACT.

$$D_i^{\text{diff}} = \phi \cdot \tau_i \cdot S_i \cdot D_i^0$$

$$D_s^{\text{diff}} = \phi \cdot \tau_s \cdot S_s \cdot S^{\text{EXPS}} \cdot D_s^0$$

$$\tau_s = \tau_0 \cdot \left( \frac{\phi}{\phi_s} \right)^n$$

(3)

(4)

(5)

The initial hydraulic properties for the van Genuchten model were based on the observed soil texture and published values for different texture classes (Carsel and Parrish, 1988; Brown, 2003). Accordingly, the different strata were described as "sandy loam" and "silt loam" assuming the following soil hydraulic properties: Sandy loam: porosity = 0.41, permeability = $1.2 \times 10^{-12}$ m$^2$/s, $\lambda = 0.471$, $\alpha = 7.65 \times 10^{-4}$ Pa$^{-1}$, and residual water saturation = 0.158. Silt loam: porosity = 0.41, permeability = $1.15 \times 10^{-13}$ m$^2$/s, $\lambda = 0.291$, $\alpha = 2.04 \times 10^{-4}$ Pa$^{-1}$, and residual water saturation = 0.149. The critical gas saturation was set to 0.05. Changes in hydraulic permeability due to changes in porosity were initially modeled with the simplified cubic law (Eq. (6), e.g. Xu et al., 2004), which is implemented in both codes, and thus can be used to compare results between codes. Parameter $k$ represents the hydraulic permeability, subscript $i$ refers to the initial values.

$$k = k_i \cdot \left( \frac{\phi - \phi_c}{\phi_i - \phi_c} \right)^3$$

(6)

As Eq. (6) may not reflect the complex relationship between porosity and permeability in cemented layers, TOUGHREACT was additionally used with the Verma–Pruess permeability–porosity relationship, which also takes into account the convergent–divergent nature of natural pore channels, where pore throats can become clogged by precipitation while disconnected void spaces remain in the pore bodies (Eq. (7), Verma and Pruess, 1988).

$$k = k_i \left( \frac{\phi - \phi_c}{\phi_i - \phi_c} \right)^m$$

(7)

Parameter $\phi_c$, a medium-dependent "critical" porosity at which permeability goes to zero, was estimated to be 15% for cemented layers (see Section 3.2). Parameter $m$, also medium-dependent, was set to 3.0.

3. Results and discussion

3.1. Bulk tailings properties

Bulk chemical compositions and particle sizes of various unoxidized samples from the Muenzbachtal tailings site are summarized in Table 1, including (i) the 300 L sample, (ii) an historical tailings sample (ACD-report, 1993), (iii) sediment from the unoxidized zone of the SE part of the tailings dam (Graupner et al., 2007), and (iv) the Freiberger gneiss (Scheinert et al., 2009). The bulk chemistry of the sediment samples is dominated by SiO$_2$ and Al$_2$O$_3$. Significant amounts of Fe$_2$O$_3$, CaO, SO$_3$, and K$_2$O as well as Ba, As, Zn, Pb and Cu were also measured. The original sulfide-S content of the tailings material at the time of deposition is

