Reactive transport modelling of weathering processes in intensely stratified 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 and to retain toxic elements. Our research is based on a German tailings site, where material is intensely stratified on a mm-cm scale. The computational domain was defined as an one dimensional column the size of a microscopic thin section of 22 mm length. Detailed quantitative information on changes in mineralogical composition was obtained by mineral liberation analysis (MLA). The resulting reactive transport model was applied to simulate Acid-Rock-Drainage (ARD) formation, the interaction of ARD with the tailings sediment, the formation of cemented layers, and the fate of arsenic, zinc, and lead. The results show that the identity and spatial distribution of weathering products is strongly dependent on local variations in the primary mineral assemblage.

Key words reactive transport modelling; mine tailings; mineral liberation analysis; weathering; cemented layers; metal retention; unsaturated zone

INTRODUCTION

Sulfide-bearing mine tailings are known for their potential to form Acid Rock Drainage (ARD) upon oxidative dissolution of iron-bearing sulfide minerals (e.g. pyrite, arsenopyrite). As a result, extensive precipitation of secondary phases is usually observed in the weathered parts of tailings dumps (e.g. gypsum, jarosite, Fe-(oxy)hydroxides, amorphous Fe-As phases, and amorphous Si-(Al) phases) (e.g. Graupner *et al.*, 2007). Several studies describe a preferential precipitation of secondary phases in distinct layers, the so-called cemented layers or hardpans (e.g. McGregor & Blowes, 2002; Graupner *et al.*, 2007). Such layers may show a significant reduction in porosity, and may attenuate various metals. A possible relation between intensely stratified tailings and extensive cementation has been discussed (e.g. Dold & Fontboté, 2002; Graupner *et al.*, 2007; Meima *et al.*, 2011, 2012).

In this study, detailed quantitative mineralogical data (Redwan *et al.*, 2012) have been applied in the reactive transport model FLOTRAN (Lichtner, 2007) to investigate possible effects of stratification on the potential of sulfide-bearing mine tailings to form protective cemented layers and to retain arsenic, zinc and lead.

METHODS

Site description

Our reference site is the Davidschacht tailings impoundment within the poly-metallic sulfide mine district Freiberg, Germany, which contains sulfide- and carbonate-bearing tailings deposited from 1951 to 1964 (GEOS, 1993). Within the upper 1.5 m of this impoundment, a repetition of oxidized, cemented sediments with pH values between 2 and 3, and unoxidized sulfide- and carbonate-bearing unconsolidated sediments with pH values around 7.5 have been found (Redwan *et al.*, 2012). Redwan *et al.* (2012) have conducted detailed geochemical and mineralogical investigations on the upper 1.5 m of this site.

Modelling approach

We applied the multi-component reactive transport model FLOTRAN (Lichtner, 2007), which can model fully-coupled two-phase reactive transport processes, including equilibrium and kinetic mineral dissolution and precipitation reactions, as well as surface complexation reactions. The model is based on a continuum representation of porous media. The computational domain was defined as a 1D column the size of a microscopic thin section of 22 mm length. Forty-four nodes with a uniform grid spacing of 0.5 mm were defined. The upper boundary was defined as a constant liquid flux boundary (0.1 m year^{-1}, 20°C, and atmospheric O_2 pressure). The infiltrating water represented the pore water composition as obtained from paste extraction of a bulk unweathered sample (Table 1). The lower boundary was defined as a constant field boundary.

The primary and secondary phases considered in the model are given in Table 2. Rate expressions and specific surface areas were taken from the literature (see Meima *et al.*, 2012). Additional rate expressions for siderite and ankerite were taken from Gobulev *et al.* (2009) and Gautelier *et al.* (1999), respectively. Geochemical speciation calculations are mainly based on the EQ3/6 database (Wolery, 1992); modifications are described in Meima *et al.* (2012). Surface complexation constants were taken from PHREEQC (Parkhurst & Appelo, 1999). The soil texture resembles loamy sand. Soil hydraulic properties for the van Genuchten model were taken from Carsel & Parrish (1988): porosity = 0.41, permeability = 1.12×10^{-12} m^2, $\lambda = 0.471$, $\alpha = 7.65 \times 10^{-4}$ Pa^{-1}, residual water saturation = 0.158.

Mineralogy

The initial mineralogical composition of the tailings material was based on mineral liberation analysis (MLA) of a microscopic thin section from a depth of 125 cm (source: Redwan *et al.*, 2012). MLA generally results in a SEM-BSE-EDX (Scanning Electron Microscope–Back-Scattered Electron–Energy Dispersive X-ray) based image showing the identity and quantity of mineral particles and assemblages as well as the geometry of particles and pores (Rammlmair *et al.*, 2011).

