Modelling the Geochemical Behaviour of Desulfurized Tailings as a Moisture-Retaining Layer in Insulation Covers with Capillary Barrier Effects using MIN3P-THCm

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Abstract

A column laboratory experiment was performed to assess the hydrogeological, thermal, and geochemical behaviour of an insulation cover with capillary barrier effects (ICCBE) made of desulfurized tailings as the moisture-retaining layer and non-acid generating crushed rocks as the protective and the capillary break layer. The ICCBE was represented in a numerical model developed using MIN3P-THCm. The model simulated the thermal-hydrogeological-geochemical behaviour of the tested ICCBE. The laboratory tests and short-term modelling showed that the tested desulfurized tailings do not generate contaminants at a concentration higher than the regulatory limits and that they can be used as cover material in a typical arctic climate. The preliminary long-term modelling results also suggest that the column will not generate acidity and maintain a leachate quality below the regulatory limits.

Keywords: Insulation Cover With Capillary Barrier Effect (Iccbe), Desulfurized Tailings, Acid Mine Drainage, Freeze And Thaw Cycles, Reactive Transport Modelling

Introduction

Mining wastes produced during mining operations are sometimes sensitive to surface atmospheric conditions and prone to producing contaminant laden leachates that are classified according to their quality and nature as acid mine (or rock) drainage (AMD or ARD), contaminated neutral drainage (CND) or alkaline drainage (AD) (INAP, 2009; Plante *et al.*, 2020). The main minerals that influence the quality and the nature of the drainage are sulfide and carbonate minerals. The former generates acidity while the latter creates alkalinity that consumes the produced acidity (entirely or partly) (Bussière and Guittonny, 2020; INAP, 2014; Lottermoser, 2007).

In most cases, the problems associated with the mine drainage can be remediated through appropriate reclamation techniques. For mines operating under Arctic conditions, factors such as climate change, the presence of permafrost, remoteness, the availability of materials, and harsh climatic conditions can make the design and construction of reclamation scenarios more difficult and expensive than for mines

in temperate climates (Bussière and Hayley, 2010). While some methods are only a transfer from those used in the South, one technique called insulation covers was explicitly proposed for Arctic conditions. The technique aims at maintaining the mine tailings frozen and below a target temperature to prevent sulfide mineral reactivity and water movement (Boulanger-Martel *et al.*, 2020a; Kyhn and Elberling, 2001; Lessard *et al.*, 2018; Meldrum *et al.*, 2001). To reduce the risk of losing performance in the long term, Boulanger-Martel *et al.* (2016) proposed to add an oxygen barrier into the insulation cover (ICCBE) that would simultaneously control both parameters (temperature and oxygen flux). The moisture-retaining layer (MRL) is the main component of such a cover system that maintains a high degree of saturation (Sr) and significantly restricts oxygen flux from reaching the acid-generating tailings. The MRL is usually made of fine-grained silty materials (Bussière, 2007; Bussière *et al.*, 2007). Recent works performed in the laboratory suggest that low sulfide or desulfurized tailings could be used as MRL in an ICCBE to control oxygen migration

(Lessard *et al.* 2018; Qureshi *et al.* 2021). However, questions remain on the potential of these low sulfide or desulfurized tailings to generate contaminants when placed in an ICCBE in the long term (Qureshi *et al.*, 2021a).

Different laboratory experiments are performed on the mining wastes to determine the expected quality and nature of the drainage upon exposure to stimulating environmental conditions (Demers *et al.*, 2008; Hamberg *et al.*, 2018; Kalonji-Kabambi *et al.*, 2020a; Larochelle *et al.*, 2019; Nyström *et al.*, 2019; Pabst *et al.*, 2014; Plante *et al.*, 2014; Qureshi *et al.*, 2019). However, most of the laboratory experiments are time-constrained and are, therefore, primarily representative of the short-term response of mining waste materials under laboratory conditions. Consequently, performing in-situ test cell experiments to produce field representative results is advocated (Bussière *et al.* 2007; Boulanger-Martel *et al.*, 2020b; Qureshi *et al.*, 2016). However, the results generated from such experiments are also relatively short-term (typically 3–5 years). Therefore, reactive transport modelling has gained the interest of many researchers (Molson *et al.*, 2008; Craig *et al.*, 2021; Demers *et al.*, 2013; Kalonji-Kabambi *et al.*, 2020b; Muniruzzaman *et al.*, 2020; Wilson *et al.*, 2018) to predict the long-term behaviour of mining waste materials using multicomponent reactive transport numerical models.

