

Reactive transport modeling of metal removal by hydrozincite precipitation in an abandoned Pb-Zn mine

Max G. Giannetta Josep M. Soler Robert Benaiges Jordi Cama*

Institute of Environmental Assessment and Water Research (IDAEA)

CSIC, Barcelona 08034, Catalonia, Spain Giannetta E-mail: ORCID: number

Soler E-mail: ORCID: number

Benaiges E-mail: ORCID: number

Cama E-mail: jordi.cama@idaea.csic.es ORCID: number

*Corresponding author

ABSTRACT

In this study, an underground zinc mine in the Aran Valley (Catalonia) was chosen as a field site to showcase the processes that affect metal mobility in the environment. Most of the galleries are flooded, and the lowermost gallery exhibits a continuous output of water, whose composition reflects a flow path through the mine and overlying host rock. Our main objective was to understand the evolution of the solute concentrations and mineral reactions that occur in the mine galleries. Three sampling campaigns at the mine (3 years) provided a spatiotemporal dataset showing the evolution of solute concentrations through the system along a flow path. Rainwater from the upper catchment flows into the host rock above the mine where it dissolves ore materials (primarily Zn- and Fe-sulfides, sphalerite and pyrite, respectively, with Ni and Cd impurities) that cause elevated Zn, Ni and Cd concentrations where these waters enter the mine. From there, the precipitation of hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) along the gallery where water flows serves as a metal-removal mechanism that significantly diminishes metal concentrations (e.g. Zn from 2.4 to 0.05 mM, Ni from 6.4 to 0.5 μM , and Cd from 0.9 to 0.1 μM). Using the CrunchFlow code, a relatively simple reactive transport model was constructed to capture the processes occurring along the flow path through the system (*i.e.* rainwater infiltration and flow through the host rock, mixing of different gallery source waters and flow of water through the gallery). Results reasonably reproduce the measured concentrations. Moreover, the model predicts the formation of hydrozincite, calcite and smithsonite while maintaining their relative proportions. A sensitivity analysis for the most relevant parameter values (e.g. hydrozincite solubility, flow velocity, dispersivity and mineral reactivities) captures the range of behaviors expected, and thereby helps predict future changes to metal mobility. The model indicates that changes to flow velocity, which would translate to changes in volumetric discharge through the system caused by rain events, could be the cause of the mineral layering and metal zonation observed in hydrozincite. The model also shows that the natural metal attenuation process is expected to occur through a wide range of system perturbations. Thus, the abandoned mine poses little risk to the neighboring ecosystem.

KEYWORDS | Victoria mine. Reactive transport modeling. Hydrozincite. Metal mobility. Hydrochemistry.

INTRODUCTION

The abandoned mines around the Mediterranean pose a serious hazard to the environment (Doumas *et al.*, 2018; Esshaimi *et al.*, 2010; Khalil *et al.*, 2013; Navarro *et al.*, 2008; Rodríguez-Pacheco *et al.*, 2023). For instance, the cessation of sulfide mining in the Iberian Pyrite Belt (IPB) in southern Portugal and SW of Spain has generated vast amounts of pyritic waste, the oxidization of which results in Acid Mine Drainage (AMD) (Álvarez-Valero *et al.*, 2008; Sánchez-España *et al.*, 2008). The tailings in the Pb-Zn-(Ag-Sn) mining districts (*e.g.* Cabezo Rajao mine) in SE of Spain discharge heavy metals that are dispersed both downstream and downslope from the mine (Navarro *et al.*, 2008). In southern Tuscany in Italy, the waste from the former mining district (exploitation of pyrite bodies) is replete with toxic elements (*e.g.* Cu, Pb, Zn, As, Bi, and Cd) that are dispersed by acidic waters (Benvenuti *et al.*, 1997). In SW Sardinia, the Ingurtosu mine exploited Pb and Zn until 1968 (Podda *et al.*, 2000; Zuddas and Poda, 2005). The mine tailings are discharged into the Naracauli creek causing the water pH to vary between 6.2 and 8.5 (Medas *et al.*, 2011; Zuddas and Poda, 2005). In Morocco, the abandoned lead mines at Zeïda, Mibladen and Aouli (Upper Moulouya district) have given rise to large amounts of waste with high concentrations of lead and with an alkaline pH given the abundance of carbonate (Iovazzo *et al.*, 2012). In southern France, the water of the Reigous Creek, which drains the tailings impoundment of the abandoned Carnoulès Pb-Zn mine, is acidic (pH 2-3) and replete with Fe and As (Egal *et al.*, 2010). In Turkey, metals and sulfate in water, mine wastes, and stream sediments around the abandoned Alaşehir Hg mine contaminate the areas adjacent to the Alaşehir mining area (Gemici, 2008).

Whatever the pH of the waste drainages of these abandoned sites (*i.e.*, acidic or alkaline depending on the abundance of carbonate bedrocks), the lack of any effective measures to manage these abandoned mines, tailings piles, processing facilities and tunnel galleries seems to play down the gravity of the problem, *i.e.*, the degradation of residues that can release toxic metals into the surrounding environment. The present study is focused on the abandoned Victoria mine (Fig. 1). The Victoria mine, the largest mine in the mining district for zinc, lead, copper, silver and iron in the Aran Valley (NE of Spain; Santamaria *et al.*, 2008) ceased mining operation in 1952. In full operation, 80 tons of raw ore were extracted daily. Since then the enormous, although not quantified, quantities of waste and residues (tailings piles, processing facilities and galleries) have been abandoned. This site was chosen to showcase the processes affecting metal mobility in the environment, considering that at the moment no environmental problems have been claimed in the study area. The aim of our study is double fold: (i) to have a better understanding of the geochemical

processes affecting solute mobility in the mine that can be applied to similar abandoned mines in the Pyrenees and further afield (*e.g.* the Ingurtosu sphalerite-mine in Sardinia) and (ii) to quantify the metal mobility through the system to assess the potential risk to the associated ecosystems. To this end, quantification of the evolution of solute concentrations and mineral reactions through the mine system was performed by Reactive Transport Modeling (RTM) using the CrunchFlow code (Steeffel *et al.*, 2015). The geochemical parameters used in the modeling (*e.g.* rock and water composition) were obtained in three field campaigns in 2019, 2020 and 2021 (Giannetta *et al.*, 2023). It is worth mentioning that only a few studies used reactive transport modeling to assess metal mobility through mine impoundments, acid mine drainage stream and contamination of groundwater systems affected by abandoned mines (Brookfield *et al.*, 2005; Runkel and Kimball, 2002; Torres, 2020). This work, therefore, can help resolve potential remediation issues, and serve to improve our ability to predict harmful metal mobility in the future.

FIELD DATA AND REACTIVE TRANSPORT MODELING

Field data

The ore bodies targeted at the Victoria Mine were mainly composed of sphalerite, and also galena, chalcopyrite, pyrite and pyrrhotite (Cardellach and Alvarez-Perez, 1979; Cardellach *et al.*, 1996). The ten gallery levels of the Victoria mine are situated beneath a steep mountain slope ranging from 1300 m to 1590 m above sea level (Fig. 1), and most of the galleries are flooded (Fig. 1A, B). The various operational levels are connected by ramps, wells and shafts. The lowermost gallery (Sinçay Gallery) exhibits a continuous output of water (Fig. 1), the composition of which reflects a flow path through the mine. Rainwater is collected in a catchment above the mine, where the Melics and the Carné creeks meet. The water infiltrates the overlying host rock and flows through the galleries (*e.g.* the second lowest gallery (1330 Gallery) of ca. 400 m in length) before exiting the mine (Fig. 1). This effluent continues down the catchment, where it is diluted by other streams.

In the three sampling campaigns, water, solids (minerals and rocks) and soil/sediment microbiology along a perceived semi-continuous flow path were sampled (see details in Giannetta *et al.*, 2022, 2023). We sampled at eleven locations (above, within, and below the mine (Figs. 2; I; Table I)), which include the Carné and the Melics creeks above the mine (source water for the system (#11)), six locations within the 1330 Gallery (from #5 to #10), three locations just outside of the Sinçay Gallery exit,

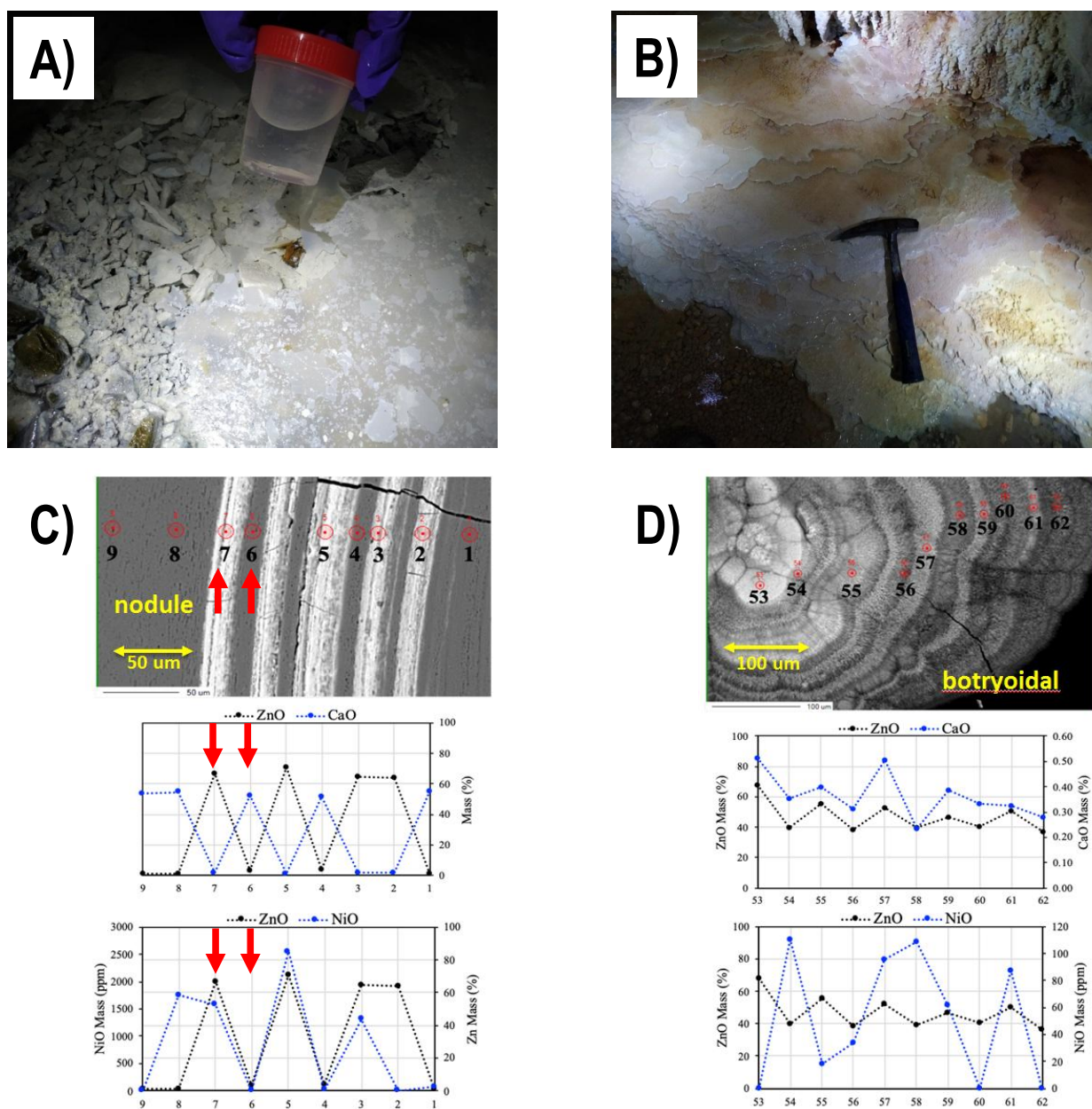


FIGURE 1. Precipitates of hydrozincite: photos taken from inside the mine that show A) hydrozincite precipitates in all areas of the mine where water was present and B) several different structures; SEM images of different morphologies of collected samples: C) nodular hydrozincite and D) botryoidal hydrozincite. The microprobe analysis shows the different contents of Zn, Ca and Ni in the different mineral bands (see also the analysis provided by [Giannetta et al., 2023](#)). The numbers on the SEM image correspond to the x-axis for each sample. Note that C) and D) are partially shown in [Giannetta et al., 2023](#).

where mine water combines with the natural catchment water (from #2 to #4), and the lower reaches of the Melics Creek (#1; [Fig. 1](#)). Sampling the upper creeks provides reliable background concentrations for the water before it infiltrates the Victoria Mine.

The sampling campaigns show that metal concentrations decrease with distance along a continuous 215 m stream on the floor of the sampled 1330 Gallery ([Fig. 2](#)). For instance, Zn and Cd decrease from 2.12 to 0.05 mM, and

from 0.90 to 0.12 µM, respectively ([Table 1](#)). Hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) was found covering the surface of the rocks in contact with the flowing water in the gallery ([Fig. 1A, B](#)). This secondary phase incorporates Ni, Cd, Fe, Pb, As, and Co as it forms ([Table 2](#); [Fig. 1B, C](#)), acting to some extent as a sink for these metals ([Giannetta et al., 2023](#)). Additionally, two sampling locations in the gallery (samples 9 and 10 at 280 m and 310 m from the gallery entrance, respectively) were identified as the principal sources of water for this 215 m flow path. The processes in the gallery

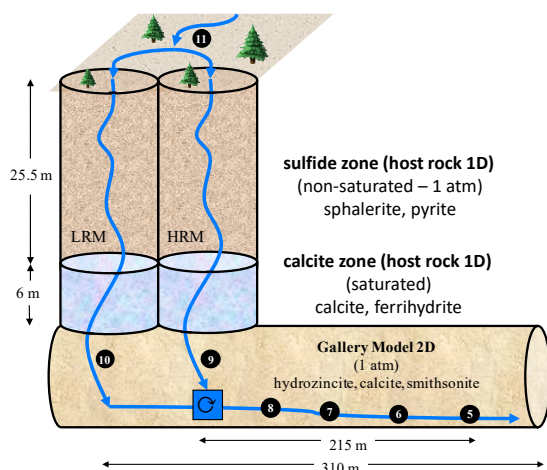


FIGURE 2. Conceptual diagram of the host rock and gallery models. The water composition at the end of the calcite zone (31.5 m) from the 1D high reactivity model (HRM) and the 1D low reactivity model (LRM) are used to inform the gallery model. Those two waters are allowed to mix inside a mixing cell () before flowing down the 250-m domain (1330 Gallery). The flux proportion of LRM/HRM equals 10. Numbers represent sampling intervals defined in Table S1 and the blue arrows denote flow direction.

lead to low concentrations of dissolved metals ([Zn], [Cd], [Al], [Ni] and [Fe] = 200, 1, 13, 2 and 12 ppb, respectively) once the water travels further down the catchment (sample 1 at lower Melics creek; Fig. 1; Table I). Metal concentrations are, therefore, lower than the accepted safe limits for Zn, Cd, Al, Ni and Fe in drinking water according to the World Health Organization, which are 5 ppm, 5 ppb, 200 ppb, 70 ppb and 300 ppb, respectively (WHO, 2003).

Conceptual model

A two-stage RTM was constructed to simulate (i) porous media flow through the host rock and (ii) surface water flow through the gallery (Fig. 2). In the first stage, rainwater infiltrates through the overlying host rock along two flow paths (Fig. 2). This water flow promotes the dissolution of pyrite (FeS_2), sphalerite (ZnS) and calcite (CaCO_3), the main minerals in the rock, which have been separated into two distinct zones (sulfide zone and calcite zone; see discussion in section Case 4: homogeneous host rock). Sampling of the two inlets in the 1330 Gallery show different chemical compositions (Table 1): sample 9 water (drip water) is more highly concentrated with respect to all measured solutes than the sample 10 water (water flowing on the floor). Also, drip waters at other locations (sample points 5, 6 and 8) show compositions similar to the other waters in the gallery (Table 1). Under the assumption that these two different inlet waters (sample points 9 and 10) originate in the Melics and Carné creeks (sample 11 composition; Table 1; Fig. 1 A) and that flow the same distance to reach the gallery, sample 9 water would be

expected to flow through a more reactive domain than sample 10. Bearing this in mind, the host rock models proposed consist of two separate domains that simulate High-Reactivity Model (HRM) and Low-Reactivity Model (LRM) flow paths to reproduce the composition of sample 9 and sample 10 water, respectively (Fig. 2). The aggregate of the two is referred to as the host rock models.