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Individual layer</th>
<th>Thickness (m)</th>
<th>Texture</th>
<th>Sulfide content relative to HOM</th>
<th>Biotite content relative to HOM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOM</td>
<td>L1 – Average bulk composition (see Table 2)</td>
<td>4.0</td>
<td>Sandy loam</td>
<td>100%</td>
<td>100</td>
</tr>
<tr>
<td>HM</td>
<td>L2a – Sandy matrix, depleted in sulfides</td>
<td>0.22</td>
<td>Sandy loam</td>
<td>20%</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>L3a – Heavy mineral layer, enriched in sulfides</td>
<td>0.3</td>
<td>Sandy loam</td>
<td>20%</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>L2a – Sandy matrix, depleted in sulfides</td>
<td>0.3</td>
<td>Sandy loam</td>
<td>20%</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>L2a – Sandy matrix, depleted in sulfides</td>
<td>2.28</td>
<td>Sandy loam</td>
<td>20%</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>L1 – Average bulk composition</td>
<td>1.0</td>
<td>Sandy loam</td>
<td>100%</td>
<td>100</td>
</tr>
<tr>
<td>HMAS</td>
<td>L2b – Sandy matrix, depleted in arsenopyrite and arsenian pyrite</td>
<td>0.62</td>
<td>Sandy loam</td>
<td>0% FeAsS, 0% arsenian pyrite</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>L3b – Heavy mineral layer, enriched in arsenopyrite, depleted in arsenian pyrite</td>
<td>0.02</td>
<td>Sandy loam</td>
<td>56753% FeAsS, 0% arsenian pyrite</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>L2b – Sandy matrix, depleted in arsenopyrite and arsenian pyrite</td>
<td>3.36</td>
<td>Sandy loam</td>
<td>0% FeAsS, 0% arsenian pyrite</td>
<td>100</td>
</tr>
<tr>
<td>MICA</td>
<td>L2c – Sandy matrix, depleted in biotite</td>
<td>0.32</td>
<td>Sandy loam</td>
<td>100%</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>L4b – Silt layer, enriched in biotite</td>
<td>0.1</td>
<td>Silt loam</td>
<td>100%</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>L2c – Sandy matrix, depleted in biotite</td>
<td>0.3</td>
<td>Sandy loam</td>
<td>100%</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>L2c – Sandy matrix, depleted in biotite</td>
<td>2.18</td>
<td>Sandy loam</td>
<td>100%</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>L1 – Average bulk composition</td>
<td>1.0</td>
<td>Sandy loam</td>
<td>100%</td>
<td>100</td>
</tr>
<tr>
<td>HET</td>
<td>L2d – Sandy matrix, depleted in both sulfides and biotite</td>
<td>0.22</td>
<td>Sandy loam</td>
<td>20%</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>L3c – Heavy mineral layer, enriched in sulfides</td>
<td>0.1</td>
<td>Sandy loam</td>
<td>1140%</td>
<td>100</td>
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<tr>
<td></td>
<td>L4b – Silt layer, enriched in biotite</td>
<td>0.1</td>
<td>Silt loam</td>
<td>100%</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>L2d – Sandy matrix, depleted in both sulfides and biotite</td>
<td>0.2</td>
<td>Sandy loam</td>
<td>20%</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>L3c – Heavy mineral layer, enriched in sulfides</td>
<td>0.1</td>
<td>Sandy loam</td>
<td>1140%</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>L4b – Silt layer, enriched in biotite</td>
<td>0.1</td>
<td>Silt loam</td>
<td>100%</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>L2d – Sandy matrix, depleted in both sulfides and biotite</td>
<td>2.18</td>
<td>Sandy loam</td>
<td>20%</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>L1 – Average bulk composition</td>
<td>1.0</td>
<td>Sandy loam</td>
<td>100%</td>
<td>100</td>
</tr>
</tbody>
</table>

Species of $1.0 \times 10^{-6}$ m$^2$/s and for gaseous species of $2.13 \times 10^{-5}$ m$^2$/s was applied.

$$P_{\text{up}}^D = \phi \cdot \tau_0 \cdot D_s^0$$

$$\tau_0 = \phi^2 \cdot S_{\text{up}}$$

(1)

(2)
Marmatite ($Zn_{0.8}Fe_{0.2}S$) was taken as a model compound for Fe-rich sulfide-S, total As, and total Zn in Table 1, cf. ACD-report, 1993). Based on the bulk chemistry of the historical tailings sample (total sphalerite, gypsum and quartz (see also Table 2). The simulated tailings mineralogy was kept as simple as possible. Specific surface areas were recalculated into $cm^2/g$ for TOUGHREACT and into $m^2/m^3$ (surface area/bulk total volume) for FLOTRAN. In order to obtain similar rate laws in TOUGHREACT and FLOTRAN, initial surface areas in TOUGHREACT were divided by the initial liquid saturation, and in FLOTRAN, the initial surface area/bulk total volume was used.