The thin section was divided into 22 layers. For each layer and for each reactive mineral, the average mineral area fraction was subsequently calculated using image analysis software.

Table 1 Properties of bulk tailings material (depth 125 cm, source: Redwan *et al.*, 2012).

Component	SiO_2	TiO_2	Al_2O_2	Fe_2O_2	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	CO_2	Ba	As	Zn	Pb
Bulk chemistry (wt -%)	69.90	0.53	9.65	6.84	0.38	1.17	2.34	0.32	2.39	0.16	3.57	1.43	4870 ppm	3170 ppm	691 ppm	505 ppm

Component	pH	Si	Al	Fe	Mn	Mg	Ca	Na	K	SO_4	HCO_3	Ba	As	Zn
Paste extraction[1] (mg L^{-1})	7.42	15.0	0.05	<0.8	<0.01	16.2	652	0.52	5.30	1680	28.0	0.012	0.034	0.27

[1] Paste extraction at tailings to distilled water ratio of 1:1 for a duration of 24 h.

Table 2 Primary and secondary minerals applied in the model.

Mineral	Formula	Abbreviation	Mineral	Formula	Abbreviation
pyrite	FeS_2	Py	gypsum	$CaSO_42H_2O$	gy
aresenian pyrite	$AS_{0.04}FeS_{1.96}$	Py(As)	calcite	$CaCO_3$	car
arsenopyrite	FeAsS	As-py	ferrihydrite	$Fe(OH)_3$	car
iron-rich sphalerite	$Fe_{0.2}Zn_{0.8}S$	Fe-sph	jarosite	$KFe_3(SO_4)_2(OH)_6$	ja
galena	PbS		kaolinite	$Al_2Si_2O_5(OH)_4$	amSiAl
biotite	$KMg_{1.2}Fe_{1.8}(AlSi_3)O_{10}(OH)_2$	bio	amorphous silica	SiO_2	amSiAl
ankerite	$CaFe(CO_3)_2$	car	amorphous ferric arsenate	$FeAsO_4.5.5H_2O$	amFeAs
siderite	$FeCO_3$	car	anglesite	$PbSO_4$	
quartz	SiO_2	qtz	zincite	ZnO	

RESULTS AND DISCUSSION

Tailings composition

Bulk tailings properties for the sample at 125 cm depth are summarized in Table 1. The material consists of grey-coloured, well-sorted, medium- to fine-grained sands with little silt and clay content. The material is very rich in SiO_2, but also contains significant amounts of aluminium, iron, sulfur, potassium and calcium. The material is also enriched in barium and arsenic. The paste solution had a pH of 7.4, and was calculated to be close to equilibrium with respect to gypsum and calcite.

Figure 1 shows the distribution of selected phases based on the classified MLA image presented in Redwan *et al*. (2012). Sulfide minerals are represented by pyrite (0.70 area %), arsenian pyrite (0.52 area %), arsenopyrite (0.65 area %), iron-rich sphalerite (0.01 area %), and galena (0.01 area %). Carbonate minerals are represented by ankerite (2.60 area %, including dolomite) and siderite (0.86 area %). Biotite (6.93 area %) represents the combined amounts of chlorite and mica-group minerals. Kaolinite (5.99 area %) represents the combined amounts of clay minerals and gels. Gypsum (0.86 area %) represents the combined amounts of gypsum and secondary sulphates. The remaining phases, which are much less reactive than the aforementioned ones, are considered as non-reactive. The porosity is highly variable.

Sulfide minerals appear to be concentrated in two distinct layers, whereas carbonate and mica-group minerals are found in many layers. The amount of iron-rich sphalerite and galena was low. The resulting cumulative mineral volume fractions that were input into the model are shown in Fig. 2. For reasons of simplicity, the porosity was made constant by adjusting the quartz volume fractions.