The overall objective of the study is to validate the hypothesis that desulfurized tailings are a viable material for the MRL in ICCBEs by assessing the thermal-hydrogeochemical behaviour of the ICCBEs in the short and long term. The results on the hydrogeological behaviour (Lessard *et al.*, 2018) and the geochemical evolution (Qureshi *et al.*, 2021a) of the column are used here for the numerical modelling part of the study. The specific objectives of this article consist of i) Calibrating a conceptual multicomponent reactive transport model in MIN3P-THCm using column leaching experiments results of insulation covers with capillary barrier effect (ICCBE) utilizing desulfurized tailings (DSTs) as a moisture-retaining layer (MRL), and ii) predicting the long-term (200 years) hydrogeochemical behaviour of the ICCBE column.

Methods

Material characterization

A tailings sample was desulfurized to a residual sulfide content of 0.4 wt% in the laboratory using the froth flotation process by Benzaazoua *et al.* (2017). Mineralogical characterization was performed using optical microscopy first and then by both scanning electron microscopy (SEM; Hitachi S-3500 N, Japan) coupled with Energy Dispersive Spectrometry (EDS; Silicon Drift Detector X-Max 20 mm^2 from Oxford, UK) microanalysis, and X-ray diffraction (XRD; Bruker AXS Advance D8, Billerica, MA, USA; XRD precision ±1%; (Bouzahzah, 2013)). The inductively coupled plasma atomic emission spectroscopy (ICP-AES; Perkin Elmer 3000 DV, Überlingen, Germany) for trace metal in particular and fusion, whole-rock analyses by borate fused disc, were used to determine the major and minor elemental composition of the desulfurized tailings. Analyses of total inorganic carbon (C) and sulfur (S) concentrations were also carried out using an induction furnace equipped with a dedicated infrared (IR) analyzer (Eltra CS 2000, Haan, Germany) with a ±0.05 to 0.1 wt% precision (CEAEQ, 2013).

Column experiment

An ICCBE was simulated in a column constructed from high-density polyethylene (HDPE) with an internal diameter of 0.14 m, a wall thickness of ≈0.022 m, and a height of 2.20 m. The column was filled with a coarse-grained non-acid generating crushed WR to a height of 1.0 m as a capillary break layer (CBL), followed by a 0.7 m moisture-retaining layer (MRL) made of desulfurized tailings and finally a 0.4m thick protective layer (PL) made of the same material from the CBL. The MRL was compacted to a porosity (n) of 0.36–0.40, and the CBL and PL layers to n=0.25. The initial unfrozen volumetric water content (θu) was 0.36 in the MRL, which corresponds to a degree of saturation (Sr) between 90–100%.

The ICCBE column was exposed to a 5 °C controlled temperature environment for 27 days, beginning with a 7-day rinse with two volumes of 1.6 L of deionized water each at 24 h intervals. At the end of
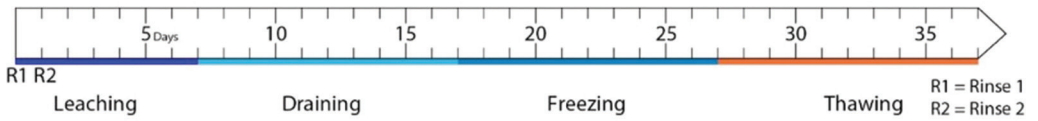
Figure 1 A typical testing cycle.

the rinse period, the collected leachates were analyzed for pH, Eh, EC, acidity, and alkalinity before chemical characterization using ICP, following the methods and protocols mentioned above. Following the flushing, the column was exposed to a 5 °C temperature for another 10 days before subjecting them to the F–T cycle of 20 days (10-day freezing and 10-day thawing). A typical cycle is presented in Figure 1. The F–T cycles were performed by exposing the column to temperature conditions inspired by those observed in the Canadian Arctic. A proportional-integral-derivative (PID) controlled industrial grade freezer was used to maintain the temperatures at -13 °C (for freezing) and 5 °C (for thawing), as applied by Boulanger-Martel *et al.* (2016, 2015) before. A total of eight such leachings and F–T cycles were performed over a period of a year.