3.2. Pore geometry of cemented tailings

Fig. 2 shows an image of the calculated pore area reduction in 2 µm erosion steps for a “gel-poor” and a “gel-rich” cemented layer. In the “gel-poor” region, the pores seem to become disconnected after eight erosion steps. In the “gel-rich” region, a disconnection of pores is observed after 14–16 erosion steps. Fig. 3 shows the remaining (normalized) pore area as a function of erosion step. For the “gel-poor” region, eight erosion steps correspond to a pore area of 17%. For the “gel-rich” region, 14–16 erosion steps correspond to a pore area of 13–15%. Therefore, the “critical porosity” in the permeability–porosity relationship (Eq. (7)) was estimated to be 15%.

3.3. Reactive minerals, rate expressions

Primary and secondary minerals were chosen on the basis of detailed mineralogical analyses of samples from field profiles C, D, and F (see Section 2.1, cf. Graupner et al., 2007), and the regional ore and wall–rock mineralogy (see Section 2.1, cf. Tichomirowa, 2001). The simulated tailings mineralogy was kept as simple as possible, which means that only phases with relevant reaction kinetics were included. As discussed below, the following set of primary minerals has been considered in the simulations: sphalerite, Fe-rich sphalerite, arsenopyrite, arsenian pyrite, biotite, anorthite, gypsum and quartz (see also Table 2).

Mineral volume fractions of sulfide-bearing minerals were based on the bulk chemistry of the historical tailings sample (total sulfide-S, total As, and total Zn in Table 1, cf. ACD-report, 1993). Marmatite ($Zn_{0.8}Fe_{0.2}S$) was taken as a model compound for Fe-rich sphalerite. The proportion of sphalerite to Fe-rich sphalerite was determined from column leaching experiments (results not shown). The average arsenopyrite content was arbitrarily set to 0.02 v/v %. Individual electron microprobe spot analyses of unoxidized samples of tailings material have shown that pyrite is often enriched in As. Therefore, the remaining As and sulfide-S content was calculated to consist of arsenian pyrite with an As content of 2.5 wt.%. This 2.5 wt.% fits well within the general compositional range of 0–10% reported for selected As-rich pyrite samples (Kolker and Nordström, 2001).

The lower Freiberg gneiss, which represents the wall rock of the mined ore veins, contributes ~10–20 vol.% to the heaped material at the study site (estimated using data from Graupner et al., 2007). The gneiss has a modal composition of ~30 vol.% of quartz, ~32 vol.% of plagioclase, ~12 vol.% of K-feldspar, ~8 vol.% of muscovite and ~14 vol.% of biotite (average of four modal mineralogy data sets in Tichomirowa, 2001). Furthermore, anorthite contents in plagioclase feldspar are up to 30% for the lower Freiberg gneiss (e.g. Walther, 1962). Based on the above assumptions, ~2.7 vol.% of anorthite and ~3.9 vol.% of biotite was estimated to be present within the unmodified sediments of the studied tailings impoundment. Muscovite, Ca-poor plagioclase, and K-feldspar were not included in the simulations, as these phases did not show significant alteration in the 40 a old weathered tailings samples (Graupner et al., 2007). The ratio of Mg to Fe in the biotite was estimated as 1.2 to 1.8, based on the MgO- and biotite-content of the lower Freiberger gneiss (Table 1).

The relatively high Ca content of the tailings compared to the gneiss (Table 1) is explained by the application of Ca-supplements during ore processing. Their reaction product would be gypsum, which was included as an additional model compound. Additional Ca may occur in locally important minerals like fluorite and calcite (according to Table 1, >0.50 wt.% CaO could be bound to fluorite and ~0.20 wt.% CaO in calcite).

The following secondary phases were allowed to precipitate: gypsum, jarosite, alunite, ferricydrhydrate, amorphous silica, amorphous ferric arsenate and kaolinite (see also Table 2). Kaolinite was taken as a model compound for Si–Al gels and clay minerals that remain after mica and plagioclase feldspar weathering.