These host rock models simulate a 1D flow path beginning in an unsaturated (*i.e.* atmospheric-pressure (atm) pyrite and sphalerite zone with variable P_{O_2} , 25.5 m length) followed by a water-saturated calcite zone (6 m length; see section Flow path length), and terminating in a short gallery zone where the water is allowed to equilibrate with the atmosphere (10 m length). Water flows at a realistic Average Linear Velocity (ALV) of 1.5 m d^{-1} (see section Water flow velocity). Note that the Average Linear Velocity (ALV) of surface flow is typically several orders of magnitude larger than that of porous media flow. It should be noted that the short gallery zones in the host rock models are implemented only to make initial interpretations of geochemical behavior at this transition zone. More detailed and realistic simulations for the gallery geochemistry are done in the gallery-specific model.

The second stage of the RTM is designed to simulate flow down the 215 meter-long gallery floor (gallery model). The 215 m corresponds to the distance from the sample 9 location to the sample 5 location (Fig. 2). This model enables comparison of measured concentrations with distance. The total length of the model domain was extended to 250 m to make additional observations. In the gallery model, water flows at a realistic yet slow surface water ALV of 0.48 m min^{-1} and is in contact with the atmosphere.

The gallery model is coupled to the host rock models via conservation of concentration. This is done by using solute concentrations at the end of the calcite zone in the host rock models (31.5 m; Fig. 2), before water enters the gallery zone, as the gallery model inputs. In practice, the gallery input composition is calculated by mixing the output waters from the two host rock models. To mix the two input concentrations from the host rock models, a 2D mesh in the gallery model is constructed (Fig. II). This method allows for the adjustment of the 1D Darcy velocities of both the HRM (V_{HRM}) and LRM (V_{LRM}) into the mixing cell at the beginning of the gallery model domain. Although the total volumetric discharge through the gallery domain is unknown, fitting to the measurement data via modification of the 1D Darcy fluxes from the HRM and LRM can help determine the relative volumetric discharges coming from each input. Once mixed, the water flows down a 1D domain that is in contact with the atmosphere. Effectively, the gallery model is 1D, but employs a 2D grid only to mix the two source waters.

TABLE 1. In-situ and ion concentration results from three sampling campaigns

Campaign date	sample position	T (°C)	pH	cond. (µS/cm)	alkalinity (mM HCO ₃ ⁻)	major elements (mM)							Minor elements (µM)					
						Na	K	Mg	S	Ca	Si	Zn	Cd	Sr	Al	Li	Ni	Fe
June 7-9 2021	1	10.7	7.9	277	1.5	0.09	0.05	0.10	0.49	1.16	0.14	0.00	0.01	1.27	0.49	0.38	0.04	0.22
	2	8.5	7.6	309	1.4	0.06	0.04	0.08	0.75	1.25	0.13	0.08	0.13	1.18	0.75	0.49	0.38	0.35
	3	6.9	7.5	986	1.7	0.25	0.07	0.70	4.65	4.37	0.15	0.15	0.20	6.28	5.02	4.91	0.72	0.24
	4	6.3	7.6	1,146	1.8	0.28	0.07	0.82	5.26	4.88	0.16	0.15	0.20	7.22	0.96	5.73	0.77	0.41
	5	5.9	8.0	845	1.4	0.21	0.06	0.61	3.96	3.72	0.11	0.05	0.12	4.22	0.34	4.74	0.55	0.66
	6	6	8.7	950	1.6	0.22	0.07	0.69	4.34	4.06	0.14	0.15	0.17	4.66	0.82	5.07	0.84	0.27
	7	6	7.9	1,049	2.2	0.21	0.08	0.66	4.24	4.01	0.14	0.16	0.16	4.64	0.66	5.01	0.90	0.77
	8	6.2	8.0	1,219	2.0	0.29	0.08	1.04	6.26	5.52	0.13	0.14	0.15	6.81	0.00	6.04	0.81	0.28
	9	6.6	7.4	2,580	2.7	0.46	0.14	3.51	17.16	11.82	0.27	2.12	0.90	11.07	0.00	18.75	6.19	1.05
	10	7.1	8.0	1,156	2.1	0.29	0.08	0.92	5.71	5.29	0.12	0.09	0.10	6.64	0.29	5.49	0.60	1.80
	11	11.55	7.9	318	2.8	0.05	0.03	0.03	0.29	1.54	0.12	0.00	0.00	1.44	1.06	0.01	0.01	0.14
	11 (σ)	0.25	0.1	8	0.4	0.01	0.00	0.01	0.16	0.05	0.01	0.00	0.00	0.03	0.11	0.01	0.01	0.06
drip water 2021	5	NA	NA	NA	NA	0.23	0.12	0.28	2.07	1.91	0.11	0.00	0.00	3.35	1.31	1.70	0.20	0.45
	6	7	8.3	468	1.4	0.15	0.05	0.31	2.84	3.33	0.15	0.00	0.00	2.57	0.64	2.74	0.37	0.21
	8	6.5	7.6	763	1.6	0.15	0.07	0.44	3.22	2.76	0.22	0.57	0.42	2.66	0.10	4.06	1.89	0.17
	9	6.6	7.5	2,580	2.7	0.44	0.12	3.52	17.44	11.54	0.18	2.37	0.93	11.24	0.00	18.96	6.43	5.36
July 14-16 2020	1	14.1	7.6	272	1.6	0.10	0.03	0.11	0.52	1.13	0.17	0.00	0.01	1.21	0.26	0.36	0.00	0.08
	2	10.7	7.1	315	1.7	0.07	0.03	0.11	0.68	1.28	0.16	0.09	0.14	1.04	0.19	0.57	0.38	0.06
	3	8.7	7.0	997	1.8	0.23	0.07	0.78	4.62	4.29	0.16	0.23	0.31	4.85	0.50	4.65	0.91	0.07
	4	7.0	7.1	1,271	1.7	0.31	0.08	1.07	6.31	5.65	0.17	0.30	0.38	7.54	0.13	6.44	1.12	0.06
	5	6.7	7.0	936	1.4	0.22	0.07	0.76	4.34	4.00	0.16	0.16	0.23	3.78	0.02	4.77	0.93	0.04
	6	6.6	7.0	1,009	1.4	0.24	0.07	0.83	4.74	4.27	0.18	0.29	0.27	4.03	0.11	5.15	1.19	0.08
	7	6.1	7.1	1,015	1.9	0.23	0.07	0.85	4.82	4.29	0.18	0.32	0.27	4.06	0.05	5.04	1.17	0.09
	8	7.0	7.9	1,279	1.8	0.34	0.08	1.19	6.65	5.98	0.18	0.23	0.19	7.28	0.00	6.72	1.20	0.00
	10	7.0	7.9	1,236	2.2	0.30	0.08	1.06	6.04	5.72	0.14	0.11	0.11	7.23	0.14	5.65	0.61	0.54
	11	11.6	8.1	328	3.1	0.05	0.01	0.05	0.20	1.76	0.14	0.00	0.00	1.56	0.13	0.03	0.00	0.28
	11 (σ)	0.5	0.1	8	0.1	0.00	0.00	0.00	0.10	0.03	0.02	0.00	0.00	0.10	0.03	0.01	0.00	0.06
Oct. 20-23 2019	1	10.1	7.4	NA	1.8	0.11	0.05	0.15	0.85	1.50	0.15	0.00	0.01	1.61	0.20	0.39	0.05	0.15
	3	6.1	7.0	NA	NA	0.29	0.07	0.82	4.95	4.91	0.16	0.15	0.20	7.02	0.07	5.27	0.72	0.05
	5	5.6	7.2	NA	NA	0.24	0.07	0.73	4.40	4.25	0.12	0.07	0.18	4.64	0.08	4.74	0.68	0.12
	8	6.3	7.1	NA	NA	0.33	0.09	1.17	6.89	6.26	0.13	0.24	0.25	7.29	0.16	7.46	1.12	0.11
	10	NA	NA	NA	NA	0.34	0.10	1.19	7.07	6.52	0.13	0.30	0.24	7.60	0.93	7.53	1.16	2.51
	11	7.4	7.4	NA	3.0	0.05	0.02	0.04	0.20	1.53	0.13	0.00	0.00	1.35	0.20	0.03	0.04	0.19
	11 (σ)	0.1	0.1	NA	0.3	0.01	0.01	0.00	0.08	0.01	0.02	0.00	0.00	0.00	0.05	0.02	0.03	0.01
detection limit		NA	NA	1	0.1	0.022	0.013	0.002	0.016	0.001	0.007	0.0003	0.001	0.002	0.074	0.014	0.003	0.358
uncertainty (±)		0.01	0.05	0.5	0.1	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%

The RTM enables us to create a reference case, where the coupled host rock and gallery models can reproduce the measured solute concentrations at both gallery inlets and along the gallery flow path with distance. Considering that mineral distribution, mineral reactivity and water flow velocity are unknown parameters in the host rock, that flow velocity is not known in the gallery and that the solubility of hydrozincite appears to vary in the gallery according to the measured saturation indexes (Giannetta, et al., 2023), these parameter values are tested to produce results that capture the possible behavior in the mine. Therefore, the RTM’s sensitivity to these parameters is evaluated in a series of four separate cases: (i) change in flow velocity through both stages of the RTM, (ii) variability in the solubility of hydrozincite (i.e. change

in K_{eq}) in the gallery model, (iii) change in dispersivity in the gallery model and (iv) possibility that the host rock is a homogenous mixture of calcite, pyrite, and sphalerite instead of two distinct mineralogical zones, as presented in the reference model. Moreover, we demonstrate the RTM's ability to predict the solute mass flux (mol d^{-1}) and discharge relationships (L min^{-1}) like those described in [Giannetta et al. \(2023\)](#). Note that this is all done in an abiotic context since the microbiological effects on both metal attenuation and aqueous geochemistry are of minor importance ([Giannetta et al., 2022](#)). Reactive transport simulations are done using the CrunchFlow code ([Steeffel et al., 2015](#)). A brief description of the RTM model is given in the Appendix.

TABLE 2. Total acid digestion results from four 0.25 g hydrozincite samples. The average values are given in ppm. The "Total (%)" is the sum of mass recovered from the digestion given in %. Since pure ideal hydrozincite is 60% Zn and 40% CO_3 and OH, a 60% recovered mass return would be expected because CO_3 was lost as $\text{CO}_2(\text{g})$ and OH is lost during this analysis. The standard deviation (σ) shows the variability between the four samples. Analytical uncertainty is $\pm 4\%$

Element	Average	σ
Zn	544388	16143
S	4259	1078
Ca	3368	346
Ni	479	35
K	225	191
Fe	195	126
Si	164	21
Mg	163	26
Pb	154	101
Cu	97	52
Cd	87	22
Al	35	25
As	34	20
Co	27	5
Mn	22	18
Sr	13	1
total (%)	55.4	1.9

MODEL SETUP AND PARAMETERIZATION

Host rock reference models

The solute concentrations at the gallery input locations (sample 9 and 10; [Table 1](#)) suggest that the upper catchment water (sample 11; [Table 1](#)) takes at least two different flow paths through the host rock before arriving to the sampling transect to 1330 Gallery ([Figs. 2; I](#)). Considering this, two gallery inlet sources were selected. One source with sample 9 composition, that was reproduced with a 1D High-Reactivity Model (HRM), and the other with sample 10 composition that was reproduced with a 1D Low-Reactivity Model (LRM).

Flow path length

The length of the flow path is based on the approximately 100 m vertical displacement between the 1330 Gallery and the upper Carné and Melics streams where samples were taken. However, water flows down the steep catchment on the creek beds for tens of meters before presumably infiltrating the host rock. In reality, the creek water most likely does not infiltrate the host rock at one or two locations, but rather simultaneously flows along the creek bed and infiltrates the rock below. Nevertheless, it can be inferred that this surface water begins to infiltrate the host rock at a height less than 100 meters above the 1330 Gallery. The total flow path length through the host rock is assumed to be 31.5 m ([Fig. 2](#)).

Mineral distribution and reactions

Based on the ore mineralogy reported by [Alvarez-Perez et al. \(1977\)](#) and [Cardellach et al. \(1996\)](#), and on the measured composition of the water in the mine (e.g. elevated zinc and sulfate concentrations; [Table 1](#)), it is assumed that sphalerite and pyrite are the most abundant/reactive metal-sulfide minerals present. It should be noted that galena (PbS) is known to exist in the Victoria Mine system. However, no significant lead concentrations were found and, therefore, galena is excluded from the model. For simplicity, silicate minerals present in the non-limestone rocks ([Fig. III](#)) have not been included in the model, since silica is not precipitating in the secondary minerals present in the gallery (hydrozincite, calcite, smithsonite). See also the gallery water compositions in [Table 1](#), which are dominated by HCO_3^- (alkalinity), Mg, S and Ca.

Two parallel pyrite reaction rate laws are used to account for effects of aqueous oxygen concentrations, Fe(III) concentrations and pH. In the case of sphalerite, two parallel sphalerite dissolution rate laws are also implemented. One that describes the normal pH-dependent dissolution, and a second neutral mechanism that

prevents dissolution rates to vanish in alkaline conditions (Table 3). Since the relative volumetric proportions of sphalerite and pyrite in the system are unknown, their respective proportions were set as equal values to make straightforward comparisons of their reactive surface areas (Table 3). Note that iron is not soluble at the observed pH range (pH = 7–8) and readily precipitates as an iron oxide in these conditions (Schwertmann, 1991). To account for this process, ferrihydrite is implemented throughout the entire model domain under a local equilibrium assumption (*i.e.*, fast precipitation). As a result, only measured sulfate concentrations may be used to determine the extent of pyrite dissolution.

Field measurements show that gallery waters are pH-buffered by bicarbonate (*e.g.* pH > 7.0 and high alkalinity) and contain dissolved calcium (Table 1). Given the existence of several limestone formations overlying the gallery (Fig. III), it is reasonably assumed that calcite exists along the host rock flow path. Calcite is added to the model to reproduce these observations, and two parallel calcite reaction rate laws are implemented to account for both acidic and neutral dissolution mechanisms. Further, calcite dissolution increases the pH and thereby inhibits sphalerite dissolution. Therefore, calcite is placed after pyrite and sphalerite in a distinct zone.

Along with dissolution and/or precipitation of pyrite, sphalerite, ferrihydrite and calcite, precipitation of hydrozincite and smithsonite are relevant to the system (Table 4), and therefore implemented into the model. Kinetic parameters (*e.g.* rate constants) for hydrozincite and smithsonite have not been previously determined for the conditions at the Victoria Mine. Therefore, like ferrihydrite, they react under the assumption of local equilibrium. The aqueous species considered in the simulations are listed in Table II. Log K_{eq} values and stoichiometric coefficients are taken from the EQ3/6 database (Wolery, 1990) included in the CrunchFlow code.

Activity coefficients were calculated using the extended Debye Hückel formulation (b-dot model) with parameters obtained from the same database.

Giannetta et al. (2023) obtained the equilibrium constant of hydrozincite dissolution at 7 °C ($Zn_5[CO_3]_2[OH]_{6(s)} + 8H^+ \rightarrow 5Zn^{++} + 2HCO_3^- + 6H_2O$; log $K_{eq} = 30.01$), which agrees with the only previously reported value for pure hydrozincite at 25 °C (log $K_{eq} = 30.14$, Schindler et al., 1969). However, using this experimentally derived value, bicarbonate measurements cannot be reproduced in the model. To reproduce measured bicarbonate concentrations, a new log K_{eq} is selected based on a speciation calculation carried out for the sample 10 location geochemistry (see Giannetta et al., 2023). The assumption is that water at this location has reacted to equilibrium with respect to hydrozincite since it has been flowing along the gallery floor allowing time for mineral reactions to take place, and hydrozincite was observed here. Accordingly, the new log K_{eq} of hydrozincite used in the reference models is 37.68 at 7 °C, which serves as the reference value for both the host rock and gallery models.

In the context of mineral distribution in space, in the hundreds of meters of vertical displacement in the Victoria Mine system, the geologic formations are composed of layers of distinct rock types (Fig. III). Therefore, the associated flow path was treated as layers of rock rather than a homogeneous porous media, and a sulfide zone is configured as a non-saturated zone closest to the surface, such that atmospheric oxygen is available for the dissolution of the sulfide minerals. The sample 9 and 10 locations always showed water flow in three years indicating perennial flow. Therefore, it is assumed that during non-rainy periods, the water table is deep below the surface, such that the phreatic level is not far above the gallery. Thus, the saturated zone is assumed to be thin relative to the total depth of the system. This saturated zone is chosen to coincide with the calcite zone, as oxygen is not required for the dissolution of calcite.