Conceptual model

A 1-D conceptual RTM was created in MIN3P-THCm using the physical and hydrogeological parameters shown in Figure 2. The model domain was discretized in 100 (CBL), 75 (MRL), and 25 (PL) control volumes. MIN3P-THCm is a multicomponent reactive transport code that is used for simulating thermo-hydro-chemical and mechanical (THCm) processes in variably saturated porous media (Mayer *et al.*, 2002). Some salient features of the code are density dependant flow and solute transport, heat and gas transport, biogeochemical reactions, and one-dimensional hydromechanical coupling (Bea *et al.*, 2012; Henderson *et al.*, 2009; Mayer *et al.*, 2002; Su *et al.*, 2020, 2017). The code includes databases from MINTEQA2 (Allison *et al.*, 1991) and WATEQf4 (Ball and Nordstrom, 1991).
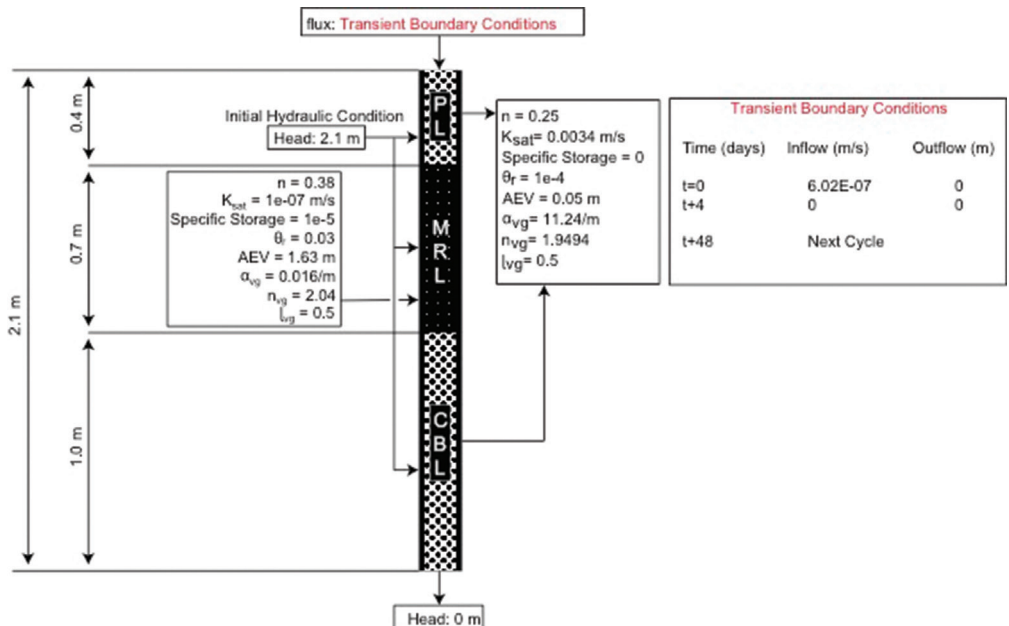

Figure 2 Illustration of the conceptual model.

Model parameters

The mineral reactivity in MIN3P-THCm can be set to remain constant or as a time-dependant mineral volume fraction (Mayer *et al.*, 2002). For sulfide minerals, however, a shrinking-core model (SCM; assuming a spherical mineral grain) which simulates O_2 diffusion-controlled sulfide mineral oxidation can also be applied (Davis and Ritchie, 1986; Mayer *et al.*, 2002). In the present research, the non-sulfide minerals that were already present in the tailings have been simulated using surface-controlled reactions, sulfide minerals using SCM and the secondary minerals are allowed to precipitate using constant reactivity (dependant upon the physicochemical changes within the system).