Rate expressions and specific mineral surface areas for kinetic mineral dissolution reactions are presented in Table 3. Rate expressions were kept as simple as possible. Specific surface areas were recalculated into $cm^2/g$ for TOUGHREACT and into $m^2/m^3$ (surface area/bulk total volume) for FLOTRAN. In order to obtain similar rate laws in TOUGHREACT and FLOTRAN, initial surface areas in TOUGHREACT were divided by the initial liquid saturation, and in the equation to update the change in surface area in FLOTRAN, the power of volume fraction was set to 1.0.

The oxidative dissolution rate for pure sphalerite from Salmon and Malmström (2006) was increased by a factor of 16 (after Weisener et al., 2003) to obtain the oxidative dissolution rate for...
## Table 5
Comparison of theoretical and measured bulk chemical compositions.

<table>
<thead>
<tr>
<th>Layer or sample</th>
<th>Sulfid-S (%)</th>
<th>Fe$_2$O$_3$ (%)</th>
<th>MgO (%)</th>
<th>K$_2$O (%)</th>
<th>Al$_2$O$_3$ (%)</th>
<th>CaO (%)</th>
<th>Zn (ppm)</th>
<th>As (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1 – Average bulk composition</td>
<td>1.4</td>
<td>4.1</td>
<td>0.8</td>
<td>0.8</td>
<td>2.6</td>
<td>2.6</td>
<td>1890</td>
<td>982</td>
</tr>
<tr>
<td>L2a – Sandy matrix, depleted in sulfides</td>
<td>0.3</td>
<td>2.7</td>
<td>0.8</td>
<td>0.8</td>
<td>2.6</td>
<td>2.6</td>
<td>378</td>
<td>196</td>
</tr>
<tr>
<td>L2b – Sandy matrix, depleted in FeAsS, only As-free pyrite</td>
<td>1.4</td>
<td>4.1</td>
<td>0.8</td>
<td>0.8</td>
<td>2.6</td>
<td>2.6</td>
<td>1890</td>
<td>0</td>
</tr>
<tr>
<td>L2c – Sandy matrix, depleted in biotite</td>
<td>1.4</td>
<td>2.9</td>
<td>0.4</td>
<td>0.4</td>
<td>2.1</td>
<td>2.6</td>
<td>1890</td>
<td>982</td>
</tr>
<tr>
<td>L2d – Sandy matrix, depleted in both sulfides and biotite</td>
<td>0.3</td>
<td>1.5</td>
<td>0.4</td>
<td>0.4</td>
<td>2.1</td>
<td>2.6</td>
<td>378</td>
<td>196</td>
</tr>
<tr>
<td>L3a – Heavy mineral layer, enriched in sulfides</td>
<td>17.5</td>
<td>23.7</td>
<td>0.8</td>
<td>0.8</td>
<td>2.6</td>
<td>2.6</td>
<td>23,060</td>
<td>11,975</td>
</tr>
<tr>
<td>L3b – Heavy mineral layer, enriched in arsenopyrite, As-free pyrite</td>
<td>10.1</td>
<td>25.6</td>
<td>0.8</td>
<td>0.8</td>
<td>2.6</td>
<td>2.6</td>
<td>1890</td>
<td>202,014</td>
</tr>
<tr>
<td>L3c – Heavy mineral layer, enriched in sulfides</td>
<td>16.4</td>
<td>22.3</td>
<td>0.8</td>
<td>0.8</td>
<td>2.6</td>
<td>2.6</td>
<td>21,548</td>
<td>11,190</td>
</tr>
<tr>
<td>L4a – Silt layer, enriched in biotite</td>
<td>1.4</td>
<td>20.7</td>
<td>6.4</td>
<td>6.2</td>
<td>5.4</td>
<td>5.1</td>
<td>1890</td>
<td>982</td>
</tr>
<tr>
<td>L4b – Silt layer, enriched in biotite</td>
<td>1.4</td>
<td>19.5</td>
<td>6.0</td>
<td>5.8</td>
<td>8.0</td>
<td>5.1</td>
<td>1890</td>
<td>982</td>
</tr>
</tbody>
</table>

Field sample Muenzbachtal heap, profile C
d. As-rich cemented layer
Field sample Muenzbachtal heap, profile Da, cemented layer
Field sample Muenzbachtal heap, profile Da, HM layer

n.a. indicates not analysed.

a See Fig. 1.
b Graupner et al. (2007).