TABLE 3. Parameters for the mineral reaction rate laws

Mineral	$k_{25^\circ C}$ (mol m ⁻² s ⁻¹)	E_a (kcal mol ⁻¹)	$(a_{H^+})^n$	$(a_{Fe^{3+}})^n$	$(a_{O_2(aq)})^n$	m_1	m_2	m_3	Reference
Calcite	-5.81	5.62	0	0	0	3	1	1	Palandri and Kharaka, 2004; Xu et al., 2012
Calcite	-0.3	3.44	1	0	0	3	1	1	same as above
Sphalerite	-6.49	15	0.54	0	0	1	1	1	Acero et al., 2007
Sphalerite	-9.73	15	0	0	0	1	1	1	assumed neutral mechanism
Hydrozincite	-6	15	0	0	0	1	1	1	assume local equilibrium (fast kinetics)
Pyrite	-7.52	13.6	-0.5	0.5	0	1	1	1	Palandri and Kharaka, 2004
Pyrite	-4.55	13.6	0	0	0.5	1	1	1	same as above
Smithsonite	-6	15	0	0	0	1	1	1	assume local equilibrium (fast kinetics)
Ferrihydrite	-5	0	0	0	0	1	1	1	assume local equilibrium (fast kinetics)

TABLE 4. Equilibrium constants (log Keq) for all mineral reactions at 7 °C

Mineral name	Reaction	Log K_{eq}
Hydrozincite	$Zn_5(CO_3)_2(OH)_6 + 8H^+ \rightleftharpoons 5Zn^{++} + 2HCO_3^- + 6H_2O$	30.01; 35.53; 37.68
Smithsonite	$ZnCO_3 + H^+ \rightleftharpoons Zn^{++} + HCO_3^-$	0.793
Sphalerite	$ZnS + 2O_{2(aq)} \rightleftharpoons Zn^{++} + SO_4^{2-}$	136.17
Calcite	$CaCO_3 + H^+ \rightleftharpoons Ca^{++} + HCO_3^-$	2.123
Pyrite	$FeS_2 + 3.5O_{2(aq)} + H_2O \rightleftharpoons Fe^{++} + 2SO_4^{2-} + 2H^+$	233.12
Ferrihydrite	$Fe(OH)_3 + 2H^+ \rightleftharpoons Fe^{++} + 0.25O_{2(aq)} + 2.5H_2O$	-4.678

Water flow velocity

No constraint on the flow velocity, porosity, or water residence time in the host rock is known for the Victoria Mine system. Accordingly, both 1D host rock models have the same ALV in order to maintain the same residence time between the two. In a similar fashion, a generic porosity value of 0.38 was assumed in all cases, with the idea of providing a framework for the calculation of water flow velocities and residence times. This value is not physically constrained by observations and would include flow through both porous rock matrix and fractures. Different values of porosity would provide the same results, as long as the implemented Darcy velocities ($m^3\ m^{-2}\ s^{-1}$) were the same. However, the corresponding ALV's would change (ALV equals Darcy velocity divided by porosity). One basic assumption made here is that the water coming from sample 9 and sample 10 locations reflects perennial flow as it was never dry. In accordance with [Arbel et al. \(2010\)](#), four different types of drip water infiltrating a 27 m vertical section of rock before entering a cave were identified: post-storm, seasonal, perennial, and overflow. These four drips were assigned ALVs, and the dominant/most frequent flow velocity for perennial flow was $\approx 5.8\ m\ d^{-1}$. Considering this value, the assumption is made that the ALV at the Victoria mine is within the same order of magnitude (e.g. 1-10 $m\ d^{-1}$). The reference host rock models are assigned an ALV of $1.5\ m\ d^{-1}$. This corresponds to Darcy velocity of $0.57\ m\ d^{-1}$ in the model.

Initial and input water composition

The amending water and initial composition in both the HRM and LRM simulations are adjusted to the sample 11 geochemistry ([Table 5](#)). This composition includes 14 primary species and eighty-six secondary species ([Table II](#)), which are incorporated into all simulations. Further, since the upper catchment water is in contact with the atmosphere, the input water is forced to be in equilibrium with atmospheric oxygen and CO_2 before entering the rock.

Construction of the host rock models

The host rock models consist of a 41.5 m domain and three zones. The first zone is a 25.5 m unsaturated sulfide zone ([Fig. 2](#)), which is composed of $500 \times 5.0\ cm$ grid cells and terminates with an additional $50 \times 1.0\ cm$ grid cells. The second zone is a 6 m saturated calcite zone, which is composed of $100 \times 5.0\ cm$ grid cells and surrounded on both ends by $50 \times 1.0\ cm$ grid cells. The third zone is a short 10 m gallery zone, which was implemented in this host rock model as a means to make initial observations of mineral reactions in the gallery (comparison with the measured compositions of samples 9 and 10) before parameterizing the 2D gallery model. This gallery zone is composed of $50 \times 1\ cm$ grid cells followed by $200 \times 5\ cm$ grid cells. The water residence time through the host rock model is $\approx 30\ d$. The runtime of each model is 60 d, such that the system experiences approximately two total water volume displacements. The temperature for all simulations was chosen to be 7 °C based on the temperature of water deep in the 1330 gallery.

The sulfide zone is composed of 30 vol% pyrite and 30 vol% sphalerite ([Table 6](#)). Artificial O_2 and CO_2 minerals were also added (1 vol% rock) to keep P_{O_2} and P_{CO_2} at equilibrium with the atmosphere, through fast dissolution/precipitation and appropriate log K_{eq} values. The water in this domain is in equilibrium with the atmosphere ($415\ ppm\ CO_2$ and 21% O_2), thus simulating an unsaturated zone (i.e. vadose zone). This promotes sphalerite and pyrite dissolution. The calcite zone is composed of 60% calcite by volume to maintain porosity and therefore, the ALV between zones. Here, water is not at equilibrium with the atmosphere (the artificial O_2 and CO_2 minerals do not react), thus simulating a water table above the gallery.

In the gallery zone, the smithsonite, hydrozincite, calcite and ferrihydrite are secondary minerals (simulations begin with a 0% volume fraction for all; [Table 6](#)). The geochemistry of an open gallery incorporates an

TABLE 5. Initial and amending water compositions (mol L⁻¹) used for all simulations. These are the pH and total concentrations of the primary species assigned in the input file. The “Sample 10/11” columns reflect the measured compositions from the corresponding sampling points. The “HRM/ LRM input” labels reflect the composition of the water at the end of the calcite zone (31.5 m) when the host rock model simulations are completed (e.g. 60 d for the reference case).

Condition:	Initial (mol L ⁻¹)		Input (mol L ⁻¹)						
Model:	Host rock 1D	Gallery 2D	Host rock (ref.)	Gallery (ref.)		Gallery (low flux case)		Gallery (high flux case)	
Composition:	Sample 11	Sample 10	Sample 11	HRM input	LRM input	HRM input	LRM input	HRM input	LRM input
pH	7.90	8.00	7.90	6.48	7.18	6.42	7.02	6.47	7.44
Na ⁺	5.07E-05	2.92E-04	5.07E-05	5.07E-05	5.07E-05	5.07E-05	5.07E-05	5.07E-05	5.07E-05
K ⁺	3.07E-05	7.66E-05	3.07E-05	3.07E-05	3.07E-05	3.07E-05	3.07E-05	3.07E-05	3.07E-05
Mg ⁺⁺	3.40E-05	9.21E-04	3.40E-05	3.40E-05	3.40E-05	3.40E-05	3.40E-05	3.40E-05	3.40E-05
Ca ⁺⁺	1.54E-03	5.29E-03	1.54E-03	1.30E-02	5.48E-03	2.47E-02	1.00E-02	6.79E-03	3.01E-03
Zn ⁺⁺	1.80E-07	9.01E-05	1.80E-07	3.61E-03	4.50E-04	9.47E-03	1.29E-03	1.23E-03	9.93E-05
Cd ⁺⁺	1.10E-10	1.70E-07	1.10E-10	1.10E-10	1.10E-10	1.10E-10	1.10E-10	1.10E-10	1.10E-10
Sr ⁺⁺	3.15E-06	1.45E-05	3.15E-06	3.15E-06	3.15E-06	3.15E-06	3.15E-06	3.15E-06	3.15E-06
Fe ⁺⁺	1.43E-07	1.80E-06	1.43E-07	1.57E-07	9.25E-08	1.65E-07	9.84E-08	1.60E-07	8.59E-08
Li ⁺	2.07E-09	1.40E-06	2.07E-09	1.10E-10	1.10E-10	1.10E-10	1.10E-10	1.10E-10	1.10E-10
Ni ⁺⁺	1.12E-07	5.93E-07	1.12E-07	1.12E-07	1.12E-07	1.12E-07	1.12E-07	1.12E-07	1.12E-07
SO ₄ ⁻⁻	2.86E-04	5.71E-03	2.86E-04	1.50E-02	4.60E-03	3.18E-02	9.36E-03	7.03E-03	2.30E-03
SiO _{2(aq)}	1.16E-04	1.22E-04	1.16E-04	1.16E-04	1.16E-04	1.16E-04	1.16E-04	1.16E-04	1.16E-04
HCO ₃ ⁻	2.00E-03	2.10E-03	2.00E-03	4.84E-03	2.44E-03	7.86E-03	4.06E-03	2.64E-03	1.15E-03

atmosphere similar to that of earth’s surface. Therefore, the same technique used to simulate the non-saturated zone is applied, and the effects of CO₂ degassing as water enters the mine can be observed. Notably, water from both sample 10 and 9 locations had some time to equilibrate with the air before sampling. This is especially true for the sample 10 location as it came from a stream on the floor and does not directly form a dripping source like sample 9.

In the host rock models, the resulting solute concentrations are a function of water residence time (determined by path length and flow rate) and mineral reaction rates. As these values are not constrained, there is no merit to altering them between the LRM and HRM. Therefore, their parameter values are held constant in both 1D reference simulations, while only the bulk surface areas (m² m⁻³ rock) of pyrite and sphalerite are different between the HRM and LRM.

Gallery reference model

A separate gallery model serves to simulate both mixing of host rock input waters and generate a realistic ALV of surface water. One objective of the gallery model is to simulate the relative mineral reaction rates of hydrozincite, smithsonite and calcite along the 1330 Gallery floor once the two source waters have mixed. In order to make straightforward comparisons, the reactive surface areas of the minerals are initially equal (Table 6).

Mixing two water sources in CrunchFlow requires a 2D domain (Figs. 2 and II). This allows for the application of a mixing cell, where waters with distinct chemical compositions can be transported into this cell. From this mixing cell, the water flows down a 1D domain while remaining in equilibrium with the atmosphere (415 ppm CO_{2(g)} and 21% O_{2(g)}). Hydrozincite, smithsonite, calcite exist in the model as secondary minerals, allowing the minerals to react although they are not present at the initiation of the simulation. Darcy velocities (V) are defined at the border of each grid cell (Fig. II) and flow can only occur along the gallery (left to right). The sum of the two input Darcy velocities into the mixing cell must be equal to the output Darcy velocity for the mixing cell and all subsequent cells, and all transverse flow velocities are set to zero to ensure mass conservation down the 1D gallery domain. The solute concentrations for each input are informed by the water compositions of the LRM (V_{LRM}) and HRM (V_{HRM}) at the calcite zone-gallery zone interface (31.5 m) (Table 6). In the case of this model, the 1D Darcy velocity through gallery is fixed at 11 m h⁻¹, such that V_{HRM} + V_{LRM} = 11 m h⁻¹. This number was selected to produce a realistic ALV of 0.48 m min⁻¹ while incorporating the 0.38 porosity value (Table 6). This was a slow-moving stream upon observations in the field. The relative proportion of the two inputs is adjusted to fit the measurement data. Specifically, V_{LRM}/V_{HRM} is set to a value reproducing sulfate concentrations, as this solute is conserved in the model.

TABLE 6. Mineral volume fractions and bulk surface areas ($\text{m}^2 \text{m}^{-3}$ rock) used in the simulations for the 1D host rock and 2D gallery models. The lower table corresponds only to the homogeneous host rock case, where the 2D gallery model is not considered. In volume fraction (vol. frac.), 0.01 of O₂ mineral and 0.01 of CO₂ mineral are considered to keep atmospheric P_{O₂} and P_{CO₂} close to local equilibrium condition

Model:	Host rock 1D (reference)							Gallery 2D	
Domain:	Sulfide zone	HRM	LRM	Calcite zone	HRM/LRM	Gallery zone	HRM/LRM	Gallery	
Parameter:	vol. frac.	bsa	bsa	vol. frac.	bsa	vol. frac.	bsa	vol. frac.	bsa
Hydrozincite	0	0.01	0.01	0	0.01	0	0.01	0	0.1
Smithsonite	0	0.01	0.01	0	0.01	0	0.01	0	0.1
Sphalerite	0.3	400	100	0	0	0.6	0	0.6	0
Calcite	0	0	0	0.6	1.5	0	0.01	0	0.1
Pyrite	0.3	12	4	0	0	0	0	0	0
Ferrihydrite	0	0.01	0.01	0	0.01	0	0.01	0	0.01
Porosity	0.38	-	-	0.38	-	0.38	-	0.38	-
Model:	Host rock 1D (homogeneous case)								
Domain:	Sulfide zone	HRM	LRM	Calcite zone	HRM	LRM	Gallery zone	HRM/LRM	
Parameter:	vol. frac.	bsa	bsa	vol. frac.	bsa	bsa	vol. frac.	bsa	
Hydrozincite	0	0.01	0.01	0	0.01	0.01	0	0.01	
Smithsonite	0	0.01	0.01	0	0.01	0.01	0	0.01	
Sphalerite	0.25	333	83.3	0.25	333.33	83.33	0.6	0	
Calcite	0.1	0.25	0.25	0.1	0.25	0.25	0	0.01	
Pyrite	0.25	10	3.33	0.25	10	3.33	0	0	
Ferrihydrite	0	0.01	0.01	0	0.01	0.01	0	0.01	
Porosity	0.38	-	-	0.38	-	-	0.38	-	

Sensitivity analyses

Case 1: Flow velocity

In the underground mine galleries the physical conditions are relatively constant through time (*e.g.* temperature, gas concentrations, input source locations). However, measurements of the mine effluent and adjacent Melics creek showed changes in the volumetric discharge (*e.g.* Melics creek (sample 3 in Fig. 1): October 2019 (37.0 L min⁻¹), July 2020 (40.4 L min⁻¹), and June 2021 (23.1 L min⁻¹; Giannetta et al., 2023). This variation could be attributed to dry and rainy seasons and rain events and affect the volumetric flux through the system, thereby changing the ALVs, and perturbing water residence time.

As the model is conceptually a 1D model, simulation of changes in volumetric discharge translates to changes in

flow velocities, assuming a fixed flow path (*i.e.* a tube). A flow velocity of half the reference ALV (low flux case) and a fast flow velocity of twice the reference (fast flow case) are tested. These two cases are applied to both the host rock and gallery models. This case generates six new sets of results: two in the LRM, two in the HRM, and two in the gallery model.

Case 2: hydrozincite solubility

Solubility experiments and speciation calculations performed by Giannetta et al. (2023) demonstrated that hydrozincite does not have a constant K_{eq} value, but rather a range of values ($30.01 < \log K_{eq} < 37.68$ at 7 °C). Under the assumption that hydrozincite was precipitating under local equilibrium conditions in the gallery (*i.e.*, SI = 0), the K_{eq} determined by the speciation calculation for the 2021 sample 10 water composition ($\log K_{eq} = 37.68$) is

used for the reference model. However, the experimental log K_{eq} (30.01) and log K_{eq} based on sample 5 speciation calculations (35.53) suggest that the apparent log K_{eq} of hydrozincite shows some variability.

One explanation for the apparent change in solubility is the observation that the hydrozincite found in the Victoria Mine was both highly heterogeneous and contained significant impurities (Fig. 1C, D). As impurities can alter the apparent K_{eq} of a mineral (Druhan *et al.* 2021; Maher *et al.*, 2006), it is reasonable to assume that samples from the mine could exhibit behavior such that the experimentally determined K_{eq} reflects an impure mineral. The log K_{eq} of hydrozincite based on the experiments (30.01) and the 2021 sample 5 speciation calculation (35.53) are examined in comparison to the reference case (sample 10 speciation calculation; 37.68), as this represents a relevant range of hydrozincite solubilities.