A total of 17 minerals were included in the simulations (Table 1), based on the mineralogical characterization of the materials, and including the secondary minerals suggested by PHREEQC (Parkhurst and Appelo, 2013) batch simulations. An initial grain radius of 9.5×10^{-7} m was used for all sulfide minerals for the SCM. The minerals' rate expressions (Table S1) and reaction rate coefficients (Table S2) for the simulations are provided in the supplementary material. The model was calibrated using reaction rate coefficients in MIN3P-THCm to simulate the laboratory observed chemical concentrations. However, the simulations were not targeted to achieve exact chemical concentration, instead to produce numerical results within the same range of the measured concentrations that represent the trends for the most important elements or components.

The porewater quality measurements for the first flushing cycle were used as the initial chemical conditions in the model, and the recharge water composition was typical of the tap water used in column experiments (Ouangrawa *et al.*, 2009) (Table 2).

Assumptions and simplifications

Some assumptions and simplifications were made to the conceptual model for its calibration. Transient inflow boundary conditions were applied to simulate the temperature effect on infiltration (assuming that no infiltration occurs under freezing conditions; Figure 2). Furthermore, these infiltration conditions were considered to repeat for 200 years in long-term simulations. However, the effect of temperature on reactive transport modelling was applied by utilizing the "define temperature field" option of MIN3P-THCm by using the laboratory observed temperature data (see Lessard *et al.* (2018) and Qureshi *et al.* (2021a) for more details). The WR in PL and CBL was assumed to be non-reactive (except for anorthite (Table 1)).

Results

Results from the reactive transport modelling of the ICCBE system were similar to the laboratory results. They showed that despite the low residual sulfur content after the desulfurization of the tailings, the column produced non-negligible concentrations of SO_4^{-2}, Ni and Zn (Qureshi *et al.*, 2021). Therefore, pH and these three parameters are considered elements of concern, and their

Table 1 Minerals' weight percentages and volume fractions1 based on mineral characterization.

Mineral	MRL		CBL, PL		Mineral	MRL		CBL, PL	
	wt%	Vf [1]	wt%	Vf [1]		wt%	Vf [1]	wt%	Vf [1]
Pyrrhotite	0.64	0.0038	n.d.	n.d.	K-Jarosite	n.d.	n.d.	n.d.	n.d.
Pentlantite	0.29	0.0017	n.d.	n.d.	Lizardite	31.81	0.3392	n.d.	n.d.
Chalcopyrite	0.25	0.0017	n.d.	n.d.	Magnetite	2.56	0.0137	n.d.	n.d.
Actinolite	29.75	0.2660	33.6	Excluded	Melanterite	2.91	0.0425	n.d.	n.d.
Anorthite	n.d.	n.d.	11.2	0.1196	Na-Jarosite	n.d.	n.d.	n.d.	n.d.
Calcite	2.17	0.0222	n.d.	n.d.	Ni-Sulfate	0.087	0.0012	n.d.	n.d.
Clinochlore	26.48	0.2770	14.7	Excluded	Thenardite	2.91	0.0304	n.d.	n.d.
Ferrihydrite	n.d.	n.d.	n.d.	n.d.	Zn-Sulfate	0.087	0.0006	n.d.	n.d.
Gypsum	n.d.	n.d.	n.d.	n.d.					

[1]Volume fraction (m^3 (mineral) m^{-3} (bulk)) = Mineral wt% × (density of rock material ÷ density of mineral) × (1 – porosity) ÷ bulk reservoir volume

n.d. = not detected

Table 2 Initial porewater and recharge water composition.