Simulation results

Figure 2 shows the results of the reactive transport simulation after a run time of 40 years. The model predicts extensive weathering in the two regions with the highest sulfide concentrations. In these regions, a significant reduction in pH is observed, because carbonate minerals were depleted before sulfide minerals were depleted. Extensive precipitation of amorphous gels (mainly amorphous

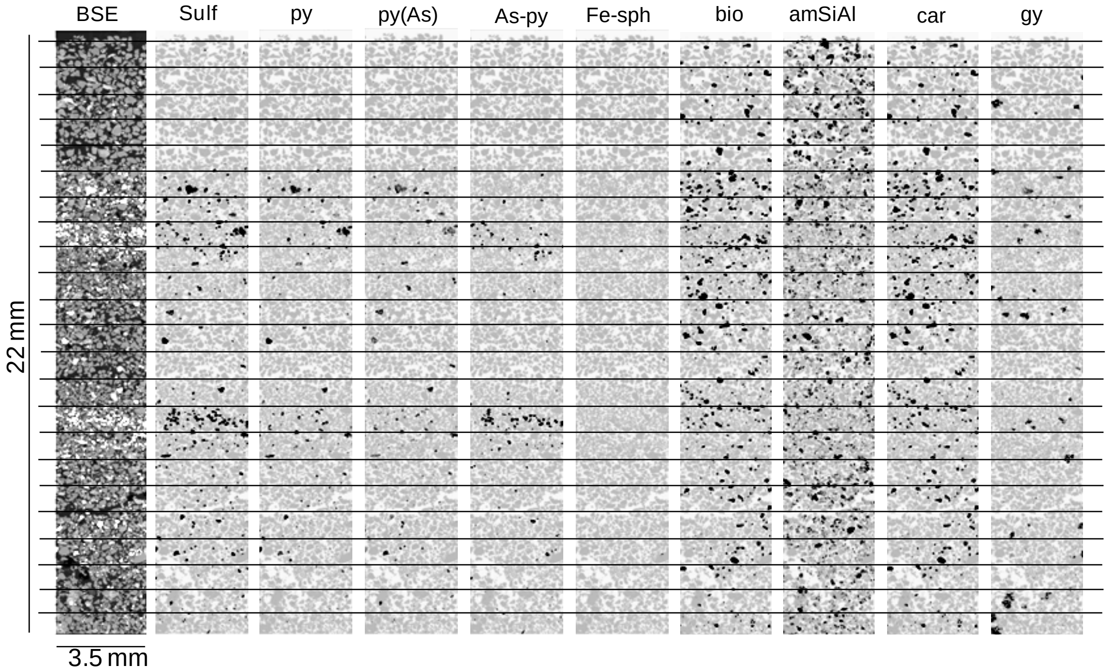

Fig. 1 BSE image (left) and selected MLA images of the thin section of relatively unweathered tailings material that was used as input for the modelling (Redwan *et al*., 2012). Horizontal lines represent model layers. Abbreviations (see also Table 2): sulf: all sulfide minerals, car: all carbonate minerals. In the MLA images, classified minerals are shown in black, other minerals in grey, and pores in white.