Case 3: dispersivity

Hydrodynamic dispersion (dispersivity) attempts to account for the effects resulting from variation in the water flow velocity along a flow path (Eq. I). The model sensitivity to changes in dispersivity are examined. A typical value assigned for porous media is a distance equal to 10% the domain length, but the gallery is a surface water and therefore could reasonably differ. As such, the reference case dispersivity is selected to be 1% of the domain length (2.5 m). High and low dispersivity cases are given values equal to 10% and 0.1% of the domain length (25 m and 0.25 m), respectively.

Since no data exists along the host rock flow path to constrain the shape of the solute concentration curve, this case will not be applied to the host rock models. Instead, the three dispersivity values will be compared only in the gallery model domain, where concentrations with distance were constrained with measurements. This case generates two sets of new results in the gallery model.

Case 4: homogeneous host rock

Earlier geological mapping shows that distinct rock formations exist above the Victoria Mine (Fig. III). However, little is known about the physical distribution of minerals along the flow path(s) taken by waters that infiltrate the mine. When mineral distribution in porous media is unknown, it is often assumed to be homogeneous. Comparing a homogeneous case to the layered reference case can give insight towards the real mineral distribution that exists in the host rock at the Victoria Mine.

In this case, the assumption remains that there are non-saturated and saturated zones above the mine. Therefore, the

two zones defined in the reference case will be maintained, such that the first 25.5 m is non-saturated porous media, while the remaining 6 m is saturated porous media (Fig. 2). The gallery zone is not altered in any way, as it does not contain any initial volume of reactive minerals.

The fundamental modification is that the total volume fraction and reactive surface area of pyrite, calcite, and sphalerite in the reference case are mixed uniformly across the 31.5 m domain. Specifically, the total surface reactivity ($m^2 m^{-3}$ rock) assigned to each mineral in the LRM and the HRM is conserved in the homogeneous case of each model (Table 6). Further, the flow and initial and input conditions are identical to that of the reference case (Table 5). This case results in two new sets of results; the mixed HRM and the mixed LRM.

Solute mass flux and discharge

An important goal of this modeling study is to quantify solute mass flux out of the gallery based on the various conditions imposed on the system, and compare the solute flux versus discharge relationships to those measured outside of the mine (Giannetta *et al.*, 2023). Although this is a 1D model, the concentrations at the end of the gallery model in all cases can be multiplied by an estimated volumetric discharge to produce a solute mass flux.

The only data that exist to support a realistic estimation for the gallery discharge rate are the discharge measurements (discharge rates = 37.0, 40.4, and 23.1 L min^{-1} in 2019, 2020, and 2021, respectively; Giannetta *et al.*, 2023), which reflect the combined discharge from the mine effluent and the adjacent Melics Creek. Using this data, two assumptions must be made to assign a reference discharge to the gallery: (i) the mine effluent and Melics Creek discharges are equivalent and (ii) the mine effluent discharge is equal to that of the 1330 Gallery discharge. Considering the minimum and maximum measured discharges (23.1 L min^{-1} and 40.4 L min^{-1}), the average is 31.8 L min^{-1} . Based on the assumptions, the assigned gallery discharge is 15.9 L min^{-1} . This value is changed only in the flow velocity test, in which the discharge is 31.8 L min^{-1} and 7.95 L min^{-1} in the high and low flux cases, respectively.

RESULTS AND DISCUSSION

Host rock reference

The results of the LRM and HRM (Fig. 3) are produced by altering the bulk surface areas assigned to pyrite and sphalerite (Table 6), while all other parameters remained constant. Model fitting for the LRM is accomplished with

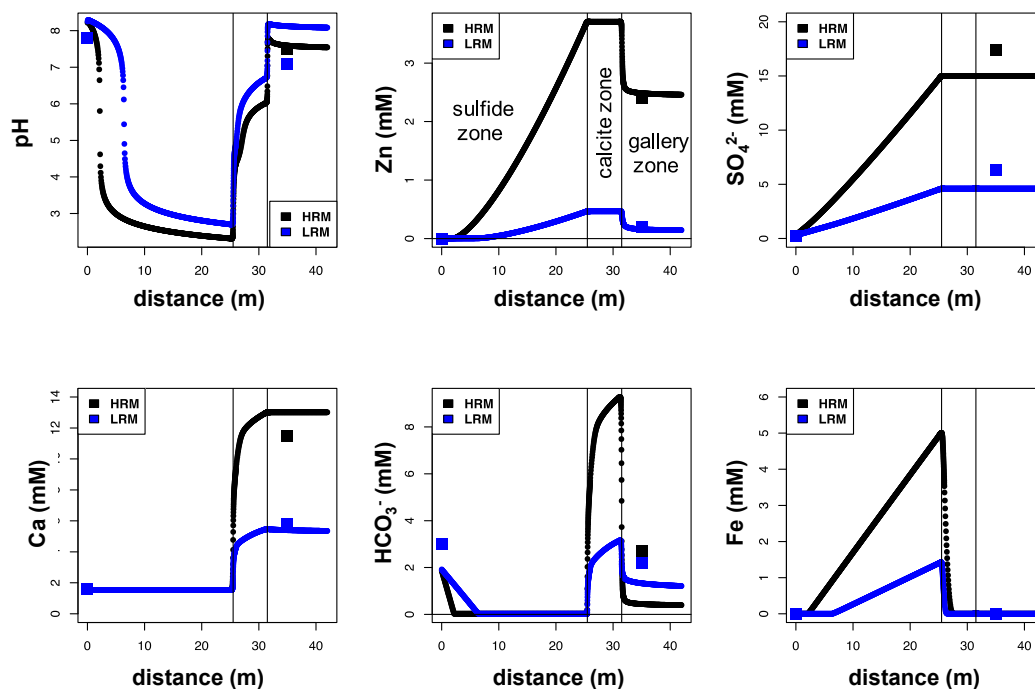


FIGURE 3. Simulated variations in pH and metal concentrations in the host rock reference case. Flow goes from left to right with an ALV of 1.5 m d⁻¹. Results from the High Reactivity Model (HRM) and Low Reactivity Model (LRM) are plotted as a function of distance at $t = 60$ d, where the residence time of the system is 30 d. The vertical lines divide the three zones as described in Fig. 2 (the non-saturated sulfide zone exists from 0 to 25.5 m, the saturated calcite zone exists from 25.5 m to 31.5 m, and the gallery zone exists from 31.5 m to 41.5 m). This is the same for all host rock models. Measured sample 9 and sample 10 water compositions are plotted at 35 m with black and blue squares, respectively. The sample 11 data are plotted at 0 m.

bulk surface areas of 4 m² m⁻³ rock (pyrite) and 100 m² m⁻³ rock (sphalerite), whereas model fitting for the HRM is accomplished with bulk surface areas of 12 m² m⁻³ rock (pyrite) and 400 m² m⁻³ rock (sphalerite). The pyrite and the sphalerite in the HRM are 3 and 4 times more reactive, respectively, than that of the LRM. Notably, calcite reactivity is not altered (1.5 m² m⁻³ rock; Table 6), with calculated calcium concentrations consistent with measured values.

In general, pH, zinc, sulfate, bicarbonate and total iron concentrations measured in the field (2021 campaign) are reproduced by the model (Fig. 3). Specifically, the LRM reproduced solute concentrations that correspond to those of sample 10, while the HRM reproduced solute concentrations that correspond to those of sample 9. Further, the results from the LRM and HRM follow the same patterns, and differ only in that the mineral reactions are faster in HRM (Fig. IV A). Each model displays a distinct yet constant pyrite dissolution rate despite the large changes in pH and iron concentrations. The oxidative dissolution of pyrite dominates the overall dissolution rate of pyrite (Fig. IV B). Oxygen partial pressure is initially 0.21 bar. Thereafter, the slight deviation from 21% pO₂ is caused by oxygen consumption, where the magnitude of this deviation is proportional to the rate of consumption (*i.e.*, at local equilibrium conditions). As the acidic

dissolution mechanism of sphalerite dominates over the neutral mechanism the sphalerite dissolution rate increases with distance (Fig. IV B). As the pH decreases, due to the dissolution of pyrite, the acidic dissolution mechanism for sphalerite takes over, thereby increasing the overall rate. This also explains the non-linear oxygen consumption curve. The total deviation from 21% pO₂ is due to both sphalerite and pyrite dissolution, but dissolution of the former consumes more oxygen as pH increases, causing the non-linearity of the curve (Fig. IV B).

In both models, the acidic waters from the sulfide zone enter the calcite zone causing calcite to dissolve rapidly. The carbonate product neutralizes the acid, increasing rapidly the pH to ≈ 5 (Fig. 3), and then increases more slowly until the water reaches the gallery zone. Ferrihydrite begins to precipitate rapidly once the water enters the saturated calcite zone because the pH increases and there is dissolved iron in solution. The rate of ferrihydrite formation subsequently falls to zero because iron is consumed (Fig. IV A). CO₂ is also supplied in the model. In the sulfide zone and the gallery zone, pCO₂ is constant in non-saturated domains (Fig. IV B). In the calcite zone, high partial pressures indicate a solution that is highly saturated in CO_{2(aq)}. This is confirmed by the bicarbonate concentrations through the calcite zone (Fig. 3), showing a solution highly saturated with respect to bicarbonate.

The gallery zone marks a transition from a saturated zone to a non-saturated zone where an O_2/CO_2 atmosphere is imposed. This process can be observed via the rapid rate of CO_2 degassing (Fig. IV B), which is analogous to the water re-equilibrating with the atmosphere. This effect causes precipitation of hydrozincite and smithsonite (Fig. IV A). A small amount of calcite precipitates as well, but the rate is slow compared to that of hydrozincite. Therefore, hydrozincite consumes bicarbonate before any significant calcite can form. This explains the flat calcium concentration curve in the gallery (Fig. 3). The precipitation of hydrozincite and smithsonite carbonate minerals controls the zinc and bicarbonate concentrations in the gallery zone although hydrozincite precipitation dominates because it has a 100 times faster rate. It appears that water reaches equilibrium with respect to hydrozincite faster than with respect to smithsonite, because smithsonite continues precipitating further down the gallery zone (Fig. IV A).

Gallery reference

The results of the gallery reference model (Figs. 4; 5) are produced by mixing the LRM and HRM water compositions at the end of the calcite zone (Table 6) at a proportion of

10:1 ($V_{LRM}/V_{HRM} = 10$). In a 3D context, this implies that the volumetric discharge of the LRM is 10 times greater than that of the HRM into the gallery. This proportion is principally determined based on the assumption that sulfate is conserved through the gallery. In other words, mixing and dilution are the only processes that can affect its concentration, not reaction. In general, the measured pH and the concentrations of bicarbonate and zinc are approximately reproduced by the model (Fig. 4), despite the very simple one-dimensional flow and reaction model. Variability in the data can probably be attributed in a large degree to a more complex flow distribution in both host rock and gallery.

The measured calcium and sulfate concentrations decrease in a similar fashion after ~100 m and remain fairly constant after the initial decrease. The model does not reproduce this behavior because no sulfate reaction mechanism is considered, and calcite precipitation is slow and contributes to a ~0.02 mM decrease across the gallery domain. If gypsum ($CaSO_4 \cdot 2H_2O$) is considered, the model results in a solution highly undersaturated with respect to it (no precipitation inside of the Victoria Mine). This consistent decrease in calcium and sulfate (sample 8 location) suggests dilution and/or mixing with another water beyond this point.

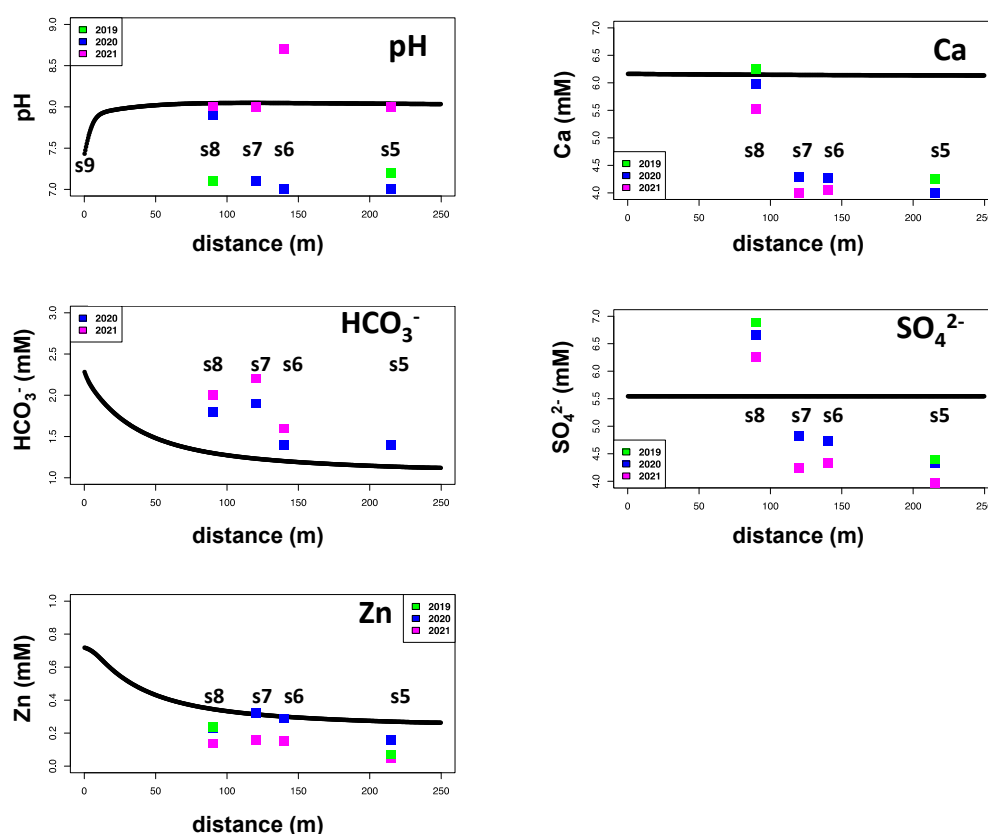


FIGURE 4. Results for the gallery model reference case plotted as a function of distance at $t = 5$ d together with measurements from three sampling campaigns. Flow goes from left to right ($ALV = 0.48 \text{ m min}^{-1}$) and the measured values plotted correspond to real distances along the gallery (samples 8, 7, 6, and 5 correspond to 90, 120, 140, and 215 m from the sample 9 (drip water) location, respectively).

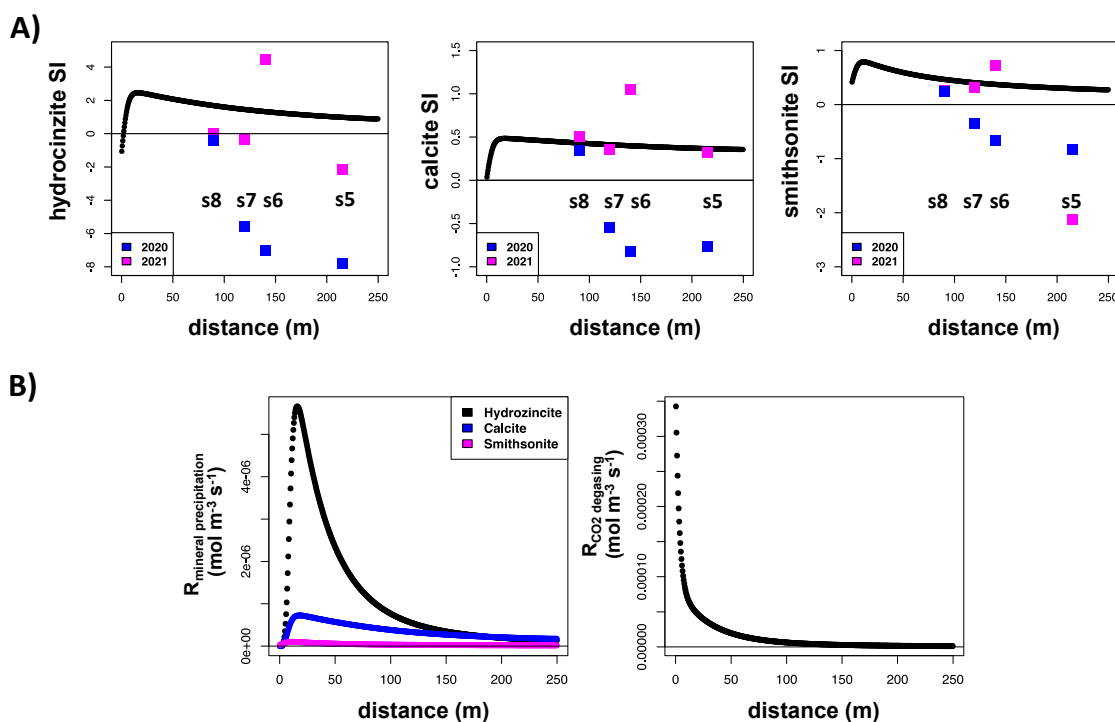


FIGURE 5. Results for the gallery model reference case plotted as a function of distance at $t = 5$ d: A) saturation state of the solution; B) mineral precipitation and rate of CO_2 degassing. Flow goes from left to right with ($\text{ALV} = 0.48 \text{ m min}^{-1}$ and water residence time = 8.7 h) and the measured values plotted correspond to real distances along the gallery. The calculated SI values from the 2020 and 2021 water measurements are done using a $\log K_{\text{eq}} = 37.68$ for hydrozincite.