Initial porewater		Recharge water	
Element	Concentration	Element	Concentration
Ca^{+2} (mol L^{-1})	1.36E-02	Ca^{+2} (mol L^{-1})	2.20E-05
K^{+1} (mol L^{-1})	1.16E-04	K^{+1} (mol L^{-1})	2.00E-05
H_4SiO_4 (mol L^{-1})	1.86E-03	H_4SiO_4 (mol L^{-1})	1.00E-20
Al^{+3} (mol L^{-1})	1.59E-06	Al^{+3} (mol L^{-1})	1.00E-20
CO_3^{-2} (mol L^{-1})	1.00E-13	CO_3^{-2} (mol L^{-1})	0.000317
Fe^{+2} (mol L^{-1})	7.16E-07	Fe^{+2} (mol L^{-1})	1.00E-10
SO_4^{-2} (mol L^{-1})	2.58E-02	SO_4^{-2} (mol L^{-1})	1.00E-05
Fe^{+3} (mol L^{-1})	1.00E-10	Fe^{+3} (mol L^{-1})	2.00E-05
Ni^{+2} (mol L^{-1})	1.72E-06	Ni^{+2} (mol L^{-1})	1.00E-10
Cu^{+2} (mol L^{-1})	1.57E-07	Cu^{+2} (mol L^{-1})	1.00E-10
Mg^{+2} (mol L^{-1})	1.03E-02	Mg^{+2} (mol L^{-1})	8.20E-07
Zn^{+2} (mol L^{-1})	4.07E-06	Zn^{+2} (mol L^{-1})	1.00E-10
Na^{+1} (mol L^{-1})	2.26E-03	Na^{+1} (mol L^{-1})	2.00E-05
HS^{-1} (mol L^{-1})	1.00E-10	HS^{-1} (mol L^{-1})	1.00E-12
pH (-)	7.89	pH (-)	7.0
O_2 (pe)	8.55	O_2 (pO_2)*	0.21

* pO_2 and pCO_2 are atmospheric O_2 and CO_2 concentrations, respectively.

simulated hydrogeochemical behavior is reported in the following sections.

Model calibration

The calibration results of the model for pH, SO_4^{-2}, Ni and Zn are in good agreement with the observed laboratory values (Figure 3). The calibrated model almost accurately reproduced the pH. Similarly, sulfate concentrations were also well reproduced by the model. However, some noticeable differences are present in Ni and Zn; Ni was under-estimated between 50 and 100 days and over-estimated between 200 and 259 days. Similarly, Zn was over-estimated between 25 and 75 days. Other researchers have also observed these differences while performing reactive transport modelling (Demers *et al.*, 2013; Kalonji-Kabambi *et al.*, 2020b; Wilson *et al.*, 2018). Since the objective of the calibration was to produce trends in the same concentration ranges rather than reproducing the absolute values, the model duration was extended to 200 years for long-term predictions.

Long-term predictions

As shown in Figure 4, the long-term simulations are encouraging for the use of desulfurized tailings in the tested ICCBE. They indicate that most of the leachate quality concerns are relatively short-term.