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**Fig. 4.** Simulation results for scenario “HOM”. (a) Initial cumulative mineral volume fractions; (b) cumulative mineral volume fractions, pH, and O$_2$(g) after a simulated run time of 40 a calculated with FLOTRAN and (c) TOUGHREACT. (d) Simulated total dissolved concentrations calculated with FLOTRAN, including sorption processes. The color legend is included in Figs. 6 and 8.
Fe-rich sphalerite (containing 16.7 wt.% Fe). According to their experiments, the dissolution rate for Fe-bearing sphalerite (containing 11.4% – 12.9 wt.% Fe) was 16–36 times as fast as the rate for Fe-poor sphalerite (containing 0.45 wt.% Fe) at pH 1.0. The oxidation rate for arsenian pyrite, which was based on the rate expression of Williamson and Rimstidt (1994), was increased by a factor of two in accordance with experiments by Lehner and Savage (2008). In their experiments, the oxidation rate of arsenian pyrite with 1.7 wt.% As was twice as fast as for pure pyrite. Furthermore, the rate expression of Williamson and Rimstidt (1994) was simplified by making it pH-independent, assuming an average pH of 3.0. This simplification does not significantly influence the modeling results discussed in this paper, and ensures the correct implementation of the rate expressions in both reactive transport codes. The dissolution of anorthite and biotite is strongly dependent on pH, and therefore, pH-dependent rate expressions were applied (see Table 3). The rate expression for biotite dissolution is based on the average pH-dependent release rates of Si, Fe, Mg and Al measured by Malmström and Banwart (1997). Malmström and Banwart (1997) have also shown that K⁺ is released significantly faster than any of the other elements. Therefore, a separate pH-dependent rate expression for the release of K⁺ from biotite was included.

3.4. Definition of scenarios

Five scenarios have been defined in order to explain the cemented layer formation processes observed in the field. Table 4 presents an overview of the characteristics of each scenario. The total amount of reactive material is similar in each scenario, as stratification was realized by a redistribution of the available reactive material.

**Scenario HOM** (i.e. homogeneous) was run with the average bulk composition as given in Table 2, without any further stratification. **Scenario HM** (i.e. heavy mineral) was run with two heavy mineral-enriched (HM) layers, containing high concentrations of sulfides. Thereto, the sulfide content of the bulk matrix was reduced to 20%, and the remaining 80% was concentrated in the two HM layers. **Scenario HMA** was run with one HM layer containing all As as arsenopyrite. Thereto, the bulk matrix was
depleted in As, yielding As-free pyrite and zero arsenopyrite. This scenario refers to field profile C, which contains mm-thick heavy mineral-rich layers with originally high concentrations of arsenopyrite (Graupner et al., 2007). Scenario MICA was run with two silt layers with increased biotite concentrations. Thereto, the biotite content of the bulk matrix was reduced to 50%, and the remaining 50% was concentrated in the two silt layers.

Scenario HET (i.e. heterogeneous) was run with two HM layers situated on top of two silt layers. Thereto, the sulfide and biotite content of the bulk matrix were reduced to 20% and 50%, respectively, and the remaining sulfide and biotite were concentrated in the respective layers.

Although several profiles of the weathered tailings have been analyzed in detail (Jung et al., 2001; Graupner et al., 2007), the exact mineral composition of originally unweathered layers remains largely unknown. In Table 5 some analysis results for characteristic weathered layers studied at the heap are compared to the theoretical composition of the layers defined in Table 4. For example, the MgO and K2O contents of the proposed silt layer (L6) are much higher than measured in any of the weathered layers at the heap. Furthermore, the As and Zn contents of the proposed HM layers (L5a and L5b) are much higher than measured in any of the weathered layers in the field. Of course, during 40 a of weathering, a significant part of these components (especially Zn) was lost. It should be emphasized, that the individual scenarios may represent extreme stratification, meant to qualitatively investigate possible mechanisms of cemented layer formation.