The model reproduces the decreasing trend in the calculated SI values for hydrozincite, calcite, and smithsonite with distance (Fig. 5A). This is due to the precipitation of the three minerals, forcing the water closer to equilibrium. In these simulations, hydrozincite precipitation controls the concentrations of zinc and bicarbonate as it precipitates approximately 10 times faster than calcite, and almost 20 times faster than smithsonite (Fig. 5B). This is consistent with the analyses of solid samples from the mine, which were composed almost exclusively of hydrozincite (Giannetta *et al.*, 2023).

The model most accurately reproduces the saturation state of all three minerals in 2021. However, the model does not predict negative SI values, which are apparent in both 2020 and 2021 (Fig. 5A). Further, the SI values calculated from measurements typically result in negative values after 100 m. This is especially true in 2020, as SI values for all minerals are typically lower for that year.

The mechanism for the precipitation of these carbonate minerals relies on the degassing of the water as it enters the gallery (Fig. 5B). Prior to this transition, water is highly saturated with respect to CO_2 . Thus, it has a lower pH ($\text{pH}_{\text{LRM}} = 7.18$ and $\text{pH}_{\text{HRM}} = 6.48$, Table 5). As the water enters the open gallery and CO_2 degasses, the pH increases rapidly (Fig. 4), thus decreasing the carbonate mineral solubility and forcing precipitation.

Sensitivity to flow velocity

Host rock model

The ALV through the host rock models is doubled (3 m d^{-1} , high flux case) and halved (0.75 m d^{-1} , low flux case) with respect to the reference case generating two new results in the HRM (Fig. 6) and the LRM (Fig. V). For each flow velocity case, the concentrations at the calcite-gallery interface (31.5 m) are used as the two input water concentrations for the gallery model.

In both the LRM and the HRM, the pyrite dissolution rate remains constant regardless of the flow velocity, indicating that the oxidative dissolution mechanism mainly controls the overall rate. However, even though the dissolution rate is constant in each model, the high flux cases produce lower sulfate and iron concentrations (Figs. 6; V A), while the low flux cases produce higher sulfate and iron concentrations when compared to the reference cases. Although the rate of sulfate and iron liberation from pyrite dissolution remains unchanged, the time spent by a volume of water in the sulfide zone increases as a result of increased residence time. Therefore, the water has more time to accumulate solute as it passes over the reactive mineral surfaces. This can also explain the linear shape of the sulfate and iron curves, such that a constant flux of solute mass is being added to the water, regardless of flow velocity.

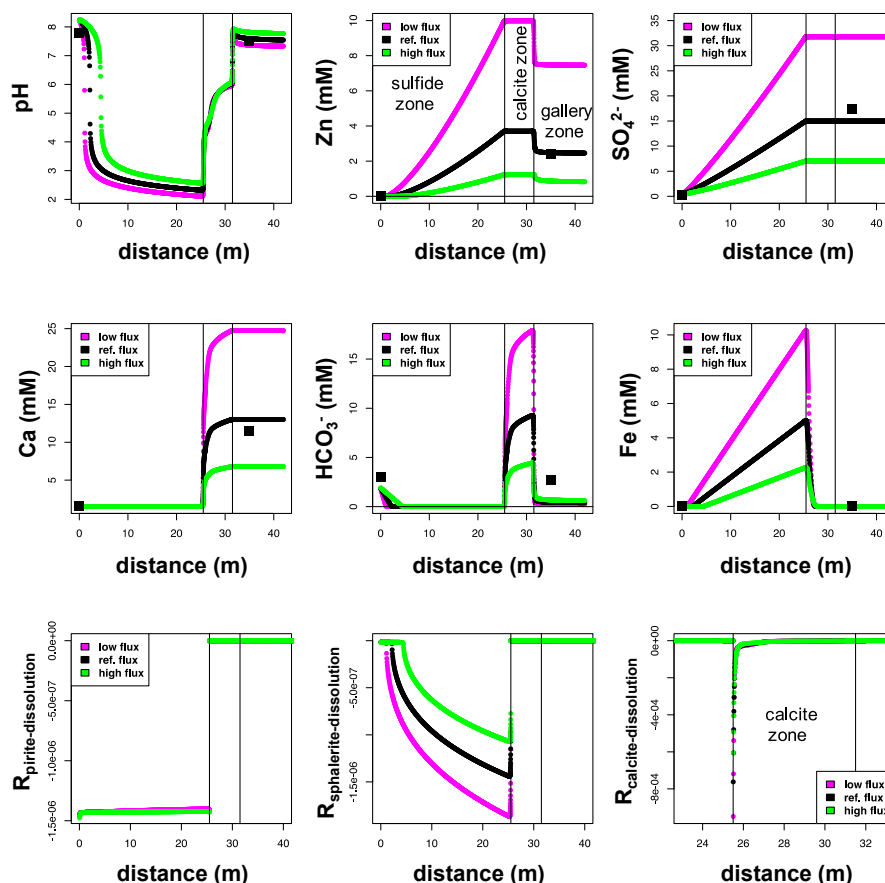


FIGURE 6. HRM simulations for the host rock high flux case and low flux case: variation in pH, elemental concentrations and mineral dissolution rates with distance. Flow goes from left to right at 0.75 and 3 m d⁻¹ for the low and high flux case, respectively. The HRM reference case is also plotted and corresponds to the HRM results (black) in Figure 3. In the high flux case, results are plotted as function of distance at $t = 30$ d (residence time = 15 d). The low flux results are plotted as a function of distance at $t = 120$ d (residence time = 60 d). The sample 11 data are plotted at 0 m and the sample 9 data are plotted at 35 m as black squares. Mineral dissolution rates ($R_{\text{mineral-dissolution}}$) are in mol m⁻³ s⁻¹.

The sphalerite dissolution rate is indirectly affected by flow velocity because slow flow produces high rates and vice versa (Fig. 6). The rate of sphalerite dissolution at these conditions is dominated by the pH. Therefore, the decrease in pH due to pyrite dissolution remains as the dominant mechanism by which sphalerite dissolves. Further, as the pH decreases with decreasing flow velocity (Fig. 6), the rate of sphalerite dissolution would be expected to increase. This occurs in both host rock models, confirming that they behave correctly. Additionally, non-linear sphalerite rate curves explain the corresponding non-linear zinc concentration curves for all cases in the host rock models (Figs. 6; V A). In the calcite zone, the initial rate of calcite dissolution is faster in the low flux case and slower in the high flux case when compared to the reference case. This is explained by the pH of the water entering the calcite zone since the dominant dissolution rate law is pH dependent (Table 3). However, within ≈ 2 m, rates in all three cases become almost indistinguishable, suggesting that the slower, neutral mechanism becomes relevant to the overall dissolution rate. This is true in both host rock models.

In conclusion, the host rock models behave similarly in the high and low flux cases. The low flux case results in higher concentrations at the end of the calcite zone in both models. This is attributed to the increase in water residence time, which demonstrates these models are sensitive to flow velocity.

Gallery model

The high flux case brings water into the gallery with lower solute concentrations as the flow velocity is doubled ($ALV = 0.96$ m min⁻¹). As a result, hydrozincite, calcite and smithsonite precipitation rates decrease by approximately 2 orders of magnitude when compared to the reference (Fig. 7A). On the other hand, the low flux case brings water into the gallery with higher solute concentrations as the flow velocity is halved ($ALV = 0.24$ m min⁻¹), resulting in a mineral precipitation rate increase of 40 times. In the context of mineral rates, the low flux and reference cases show similar patterns (the rate of hydrozincite > calcite > smithsonite, whereas in the high flux case, smithsonite precipitation is faster than that of calcite (Fig. 7B).

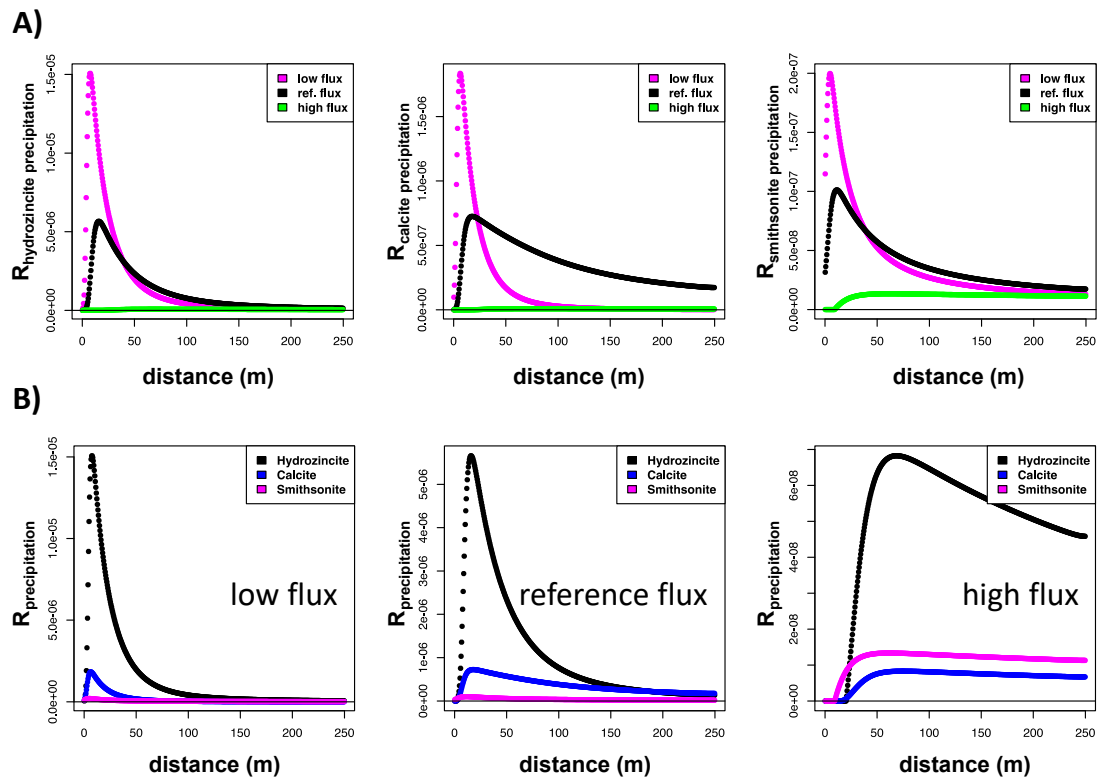


FIGURE 7. Variation in mineral precipitation rates ($R_{\text{mineral-precipitation}}$ in $\text{mol m}^{-3} \text{s}^{-1}$) from the 2D gallery model informed by the low and high flux host rock cases. Rates are plotted as function of distance at $t = 5$ d. Flow goes from left to right. The ALV are 0.24, 0.48, and 0.96 m min^{-1} for the low, ref., and high flux cases, respectively.

Moreover, the high and low flux cases result in changes to the relative mineral precipitation rates. For instance, in the high flux case, smithsonite and calcite make up a larger proportion of the total mineral precipitation (*i.e.* total rate = rate of hydrozincite + rate of smithsonite + rate of calcite). In contrast, in the low flux case, calcite and smithsonite barely contribute to the total mineral precipitation in the gallery. This suggests that the mineral composition of a theoretical solid forming in the gallery would change with water flux through the system. Specifically, as discharge increases, so does mineral heterogeneity, as more smithsonite and calcite would be expected to form with respect to hydrozincite. Congruently, as discharge decreases, the theoretical solid would contain less calcite and smithsonite, resulting in a more homogenous hydrozincite solid.

In the low flux case, mineral rates stabilize around 150 m, while in the reference case, mineral stabilize at the end of the domain (250 m). The high flux case does not show mineral rate stabilization within the domain (Fig. 7). These patterns are primarily due to the ALV, such that faster flowing water does not allow time for the minerals to reach equilibrium with respect to the fluid.

All measured concentrations of sulfate are matched by changing the flow velocity (Fig. 8). Specifically, the post-100 m data points fall between the high flux and reference cases, while the pre-100 m data points fall between the reference and the high flux cases. All measured calcium concentrations are captured by the high flux and reference cases. Further, several measured zinc concentrations are reproduced by the high flux case that were not reproduced by the reference case. In general, the high flux case more accurately reproduces zinc, sulfate and calcium measurements (Fig. 8).

The low flux case shows a lower pH than the reference and high flux case, which are similar (Fig. 8). The excess zinc in the low-flux case promotes hydrozincite precipitation, which consumes more bicarbonate (Table 4). The flattening of the zinc and bicarbonate curves reflects the fluid approaching equilibrium with respect to hydrozincite (saturation indexes in Fig. 8).

Sensitivity to hydrozincite solubility

Two distinct $\log K_{\text{eq}}$ values for hydrozincite at 7°C are applied to the gallery model and compared to the reference case. No other parameters are altered. The first is the experimentally

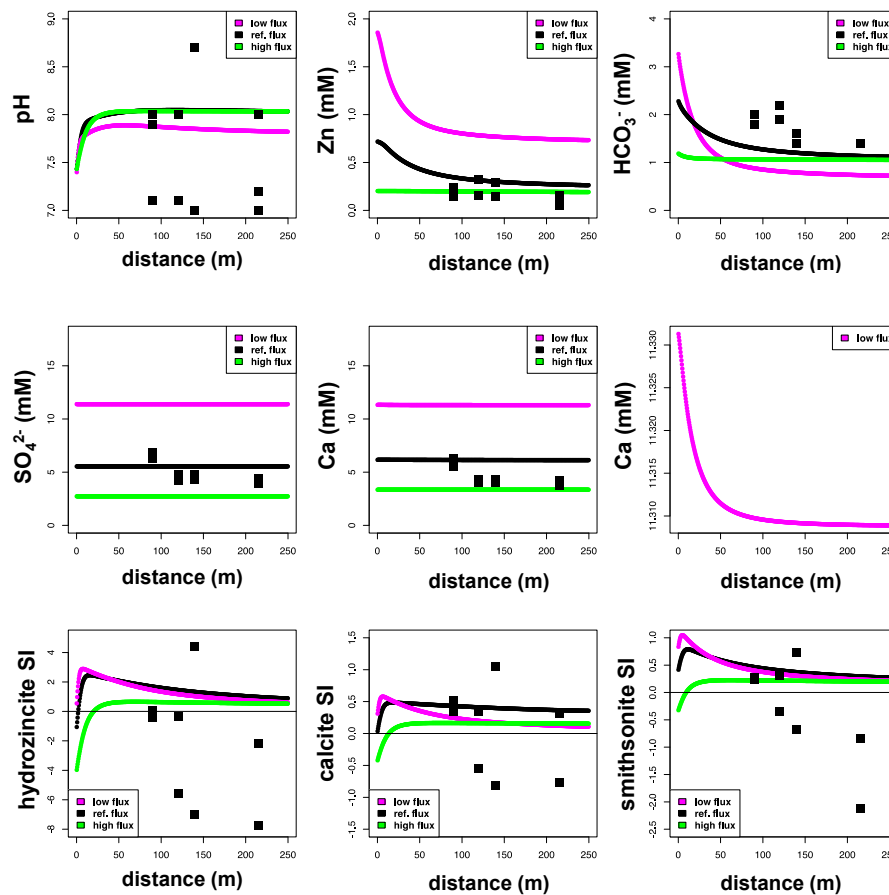


FIGURE 8. Variation in pH and elemental concentrations calculated in the 2D gallery model informed by the low and high flux host rock cases. Results are plotted as function of distance at $t = 5$ d. Flow goes from left to right. The ALV are 0.24, 0.48, and 0.96 m min^{-1} for the low, ref., and high flux cases, respectively. The data from all sampling campaigns are shown with black square markers.

determined value ($\log K_{\text{eq}} = 30.01$). The second is the value calculated under the assumption that the water at the sample 5 location was in equilibrium with hydrozincite ($\log K_{\text{eq}} = 35.53$).