The simulations show that the pH spikes above 7.5 after about 30 years, followed by a constant declining trend, which finally stabilizes after 100 years to circumneutral values. Sulfate was one of the most critical concerns from the laboratory experiments, but the simulation shows that, although the sulfate concentrations could remain relatively high initially, they will stabilize to a few mg L^{-1} after four years. This is because of the slow reaction of sulfide minerals and the depletion of thenardite ($Na_2SO_4^{-2}$), which seems to be the main contributor towards the sulfate leaching in the column (see Figure S1 in supplementary material). Sulfide minerals' reactivity appeared negligible, as shown by the sulfide minerals' mineral volume fraction (Figure S2 in supplementary material), probably due to the high degree of saturation maintained by the capillary barrier effects (which restricts oxygen supply) and the low-temperature conditions to which the column was exposed (Lessard *et al.*, 2018; Qureshi *et al.*, 2021). Nickel and Zn concentrations, on the other hand, remain present for a longer duration, but the predicted concentrations shall not be higher than the provincial allowed effluent concentrations for mining operations in Québec (0.5 mg L^{-1} for both Ni and Zn in Directive 019). More specifically, Ni shall stabilize with a maximum concentration of 1.50×10^{-06} mol L^{-1} (or 0.09 mg L^{-1}) after
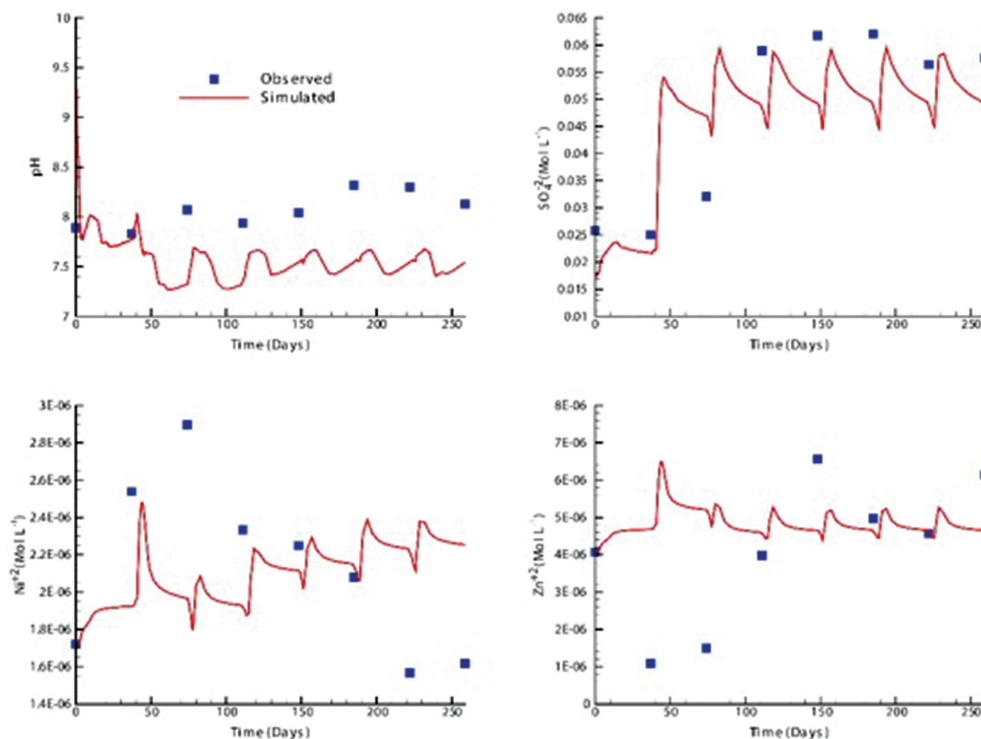
Figure 3 *Calibration of the RTM with the laboratory observations.*

≈50 years. Similarly, Zn will be leached with a maximum concentration of $3.5 \times 10\text{-}06$ mol L^{-1} (or 0.2 mg L^{-1}) after ≈50 years and shall finally become stable at $4.0 \times 10\text{-}09$ (or 0.00026 mg L^{-1}) after ≈145 years.

Conclusions

A conceptual multicomponent reactive transport model was created to predict the long-term behaviour of an ICCBE system utilizing desulfurized tailings as an MRL and non-acid generating crushed WR as PL and CBL. The model was first calibrated with the laboratory observed concentrations of the main elements of concern (Zn, Ni, SO_4^{-2}, and pH). The calibrated model was then used to perform long-term simulations that show that the ICCBE system can maintain a circumneutral pH for 200 years. The sulfate concentrations shall drop to a few mg L^{-1}, with Ni and Zn concentrations maintained below provincial allowable concentration in Québec for 200 years. These results confirm a low risk of contamination from the MRL made of desulfurized tailings and that this material

could be used to build an ICCBE in cold climatic conditions. However, a sensitivity analysis is underway to assess the robustness of the calibrated conceptual model further.