3.5. Modeling results and discussion

Modeling results are presented for cumulative mineral volume fractions, O2(g), pH, and dissolved concentrations down to a depth of 2 m and after a simulated run time of 40 a (Figs. 4–8). The corresponding color legend is included in Figs. 6 and 8. The simulation results obtained with TOUGHREACT and FLOTRAN basically match well, which confirms the proper working of both codes. Small differences in simulated [O2(aq)], pH and mineral volume fractions are observed, which, however, do not significantly affect the cemented layer formation processes. The discrepancies are related to different O2 diffusion rates (compare Eq. (1–5)). For example, in Fig. 8, the dissolved O2 concentration in the heavy mineral layer at
0.7 m depth was calculated to be $6.3 \times 10^{-6}$ M for TOUGHREACT and $1.1 \times 10^{-5}$ M for FLOTRAN. The higher dissolved O$_2$ concentration in FLOTRAN resulted in faster sulfide oxidation rates compared to TOUGHREACT, which explains the development of lower pH values and higher amounts of secondary minerals at this depth as compared to TOUGHREACT.

**Scenario “HOM”** is presented in Fig. 4. The oxidation front was calculated to move downward continuously, as a result of ongoing sulfide oxidation. After 40 a of simulation time, almost all sulfides were oxidized down to the water table at 3.8 m. Simulated pH values initially decreased to values below 5.0, then gradually increased to values between 5.5 and 5.8 due to replacement of the sulfides and biotite weathering. The K released as a result of biotite weathering resulted in the precipitation of jarosite. The anorthite weathering rate was not significant here (<2 vol.%) because of the moderate pH conditions. In scenario “HOM”, secondary phases were not concentrated in distinct layers, but were calculated to precipitate over the entire length of the unsaturated profile (cf. Graupner et al., 2007). At the top of the profile, secondary phases were washed-out by rainwater input.

In **scenario “HM”** (Fig. 5), a sequence of three cemented layers has been simulated, situated at the interfaces between the sulfide-rich layers and the mica-containing sandy layers. The porosity was predicted to decrease from 0.41 to 0.29. The cemented layers mainly represent an accumulation of jarosite, ferrihydrite, gypsum and amorphous silica, which is in accordance with field observations (Graupner et al., 2007). The precipitation of jarosite at the interfaces between the layers is explained by the availability of potassium. The weathering rate of biotite and plagioclase strongly increases with decreasing pH (Table 3), resulting in the highest release of Ca and K in the immediate vicinity to the source of the ARD. The cemented layers have developed as relatively broad layers. This is explained by the movement of the reaction zone to gradually greater depths upon depletion of biotite and anorthite.

In **scenario “HMAS”** (Fig. 6), a single cemented layer mainly consisting of amorphous ferric arsenate was predicted to precipitate within the arsenopyrite-rich layer. The solubility of amorphous ferric arsenate is lowest under acid conditions (pH 3–5), and its molar volume is up to 4.2 times larger than that of arsenopyrite (Table 2). The porosity within this cemented layer was
predicted to decrease from 0.41 to <0.15 in less than 10 a simulation run time, which is below the “critical porosity”. Cemented layers dominated by amorphous As–Fe–Si-gel phases have indeed been observed in the field (Lee et al., 2005; Graupner et al., 2007) as well as in column experiments (Jung et al., 2001; Rammlmaier et al., 2001). Fig. 6d shows simulation results for the same scenario, with the Verma–Pruess relationship (Eq.(7)) activated. After a simulated run time of less than 10 a, the porosity has decreased to 0.15, which resulted in a strong retardation of the downward diffusion of O\textsubscript{2}. The simulations based on the cubic permeability–porosity function (Fig. 6b and c), do not show such a significant decrease in the downward diffusion rate of O\textsubscript{2}, because according to Eq.(6), a strong reduction in permeability is only possible when the porosity approaches zero.