The K_{eq} for hydrozincite is calculated according to $[K_{\text{eq}} = (a_{\text{Zn}^{++}})^5 \cdot (a_{\text{HCO}_3^-})^2 / (a_{\text{H}^+})^8]$, meaning that decreasing the $\log K_{\text{eq}}$ value decreases solubility. In the reference case ($\log K_{\text{eq}} = 37.68$), hydrozincite is the most soluble, while it is least soluble using the experimentally determined value ($\log K_{\text{eq}} = 30.01$). Two model behaviors are expected based on this observation. First, as solubility decreases, the rate of precipitation increases under the local equilibrium assumption, given that the initial concentrations remain constant (Eqs. III; IV). Second, zinc and bicarbonate would approach lower concentrations as the water approaches equilibrium with respect to hydrozincite.

The rate of hydrozincite precipitation doubles when the experimental $\log K_{\text{eq}}$ is applied (Fig. 9A). This drives the bicarbonate to $\sim 0.75 \text{ mM}$ and zinc to below 0.1 mM before 150 m down the gallery (Fig. 9B), where hydrozincite precipitation slows to effectively zero. The consumption of

bicarbonate to this concentration effectively inhibits calcite and smithsonite precipitation. This can be more clearly seen in Figure 9C: as the solubility of hydrozincite decreases, the calcite and smithsonite precipitation becomes less important. Calcium and sulfate concentrations remain approximately the same as in the reference case (not shown). There is, however, a small decrease in calcium due to calcite precipitation.

Most importantly, this analysis demonstrates that as hydrozincite solubility decreases, calcite and smithsonite precipitation becomes less relevant. In other words, hydrozincite precipitation increasingly dominates geochemistry of the gallery as its solubility decreases. Given this, the use of the experimental $\log K_{\text{eq}}$ value effectively shuts-off calcite and smithsonite precipitation.

Sensitivity to dispersivity

The changes to the gallery reference case based on a variation in dispersivity (0.25 m , 2.5 m , 25 m) produce two new sets of results (Fig. VI). The results of these parameter changes

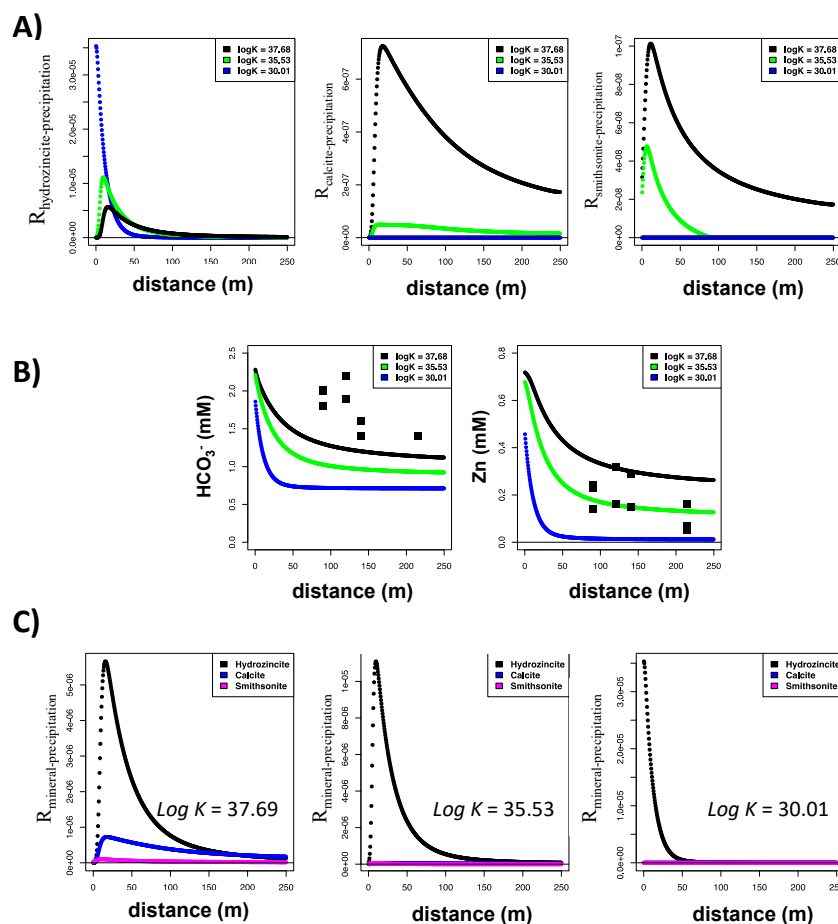


FIGURE 9. Results of the variable K_{eq} of hydrozincite cases in the 2D gallery model plotted with distance at $t = 5$ d: A) precipitation rate of carbonate minerals; B) bicarbonate and zinc concentration and C) comparison between precipitation rates. Flow goes from left to right at an ALV of 0.48 m min^{-1} . Bicarbonate and zinc concentration data (black square markers) is from all sampling campaigns. Mineral precipitation rates ($R_{\text{mineral-precipitation}}$) in $\text{mol m}^{-3} \text{ s}^{-1}$.

show that concentration, solubility, and reaction rate curves tend to flatten across the domain in all the cases. This demonstrates that dispersivity is a relatively insensitive parameter, such that no significant change to solute concentrations is observed (only small changes in the first 30 m).

Effect of assuming a homogeneous rock model

A new host rock model case is constructed by creating a homogeneous mixture of calcite, sphalerite and pyrite. This refers to the reactive solids from the beginning of the sulfide zone to the end of the calcite zone (31.5 m; Fig. 2), such that the total mineral volumes and reactive surface areas from the reference case are maintained. This creates a new homogeneous case result in the HRM (Fig. 10), and a homogeneous case result in the LRM (Fig. VII).

The dominant effect of the homogeneously distributed minerals is the slower mineral dissolution rates, namely sphalerite. The reduced reaction rates result in lower solute

concentrations once the water enters the gallery zone. This is shown by the pH plots in both host rock models (Figs. 10; VII), where the lowest pH values are much higher than in the reference case, and both reach a constant value.

The pyrite rate is not affected as much at the sphalerite rate because pyrite's fastest reaction mechanism in the model is oxidative dissolution. This process is particularly evident in the pyrite rate plot (Fig. 10). As water reaches the saturated zone, no oxygen source is present causing pO_2 to fall to zero due pyrite dissolution, which shuts down pyrite dissolution.

On the other hand, the overall sphalerite rate is much slower because the acidic (pH dependent) mechanism dominates the sphalerite dissolution (Table 3). The cause of this discrepancy in the sulfide-mineral rates is simultaneous calcite dissolution. The dissolution of calcite causes a fast increase in pH, which affects mostly sphalerite dissolution (pH dependent). Pyrite dissolution depends more strongly on $O_{2(aq)}$ and is not affected as much.

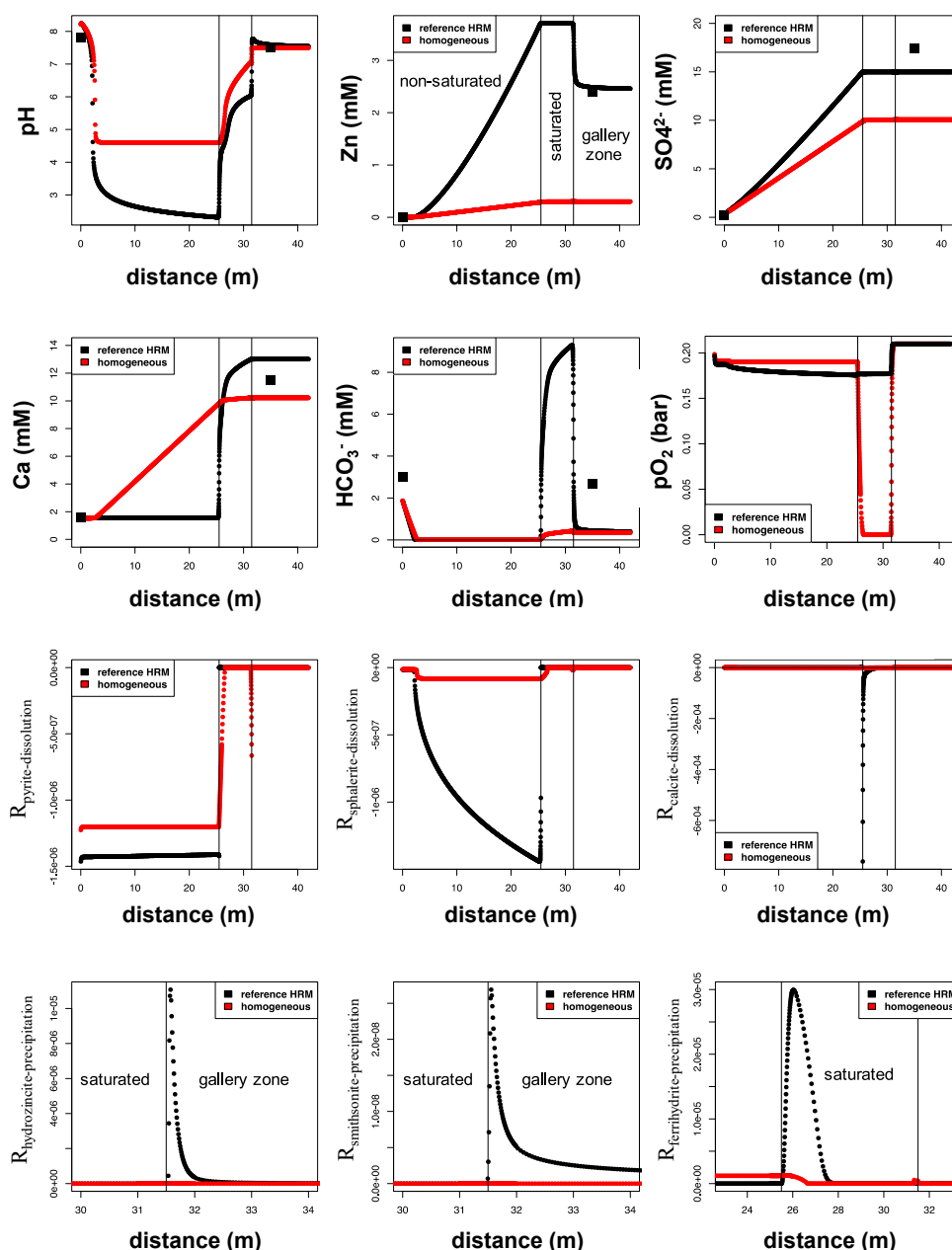


FIGURE 10. CrunchFlow simulation results in the HRM comparing the homogeneous host rock case and the layered host rock (reference) case. Results are plotted as a function of distance at $t = 60$ d. Flow goes from left to right ($ALV = 1.5 \text{ m d}^{-1}$). The vertical black lines represent zones of saturated and non-saturated conditions rather than mineralogical composition since this model is mineralogically homogeneous. The gallery zone remains as an effectively non-saturated zone (flowing water is in contact with the atmosphere). The plots for calcite, hydrozincite, smithsonite and CO_2 degassing rates have been scaled on the x-axis to more clearly visualize the model behavior. These five rates remain at zero outside of the visible range, except for smithsonite, which is slightly above zero ($\approx 5.0 \cdot 10^{-9} \text{ mol m}^{-3} \text{ s}^{-1}$) in the reference model. The ferrihydrite precipitation rate is $1.2 \cdot 10^{-6} \text{ mol m}^{-3} \text{ s}^{-1}$ from 0 m to 27 m and then drops to zero. Mineral dissolution ($R_{\text{mineral-dissolution}}$) and mineral precipitation rates ($R_{\text{mineral-precipitation}}$) in $\text{mol m}^{-3} \text{ s}^{-1}$.

Hydrozincite, smithsonite, and calcite do not precipitate in the gallery zone as a result of the low bicarbonate and zinc concentrations in the water (Fig. 10). Therefore, using a homogeneous mineral distribution does not reproduce the behavior seen in the Victoria Mine. This implies that the real flow path likely contains layers of rock, similar to those applied in the host rock reference case.

Effect of flow velocity and discharge on solute mass fluxes

Under the assumption that the gallery model reference case exhibits a discharge of 15.9 L min^{-1} (see section Solute mass flux and discharge), the concentrations at the end of the domain (250 m) are used to calculate

TABLE 7. Solute mass fluxes (mol d⁻¹) leaving the gallery model for seven different simulations.

Discharge (L min ⁻¹)	15.9	7.95	31.8	15.9	15.9	15.9	15.9
Model case	reference	low flux	high flux	Log <i>K</i> = 30	Log <i>K</i> = 35	high disp.	low disp.
Zinc	6.0	8.4	8.8	0.5	2.9	6.8	5.9
Bicarbonate	25.7	8.3	48.2	16.7	21.1	27.0	25.4
Calcium	140.5	129.5	153.6	141.1	141.1	140.4	140.5
Sulfate	127.0	130.5	125.0	127.0	127.0	127.0	127.0

solute mass fluxes (Table 7). Further, the volumetric discharge and mass fluxes of zinc, calcium and sulfate measured in the field over three years are compared to the results of the model (Fig. 11). It should be noted that these flux versus discharge relationships predicted by the model are qualitative, and associated with a high degree of uncertainty.

Zinc mass flux does not show a strong correlation with discharge when considering the high and low flux cases. The reference model discharge shows the lowest zinc flux, while the high and low flux cases show higher zinc fluxes (Table 7). Zinc flux is not highly dependent on flow rate in the model. This does not capture entirely the natural behavior from the mine, which shows an increase of zinc with discharge (Fig. 11). However model zinc fluxes are similar to the measured values.

The bicarbonate mass flux and discharge relationship from both model and measurements show a similar trend and similar slopes of the lines (Fig. 11), indicating that the model captures the overall behavior of the Victoria Mine. Note that only mass flux data from 2020 and 2021 are available. Calcium mass flux increases with increasing discharge in both the model and at the Victoria Mine (Fig. 11). The calcium fluxes produced by the model are similar to those produced by the mine at the lower range of discharge. However, at the mine, more calcium leaves the mine per unit increase in discharge. Sulfate mass flux from the model is significantly higher than what is observed at the Victoria Mine; approximately 100 mol d⁻¹ more. Further, the sulfate flux tends to decrease slightly with increasing discharge in the model, while the opposite is true at the mine. Notably, sulfate is conserved through the gallery model, and its concentration is a result only of the pyrite dissolution in the host rock models. In contrast, zinc, calcium, and bicarbonate are involved in mineral reactions through the gallery model. In general, the model does not capture the sulfate flux or discharge relationships.

CONCLUSIONS

Simple one-dimensional reactive transport modeling has proved useful to simulate the geochemical processes at the Victoria Mine system and provide a conceptual basis for the formation of the secondary minerals observed in the investigated mine gallery. Zinc was used to make interpretations towards metal mobility, as trace metal mobility is directly linked with hydrozincite precipitation, the dominant metal attenuating mineral in the Victoria Mine.

Given the limited accuracy of the boundary conditions, detailed mineralogical distribution and associated mineral reactivity, and information regarding the water residence time and volumetric discharge (*i.e.*, a model that is not particularly well-constrained), the conceptual framework and sensitivity analyses of these parameter values serve to help understand and quantify the geochemical processes that affect both mineral precipitation and metal mobility.

Regarding the host rock, the model demonstrates that a homogeneous mineral distribution cannot reproduce the solute concentrations measured as input of the gallery. As for the gallery itself, simulations highlight the relevant aspects concerning metal attenuation via precipitation: (i) The more concentrated/toxic water serves to increase the saturation state of the water with respect to hydrozincite. (ii) Calcite and smithsonite precipitate alongside hydrozincite due to CO₂ degassing as the water enters the gallery. (iii) The precipitation rates indicate that, although composed mostly of hydrozincite, a theoretical solid would contain some smithsonite and calcite. (iv) As flow velocity increases, so does the overall proportion of calcite and smithsonite in the solid with respect to hydrozincite, which explains some of the heterogeneity observed in the hydrozincite samples. (v) In the case of apparent changes in hydrozincite solubility due to impurities, any solubility below that calculated using gallery water would produce a theoretical solid that would be almost completely hydrozincite. A change in the hydrodynamic dispersivity would not induce significant changes to the theoretical solid.