Acknowledgements

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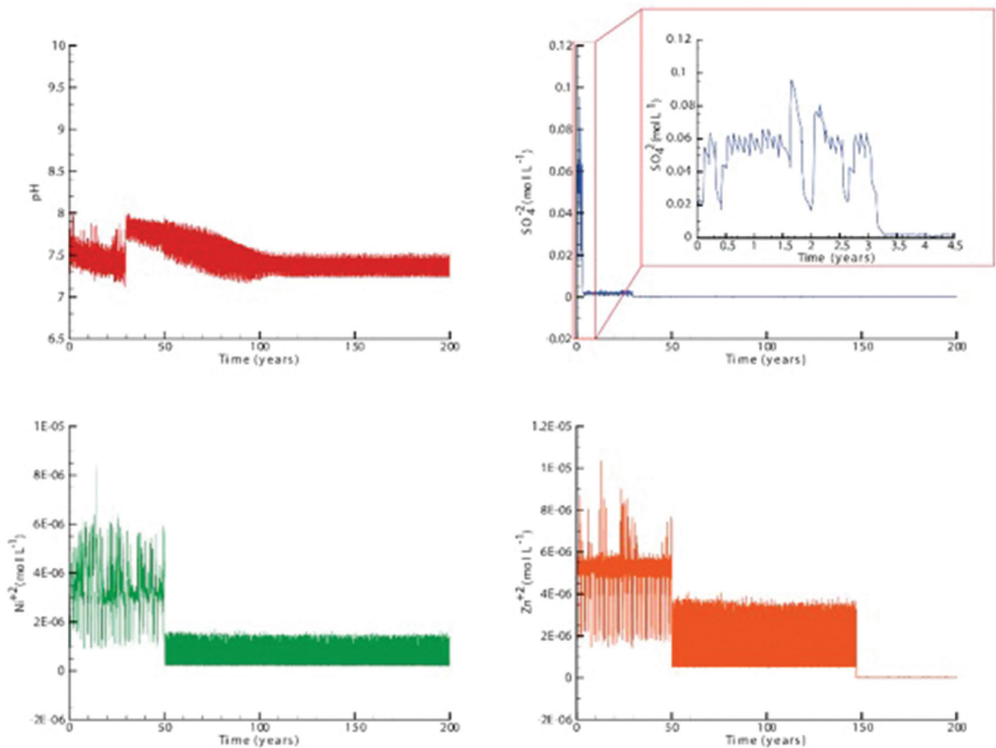
Figure 4 Long-term predictions for the conceptual ICCBE model.

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Supplementary Material

Table S1 Minerals' rate expressions

Mineral	Rate expression	Mineral	Rate expression
Pyrrhotite	SCM	K-Jarosite	$R = -K^{eff}_{K-Jarosite}\left[1 - \dfrac{IAP}{10^{9.21}}\right]$
Pentlantite	SCM	Lizardite[1]	$R = -K^{eff}_{Lizardite}$
Chalcopyrite	SCM	Magnetite	$R = -K^{eff}_{Magnetite}\left[1 - \dfrac{IAP}{10^{-3.737}}\right]$
Actinolite[1]	$R = -K^{eff}_{Actinolite}$	Melanterite	$R = -K^{eff}_{Melanterite}\left[1 - \dfrac{IAP}{10^{-2.209}}\right]$
Anorthite[1]	$R = -K^{eff}_{Anorthite}$	Na-Jarosite	$R = -K^{eff}_{Na-Jarosite}\left[1 - \dfrac{IAP}{10^{5.28}}\right]$
Calcite	$R = -K^{eff}_{Calcite}\left[1 - \dfrac{IAP}{10^{-8.475}}\right]$	Ni-Sulfate	$R = -K^{eff}_{Ni-Sulfate}\left[1 - \dfrac{IAP}{10^{-2.33}}\right]$
Clinochlore[1]	$R = -K^{eff}_{Clinochlore}$	Thenardite	$R = -K^{eff}_{Thenardite}\left[1 - \dfrac{IAP}{10^{-0.179}}\right]$
Ferrihydrite	$R = -K^{eff}_{Ferrihydrite}\left[1 - \dfrac{IAP}{10^{-3.191}}\right]$	Zn-Sulfate	$R = -K^{eff}_{Zn-Sulfate}\left[1 - \dfrac{IAP}{10^{-1.8683}}\right]$
Gypsum	$R = -K^{eff}_{Gypsum}\left[1 - \dfrac{IAP}{10^{4.58}}\right]$		