The results of scenario “MICA” (Fig. 7) resemble those of scenario “HOM” (Fig. 4). No cemented layers were formed, because the initial concentration of biotite and anorthite in the sandy layers was high enough to provide enough K and Ca for jarosite and gypsum formation in the sandy layers. The increased water saturation in the silt layers, however, has reduced the downward diffusion rate of O\textsubscript{2}. The calculated O\textsubscript{2} profile represents the sum of O\textsubscript{2} input through diffusion and O\textsubscript{2} usage through oxidation processes.
Scenario “HET” (Fig. 8) was very successful in producing effective cemented layers. The porosity of the upper biotite-rich layer was predicted to decrease from 0.41 to <0.15 in less than 10 a of simulation run time, which is below the estimated “critical” porosity. Fig. 8d shows simulation results for the same scenario calculated with TOUGHREACT, with the Verma–Pruess relationship (Eq. (7)) activated. After a simulated run time of 6 a, the porosity had decreased to 0.17, which resulted in a strong retardation of the downward diffusion of O2. Newly formed jarosite and ferrihydrite are responsible for this extensive cementation. The hydrogeochemical processes are very similar to scenario “HM”. In scenario “HM”, the zone of jarosite precipitation moved to greater depth upon depletion of the K source. In scenario “HET”, however, the availability of K immediately below the zone of ARD generation is much greater than in scenario “HM”. Consequently, jarosite could precipitate in only a narrow zone underneath the zone of ARD generation, which explains the high degree of pore clogging.

The effect of recharge rate on cemented layer formation processes has been investigated for scenario HET. Recharge rates were calculated to have no significant effect at the upper reactive interface at 0.4 m depth. However, a larger amount of soluble phases (mainly gypsum) are predicted to be washed out by increasing amounts of infiltrating rain water. At the lower reactive interface at 0.7 m depth, increasing recharge rates resulted in reduced sulfide oxidation rates. This is explained by an increased water saturation and consequently lower effective O2 diffusion rate.

The simulated dissolved concentrations of Ca, SO4, Fe, Si, Al, and As are generally controlled by equilibrium with respect to gypsum, ferrihydrite, amorphous silica, kaolinite, and amorphous ferric arsenate, respectively. The calculated increase in the SO4 concentration with depth is explained by the formation of soluble MgSO4-species. In the uppermost layers, the dissolved concentration of various components is decreased, which is explained by leaching due to rain water infiltration. The concentration of Zn generally increases with depth, due to (oxidative) dissolution and transport. Variations in dissolved Fe concentrations are explained by the strongly pH-dependent nature of the solubility of ferrihydrite (e.g. scenario MICA, HET), and also by the absence of ferrihydrite in specific layers (e.g. in scenario HM, HET). The simulated concentrations of Ca, SO4, Fe, Al, Si, and Zn are within the ranges for sulfide-bearing tailings pore waters reported by Gunsinger et al. (2006). The simulated concentrations of As are within the range reported by Moncur et al. (2009). Simulated pH values correspond well to measured pH values at the investigated field site (pH 2.5–7.0: Graupner et al., 2007), except for the mica-enriched silt layers. The model overestimates the pH in the mica-enriched silt layers, and also the dissolved concentrations of Mg and K in layers that still contain biotite (e.g. scenario MICA). In the absence of biotite, the concentrations of Mg and K are relatively low and within the range reported by Gunsinger et al. (2006). In the presence of biotite, the concentrations of Mg and K generally increase with depth due to dissolution and transport (e.g. scenario HOM, HMAS). This is explained by the model assumption, that upon biotite dissolution, K and Mg are completely released into the pore water solution. As the model does not provide any retention mechanism for Mg or for K at neutral pH values, the concentrations of these elements increase with depth. The model could be further improved by taking into account the incongruent nature of biotite-weathering, which would also reduce the simulated pH values inside the biotite-rich layers.

FLOTTRAN has also been used to simulate possible mechanisms for As and Zn retention in the described scenarios. These attenuation mechanisms include sorption to freshly precipitated ferrihydrite and precipitation as amorphous ferric arsenate. Crystalline As phases have not been observed in the field samples (Graupner et al., 2007). Furthermore, As may precipitate in jarosite-beudantite solid solutions as observed by Gieré et al. (2003), Romero et al. (2007), and Graupner et al. (2007). However, thermodynamic data for the latter process are not available yet. Due to the prevailing pH conditions (pH 2–6), Zn retention was not significant. The best protection against Zn leaching was calculated to be the cemented layer in scenario HET, underneath which (Zn) sulfide minerals were stable under the newly developed anoxic conditions.