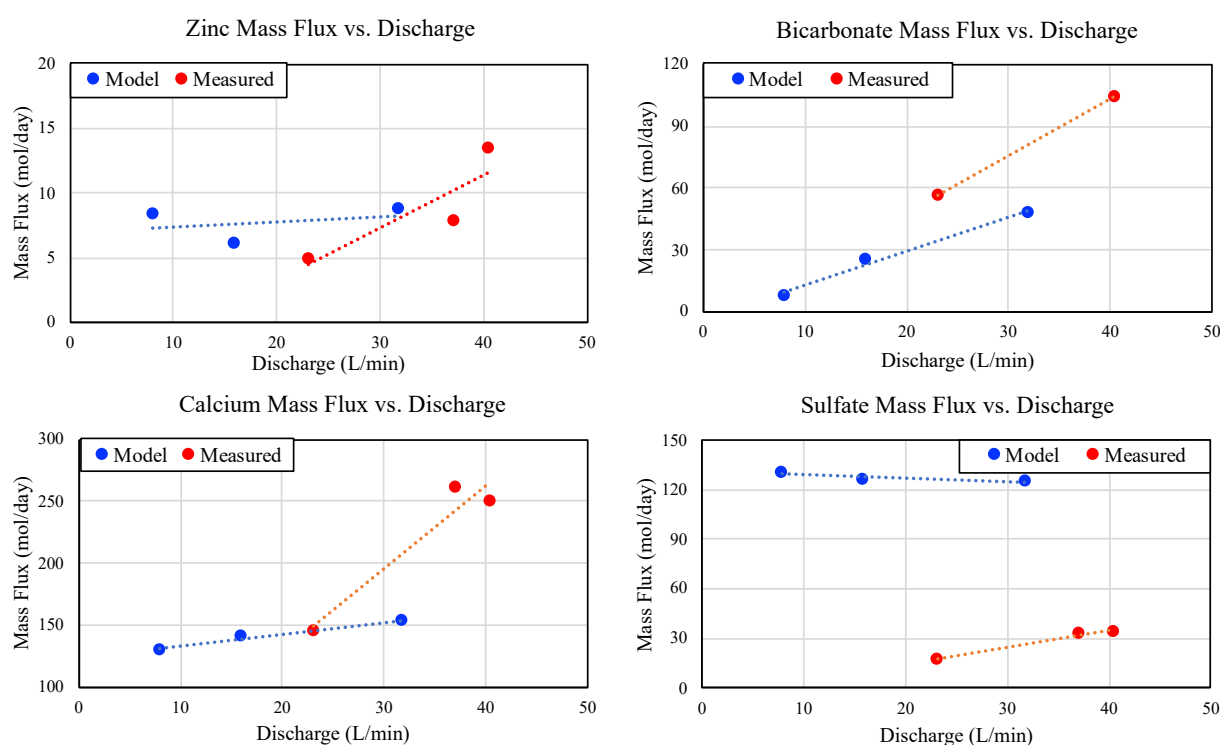


FIGURE 11. Flux-discharge relationships plotted from measurements (red) and model (blue) for zinc, bicarbonate, calcium, and sulfate. Concentrations at 250 m in the gallery model were used in these calculations. The measured values are reported in [Giannetta et al. \(2023\)](#).

The model also indicates that (vi) gypsum is highly undersaturated and therefore would not form, which corroborates the lack of Ca-bearing sulfates and (vii) that there are specific flow velocities that increase and decrease metal fluxes out of the mine. However, as this last conclusion is based on three simulations, a more extensive modeling study of flow velocities could lead to a better understanding of a relationship between discharge and mass flux through the Victoria Mine system.

To improve the modeling, further research should focus on to understanding the conditions that may perturb hydrozincite solubility, which varies based on the environment where it precipitates, and controls metal mobility. Additional sampling of the mine, characterization of the host rock, volumetric flux measurements inside the mine, and experimental work to determine the kinetic values associated with hydrozincite and smithsonite formation (and dissolution) would serve to enhance the accuracy of the study.

Model simulations of the system's response capture the behavior of metal mobility and the associated

environmental impact, indicating that the Victoria Mine poses little threat to the environment. Moreover, it is predicted to continue behaving in such a manner via secondary precipitation of hydrozincite. Such findings could be applied to other abandoned and active mining sites exhibiting similar characteristics as well as to investigate the effect of an aridification trend due to climate change on the precipitation of calcite and smithsonite alongside hydrozincite.

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APPENDIX I

Description of the RTM model

The CrunchFlow code (Steeff et al., 2015) was used for the reactive transport simulations. The code solves the advection-dispersion-reaction equations, which are based

$$\frac{\partial}{\partial t}(\phi C_j) = \nabla(D \nabla C_j) - \nabla(q C_j) + R_j \quad (\text{Eq. I})$$

$$(j = 1, 2, \dots, N_{\text{tot}})$$

on the conservation of solute mass and take the form

where C_j is the concentration of a primary species j in solution (mol m^{-3}), q is the Darcy velocity ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$), D is the combined dispersion-diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), R_j is the total reaction rate ($\text{mol m}^{-3} \text{rock/time}$) affecting component j , t is time, N_{tot} is the total number of primary species, and ϕ is porosity.

In the present simulations, the rate laws used for a mineral reaction take the following form

$$R_m = A_m \sum k_{25} \exp\left[\frac{E_a}{R} \left(\frac{1}{T_{25}} - \frac{1}{T}\right)\right] \left(\prod_i a_i^{n_i}\right) f_m(\Delta G) \quad (\text{Eq. II})$$

where R_m is the reaction rate ($\text{mol m}^{-3} \text{rock s}^{-1}$) for a given mineral m , A_m is the surface area of the mineral ($\text{m}^2 \text{m}^{-3} \text{rock}$), k_{25} is the reaction rate constant ($\text{mol m}^{-2} \text{s}^{-1}$) at 25 °C, $\prod_i a_i^{n_i}$ describes the effect of any species i on the overall rate (i.e. inhibition or catalysis), R is the gas constant ($8.3144 \text{ J mol}^{-1} \text{K}^{-1}$), E_a is the activation energy (J mol^{-1}), T is temperature (K), and $f_m(\Delta G)$ is a

function that describes the dependence of the rate on the solution saturation state with respect to that mineral. The summation term indicates that R_m may depend on other parallel rate laws for the reaction. For example, R_m can depend on the pH and/or the $\text{O}_{2(\text{aq})}$ concentration. The function $f_m(\Delta G)$ is described as

$$f_m(\Delta G) = [1 - \exp(m_2 g^{m_3})]^{m_1} \quad (\text{Eq. III})$$

where

$$g = \frac{\Delta G}{RT} = \ln \frac{\text{IAP}}{K_{\text{eq}}} \quad (\text{Eq. IV})$$

and ΔG is the Gibbs energy of the reaction (J mol^{-1}), IAP is the ion activity product of the solution with respect to the mineral and K_{eq} is the equilibrium constant for that mineral reaction. Eq. (4) serves to calculate the saturation index ($\text{SI} = \log[\text{IAP}/K_{\text{eq}}]$) of the mineral depending on the IAP. The parameters m_1 , m_2 and m_3 define the shape of the $f_m(\Delta G)$ function and are determined empirically through experiments. Otherwise, they are assumed to be 1 (Lasaga, 1998).

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APPENDIX II

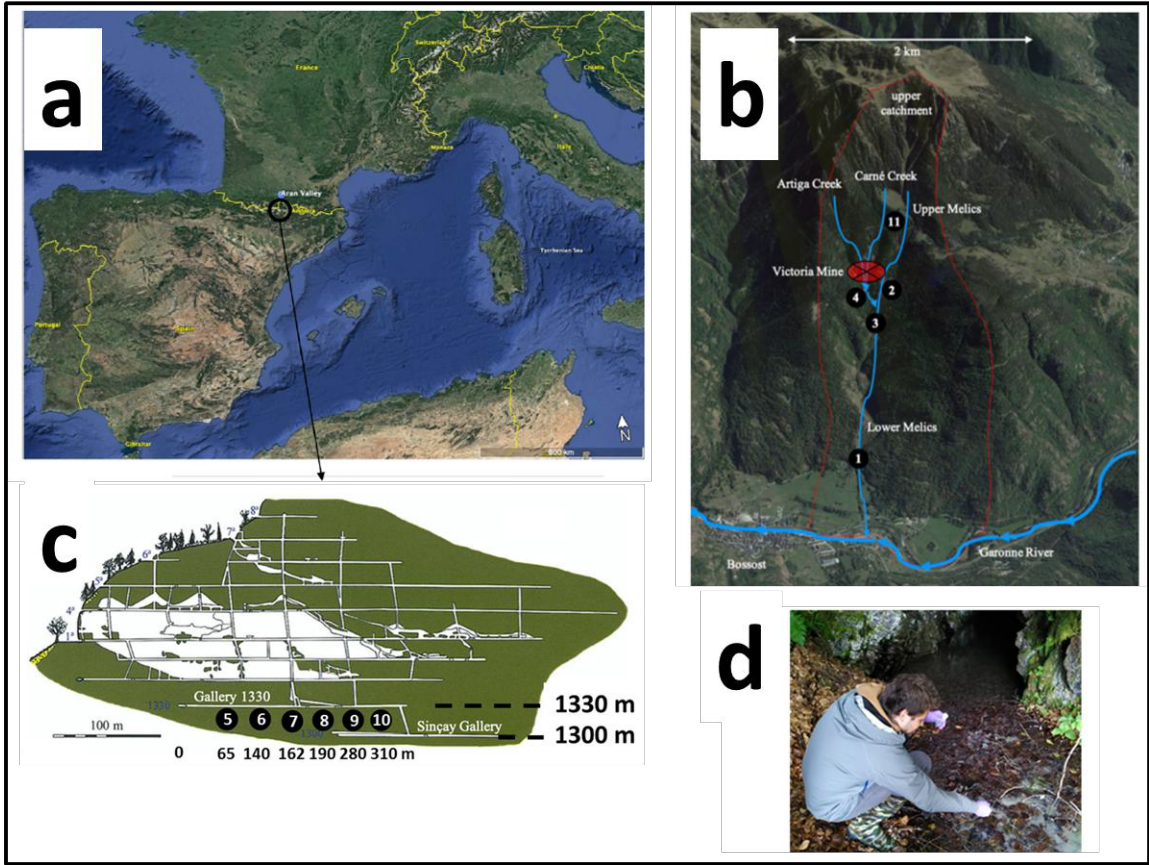


FIGURE I. Victoria Mine: A) A Google Earth image showing the location of the Aran Valley; B) Google Earth image of the Victoria Mine catchment system with a total area of 3.2 km² and locations of outdoor sampling intervals. Sampling locations (black circle with a number) correspond to Table I. The red line represents the catchment boundaries and the red oval with the “X” is the approximate location of the Victoria Mine. Carné and Melics creeks were sample. However, Artiga Creek was never sampled because it was dry during all three sampling campaigns. Blue arrows represent water and the corresponding flow direction; C) sketch of a cross section of the mine with each sample location (Table I). The second lowest gallery (1330 Gallery), sampled in October 2019, July 2020 and June 2021, resides at an altitude of 1330 m. Figure modified from Santamaria et al. (2008); D) the lowermost gallery (the Sinçay Gallery) exhibits a continuous output of water.

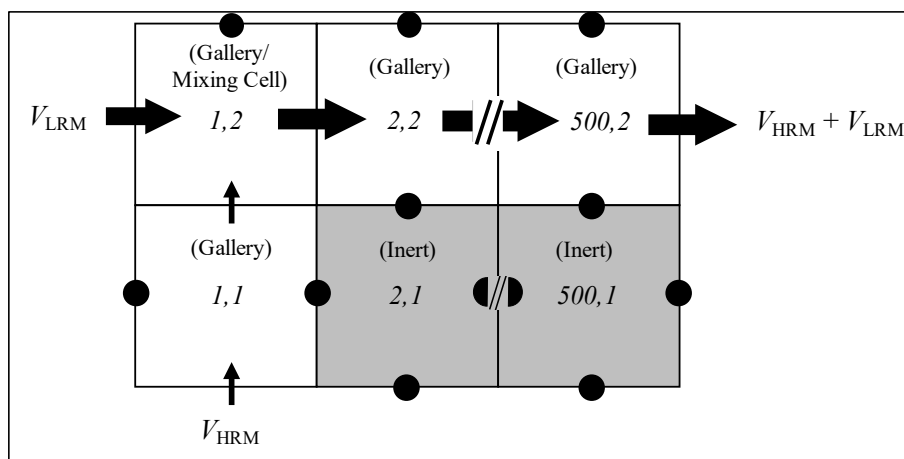


FIGURE II. Sketch of the 2D grid implemented in CrunchFlow to simulate the mixing of the resulting HRM and LRM compositions and subsequent flow down the gallery. The domain consists of 500 x 2 grid cells, each measuring 0.5 m x 0.5 m, resulting in a 250-m flow path. The two rows of 500 cells are stacked, such that y-coordinates are either 1 or 2 (y, 1-2) and x-coordinates are defined as 1 to 500 (1-500). The gallery domain is defined as (2, 1-500), which is effectively a 1D matrix stacked on top of another 1D matrix defined as (1, 1-500). The gallery domain (2, 2-500) is composed of an inert mineral resulting in a porosity of 0.38. Hydrozincite, smithsonite and calcite are allowed to react although they are not present at the initiation of the simulation. The underlying ghost domain (1,2-500; grey cells) is composed of an inert mineral with porosity of 0.001 (*i.e.* effectively solid). However, the first cell in the ghost domain (1,1) has a porosity of 0.38, identical to that of the overlying cells, and contains only an inert mineral. This cell serves as HRM water input. Darcy velocities (V), which are represented by arrows with a size that is proportional to the flux, are defined at the border of each grid cell, such that flow can only occur along the gallery (left to right), and up through the 1,1 cell. The sum of the two input Darcy velocities into the mixing cell (1,2) must be equal to the output Darcy velocity for the mixing cell and all subsequent cells as all cells are of the same size (0.5 m x 0.5 m). All transverse flow velocities are set to zero and no flow can be lost to the underlying ghost domain (1,2-500; black circles represent no-flow boundaries). Hence, mass conservation is ensured down the 1D gallery domain. The solute concentrations for each input are informed by the water compositions of the LRM (V_{LRM}) and HRM (V_{HRM}) at the calcite zone-gallery zone interface (31.5m).