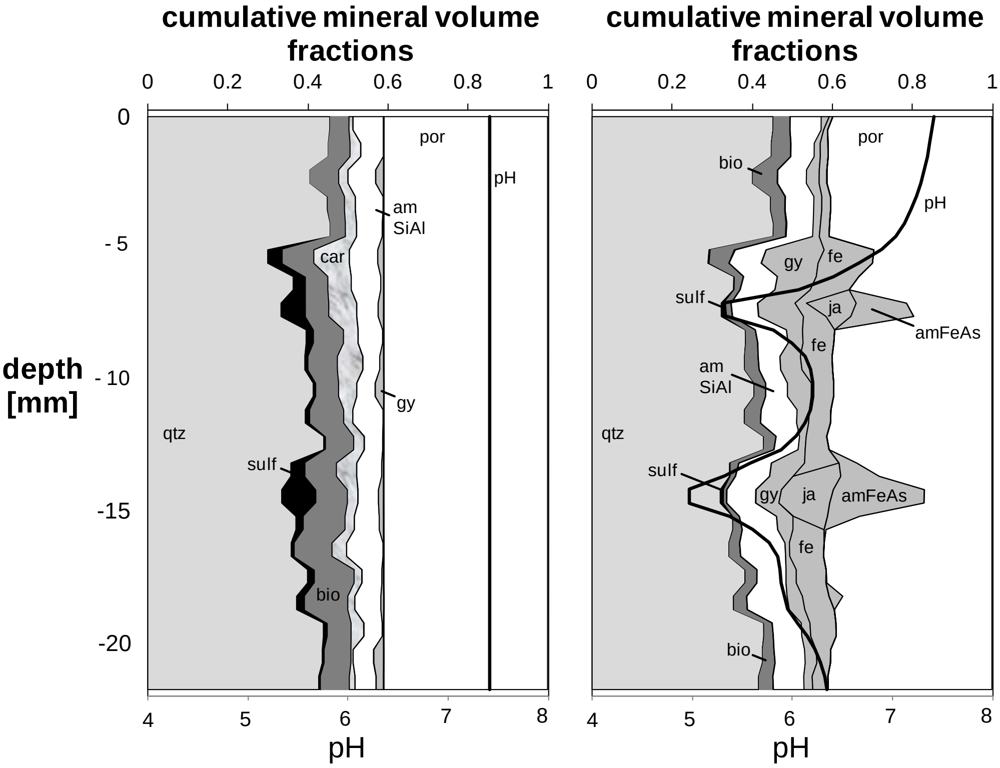

Fig. 2 Initial (left) und simulated (right) cumulative mineral volume fractions and pH after a simulated run time of 40 years. Abbreviations (see also Table 2): sulf: all sulfide minerals, car: all carbonate minerals, por: porosity.

iron arsenate, also ferrihydrite), as well as of jarosite and gypsum, have resulted in the formation of cemented layers with a significant reduction in porosity. The predicted porosity is close to the critical porosity (~15%) at which the permeability may go to zero (Meima *et al.*, 2012).

The formation of cemented layers is known to be thermodynamically favoured at geochemical interfaces characterized by sudden changes in geochemical parameters (pH, Eh, availability of specific ions, e.g. K^+). According to the simulation results, interfaces with sudden changes in pH can effectively develop around sulfide-enriched layers. Amorphous iron arsenate and jarosite, which are stable below pH~6, have accumulated in the “low-pH regions”, giving rise to the observed cemented layers. Ferrihydrite, which is not stable below pH~5, is only precipitating in “moderate-pH regions”.

The simulation results are consistent with field and microscopic observations (Redwan *et al.*, 2012) and also with previous simulations with the reactive transport code TOUGHREACT (Meima *et al.*, 2011, 2012). The predicted phases and cemented layers are similar to those observed in the field. Redwan *et al.* (2012), for example, has observed that in some regions, the pores were partly filled with gypsum, jarosite and gel phases, and that in other regions extensive precipitation of amorphous Fe-As-gels locally resulted in a clogging of pores (Redwan, unpublished results). Furthermore, gel phases were predominantly found in the direct vicinity of decomposing sulfide minerals, jarosite was predominantly found in the direct vicinity of mica-group minerals, and gypsum was found in many laminas.

After the simulated run time of 40 years, more than 99% of the arsenic, lead and zinc were released from the primary sulfide minerals. Eighty percent of the arsenic had reprecipitated as amorphous ferric arsenate, 16% was sorbed to ferrihydrite, and 3% was leached from the system. The preferred retention mechanism is strongly pH dependent. Precipitation of amorphous ferric arsenate is favoured below pH~6, whereas the extent of arsenate sorption to ferrihydrite is strongly dependent on the stability of this phase. According to our simulation results, lead and zinc do not reprecipitate as anglesite or zincite. It should be mentioned, however, that a local armouring of galena particles with anglesite, which has frequently been observed (e.g. Graupner *et al.*, 2007), cannot be simulated with the continuum representation of porous media as applied in this paper. A pore-scale modelling approach would therefore be required. According to our modelling results, 91% of the lead had sorbed to ferrihydrite and 9% was leached from the system. For zinc, only 2% was calculated to have sorbed to ferrihydrite, and 98% was leached from the system. These results reflect the different affinities of zinc and lead for sorption to ferrihydrite.

Figure 3 shows the predicted leaching of arsenic, zinc, and lead from the simulated section. Recrystallization of amorphous ferric arsenate into crystalline ferric arsenate (scorodite) would significantly reduce arsenic mobility (Paktunc & Bruggeman, 2010). The best protection against zinc leaching seems to be a return to anoxic conditions where zinc can be captured in sulfide minerals.

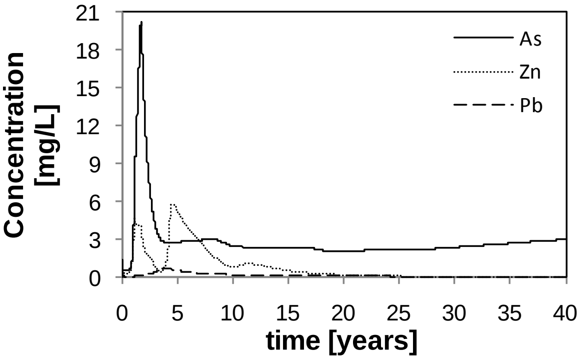

Fig. 3 Predicted leaching of arsenic, zinc, and lead from the simulated system; total dissolved concentrations at the lower boundary.

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