For As, pH conditions between pH 3 and pH 5 are very favorable for the precipitation of amorphous ferric arsenate. Fig. 9 demonstrates the strong dependence of the solubility of amorphous ferric arsenate on pH. Fig. 9 also shows that recrystallisation of amorphous ferric arsenate into scorodite would significantly reduce As mobility (see also Paktunc and Bruggeman (2010), who also measured dissolution and precipitation rates for these phases). In the upper 2 m of scenario HM and HMAS, 85–99% of the initial As was calculated to occur as amorphous ferric arsenate. In the upper 2 m of scenario HOM, HMAS and HET, up to 10% of the initial As was calculated to be sorbed to freshly precipitated ferrihydrite, and 26–65% of the initial As was calculated to have precipitated as amorphous ferric arsenate. Furthermore, significant amounts of As prevailed in sulfides underneath the cemented layer in scenario HET, where anoxic conditions could develop.

4. Summary and conclusions

Field and laboratory data from a low-sulfide, low-carbonate tailings site have been used to design multiple possible scenarios for reactive transport modeling of processes leading to the formation of cemented layers. The simulations were performed with two different reactive transport codes (TOUGHREACT and FLOTTRAN), which basically yielded similar results. Stratification was found to play a crucial role in the formation of cemented layers:

- In homogeneous systems without stratification (scenario HOM), secondary phases do not accumulate in distinct horizons. The same holds true for systems with mica-enriched layers in a matrix with a homogeneous distribution of Fe sulfide-bearing minerals (scenario MICA).
- In the system with an arsenopyrite-rich layer (scenario HMAS), amorphous ferric arsenate has been predicted and observed to precipitate. Its extremely high molar volume, which is up to 4.2 times higher than that of arsenopyrite, makes this secondary phase very effective in reducing porosity. Its precipitation is favored in the pH range 3–5. A significant amount of As was calculated to be retained in this phase, effectively controlling As concentrations in pore waters as a function of pH.
- In the mixed-layer system (scenario HET), precipitation of secondary minerals takes place immediately below the Fe sulfide-enriched layers. The more pronounced the geochemical interface between the heavy mineral rich layer and the biotite-enriched layer, the higher the extent of secondary mineral accumulation and the stronger the reduction in porosity in the resulting cemented layer.

The modeling results have demonstrated that the key processes in scenarios HET and HM are very different from those acting in scenario HMAS. In scenario HMAS, the only prerequisite is a local high initial concentration of reactive arsenopyrite in the sediment, which upon oxidation may reprecipitate as amorphous ferric arsenate. In scenarios HET and HM, however, the presence of a high amount of reactive aluminosilicates immediately below the HM layer appears to be crucial. Key processes in scenarios HM and HET are extensive ARD formation in the HM layers followed by enhanced (pH-driven) weathering of biotite and Ca-rich plagioclase immediately below the sulfide-enriched layers. This results in a
local extensive release of K, Ca, Al, Si, and in a buffering of pH, which promote the local accumulation of secondary phases as was also observed at the study site.

The simulated cemented layers in scenarios HMAs and HET acted as hydraulic barriers for the transport of pore gas, resulting in a sharp decrease in the O₂ concentration below the cemented layer. The Verma–Pruess permeability–porosity relationship has been calibrated based on scanning electron microscope analyses of samples of cemented layers. The “critical porosity” at which the pore area becomes disconnected and permeability might go to zero, has been estimated at ~15%. This “critical porosity” may be reached after ~10–40 a in the case of scenario HMAs, and after ~6–40 a in the case of scenario HET, according to the simulation results (min. value) and field observations (max. value).

The details presented on the role of stratification on the formation of cemented layers could be considered in the construction of mining heaps as a possible measure for stimulating natural attenuation.

Acknowledgements

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References