[1] Irreversible dissolution

Table S2 Minerals' reaction rate coefficients used for simulations in MIN3P-THCm

| Mineral	Rate coefficient			Mineral	Rate coefficient		
	MRL	CBL	PL		MRL	CBL	PL
Lizardite	1E-12	1E-50	1E-50	Ni-Sulfate	4.5E-15	1E-13	1E-10
Actinolite	1E-12	6E-11	1E-50	Thenardite	6E-09	1E-10	1E-10
Clinochlore	1.5E-10	5E-10	1E-50	Melanterite	2.2E-10	1E-10	1E-10
Calcite	7E-11	1E-25	1E-50	Anorthite	1E-25	1E-09	1E-50
Magnetite	1E-07	1E-10	1E-50	Ferrihydrite	1E-10	1E-10	1E-50
Pyrrhotite	3E-12	1E-12	1E-10	Na-Jarosite	1E-10	1E-10	1E-50
Pentlandite	1E-12	3.5E-12	1E-10	K-Jarosite	1E-10	1E-10	1E-50
Chalcopyrite	5E-10	1E-10	1E-10	Gypsum	1E-10	1E-25	1E-50
Zn-Sulfate	4.5E-13	4.5E-13	4.5E-13				
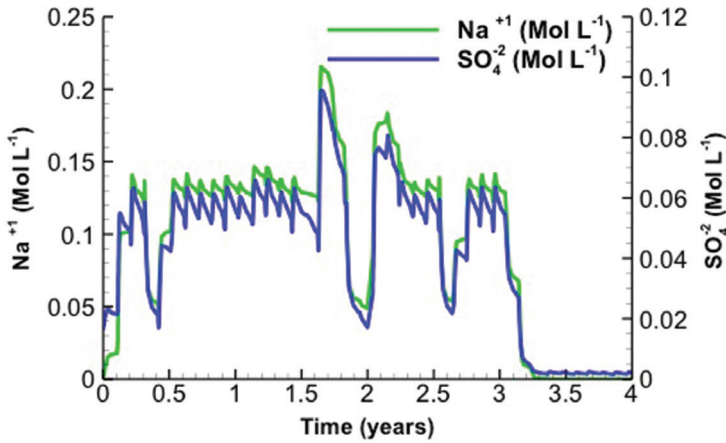
Figure S1 Leaching of sodium and sulfate
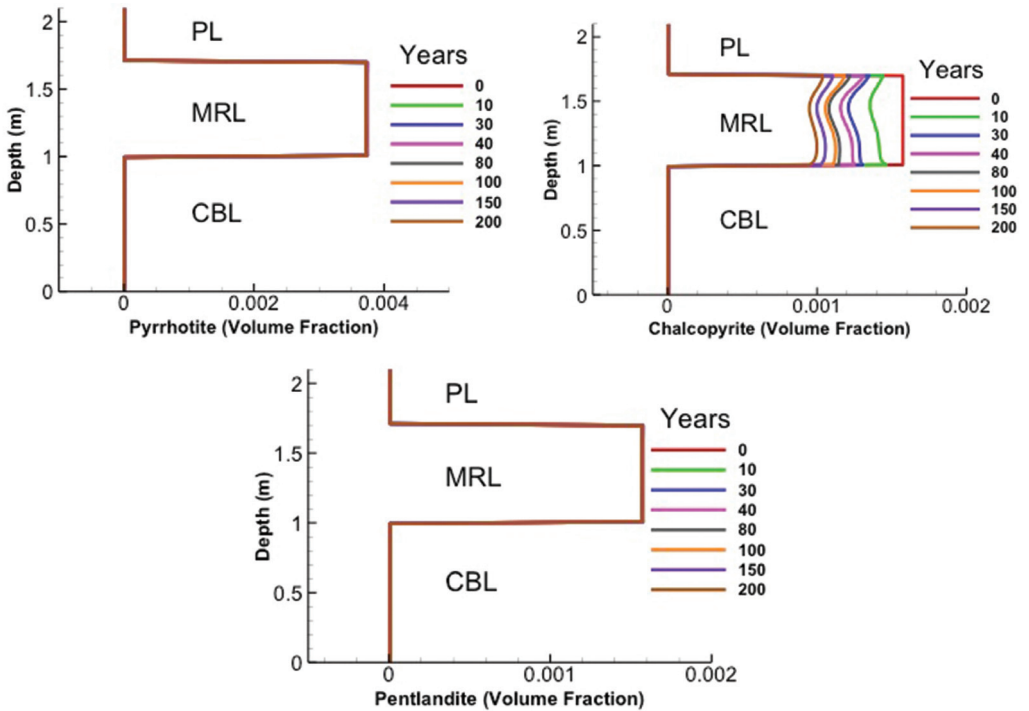
Figure S2 Change in sulfide minerals' volume fractions over time