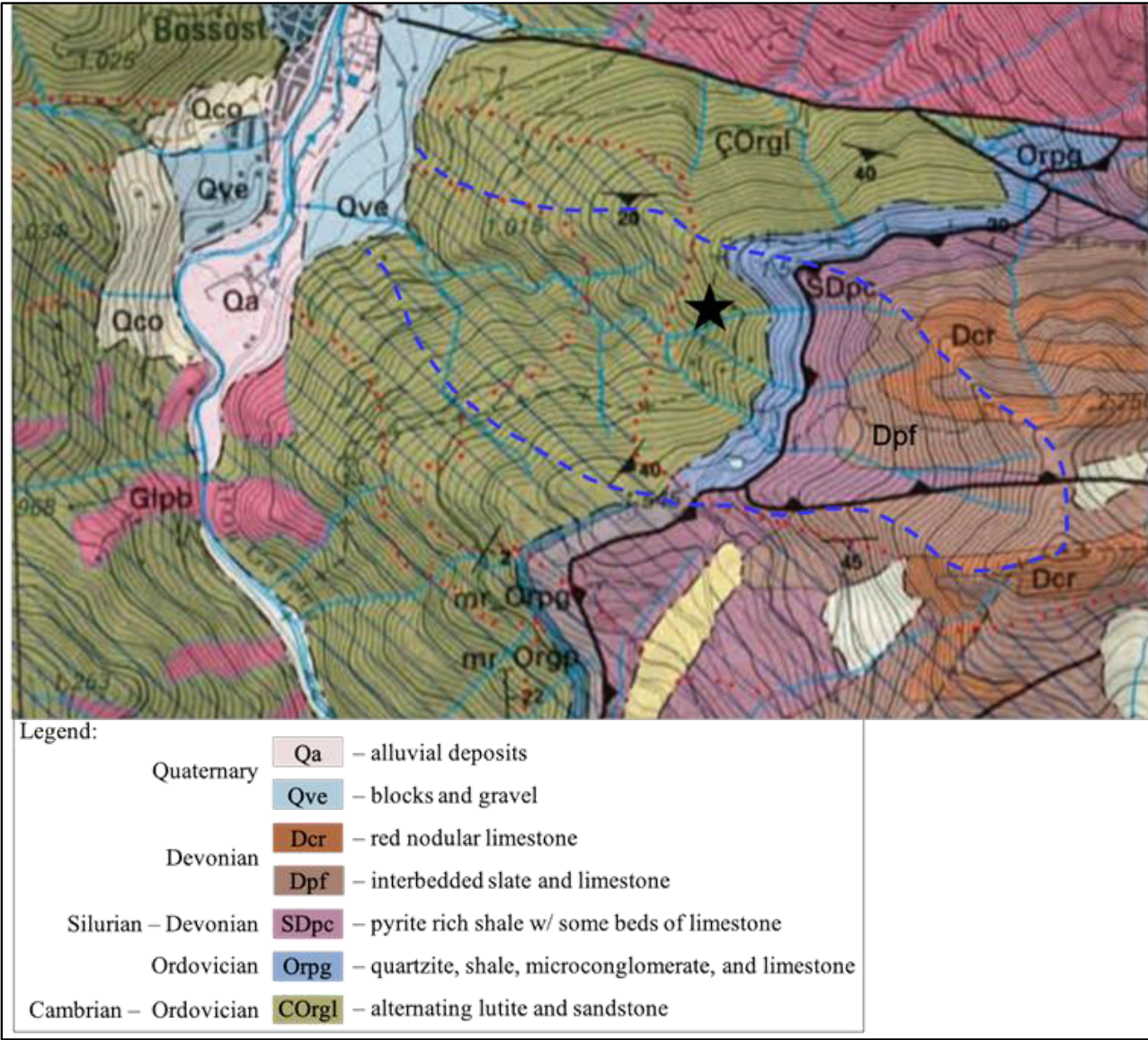
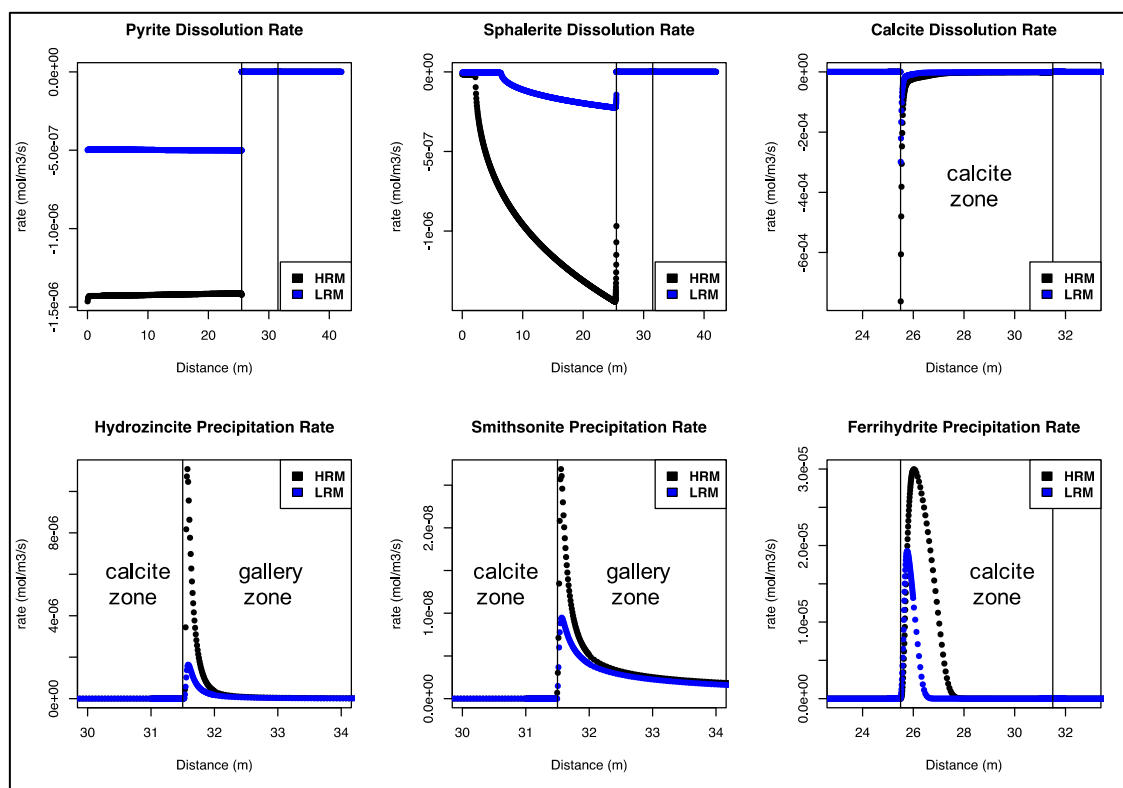


FIGURE III. A cropping of a 1:50,000 geologic map of the Victoria Mine catchment in the Bossost-Arres mining district (Geologic Institute of Catalonia, map # 39). The approximate location of the Victoria Mine is represented by the black star and catchment boundaries have been marked with a blue dotted line. Above the elevation of the mine one can find dark Devonian slates with some interbedded limestone (Dpf), Devonian red nodular limestone (Dcr), black Silurian-Devonian slates rich in pyrite with some interbedded limestone (SDpc), and an Ordovician limestone containing some quartzite, slate, and microconglomerate (Orpg). Below the elevation of the mine there is a rock unit of Cambrian-Ordovician interbedded sandstone and lutite (COrgl).

a)



b)

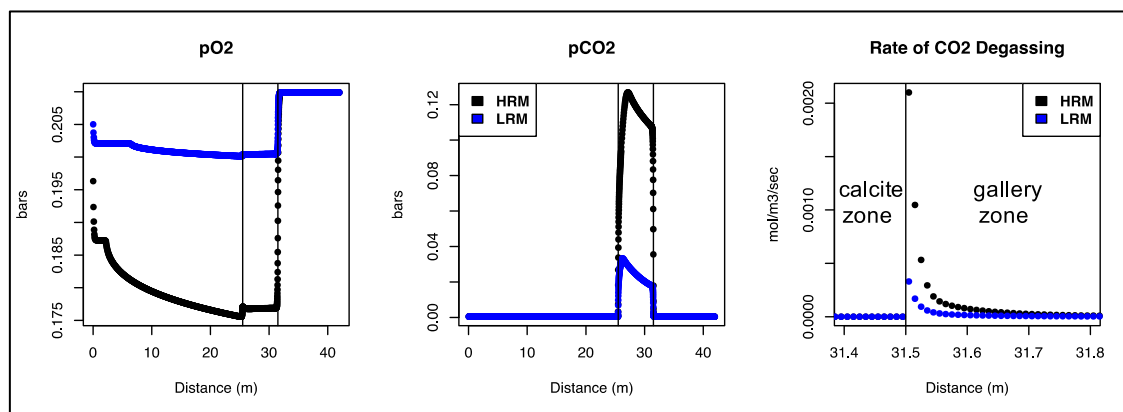


FIGURE IV. Simulations in the host rock reference case: A) calculated dissolution and precipitation mineral rates and B) calculated pO₂, pCO₂ and the rate of CO₂ degassing. Flow goes from left to right (ALV of 1.5 m d⁻¹). Results from HRM and LRM are plotted as a function of distance at t = 60 d (residence time of the system is 30 d). The vertical lines divide the three zones (the non-saturated sulfide zone exists from 0 to 25.5 m, the saturated calcite zone exists from 25.5 m to 31.5 m, and the gallery zone exists from 31.5 m to 41.5 m). The plots for calcite, hydrozincite, smithsonite and CO₂ degassing rates have been scaled on the x-axis to more clearly visualize the model behavior. These five rates remain at zero outside of the visible range.

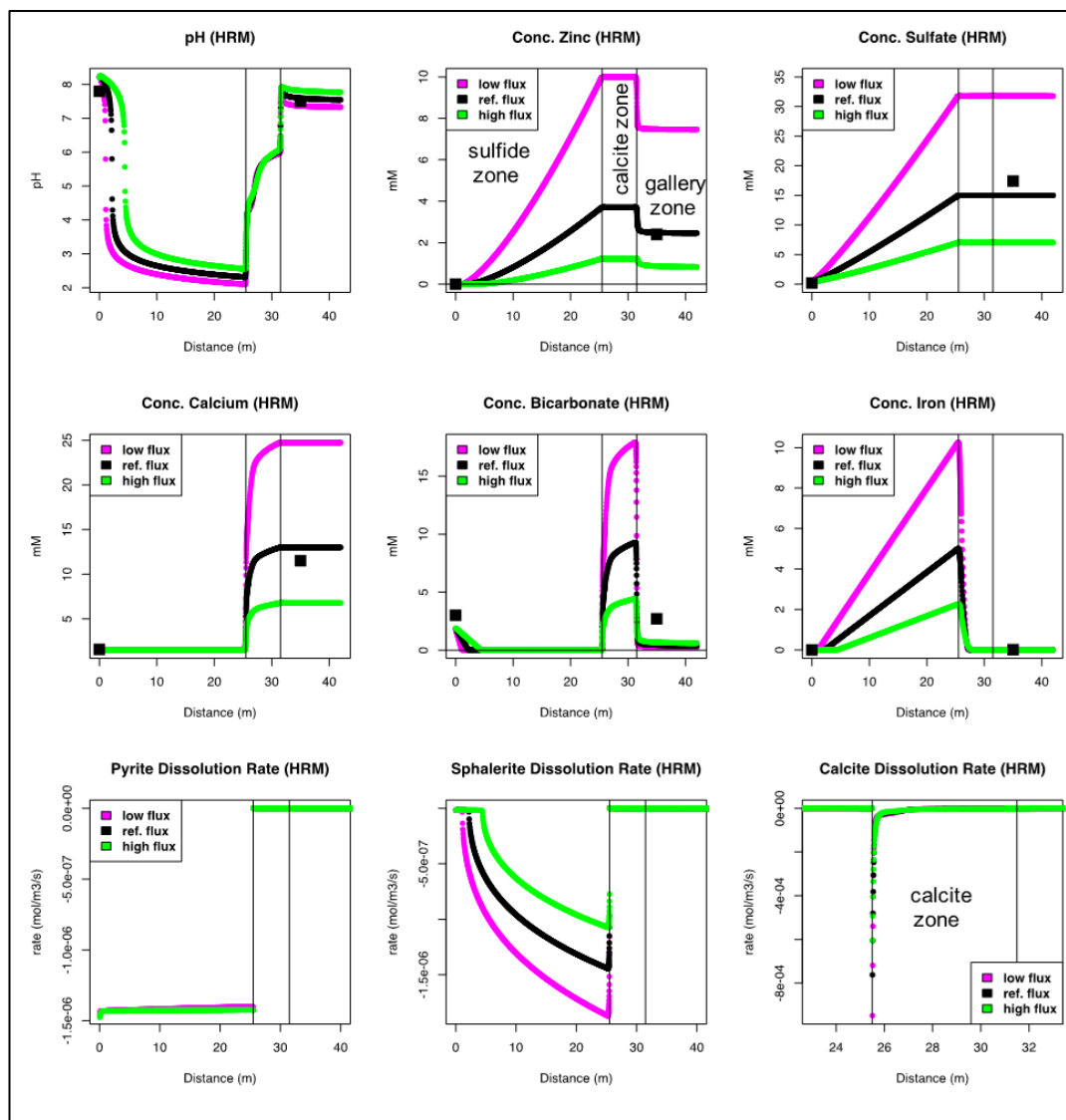


FIGURE V. LRM simulations for the host rock high flux case and low flux case: variation in pH and elemental concentrations and dissolution rates with distance. Flow goes from left to right at 0.75 and 3 m d⁻¹ for the low and high flux case, respectively. The LRM reference case is also plotted and corresponds to the LRM results (blue) in [Figure 3](#) (main text). In the high flux case, results are plotted as function of distance at t = 30 d (residence time = 15 d). The low flux results are plotted as a function of distance at t = 120 d (residence time = 60 d). The sample-11 data are plotted at 0 m and the sample-10 data is plotted at 35 m as black squares.

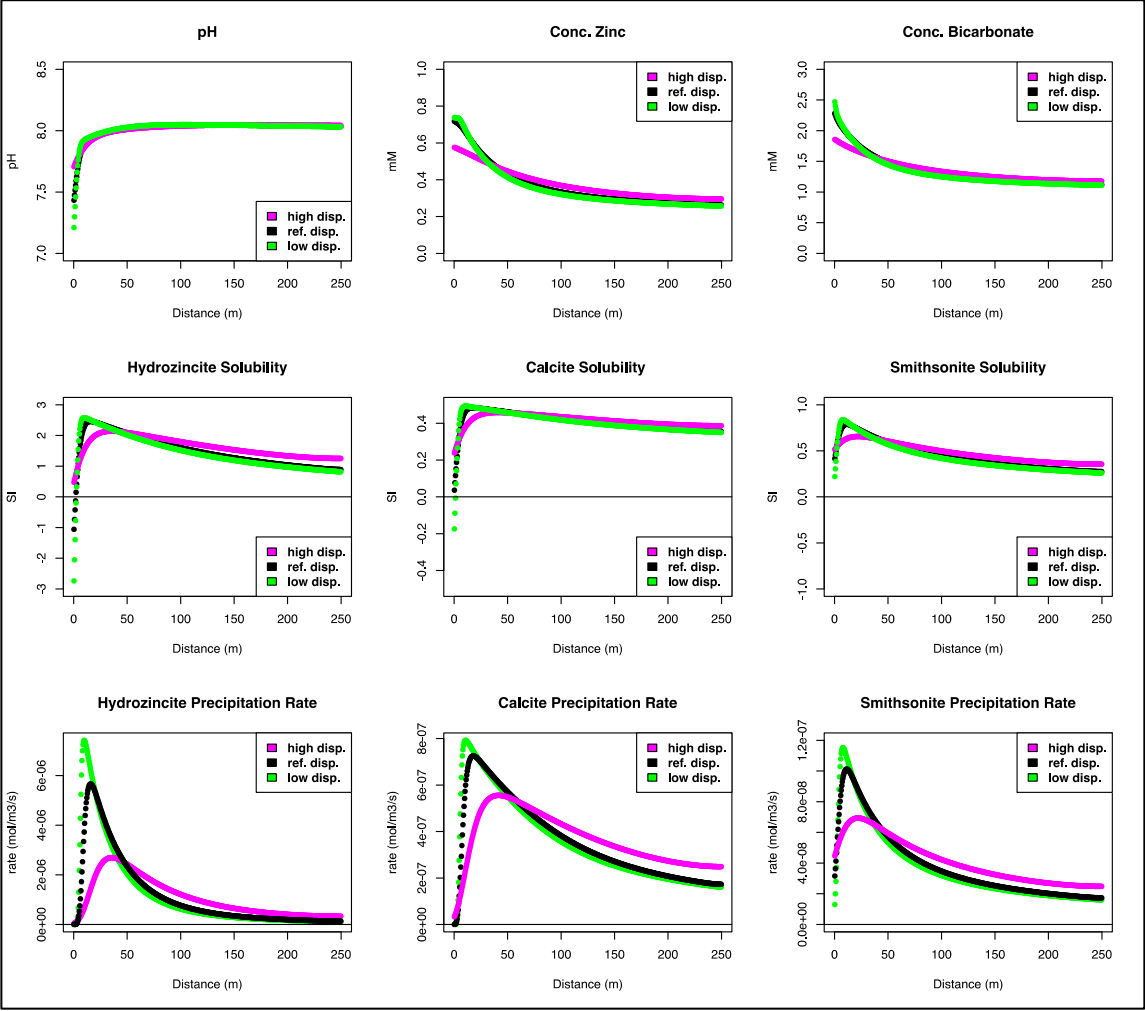


FIGURE VI. The results plotted as a function of distance at $t = 5$ d of three 2D gallery model simulations where only the dispersivity values were changed. Flow goes from left to right ($ALV = 0.48 \text{ m min}^{-1}$). High disp. = dispersivity set to 25 m (10% of the domain length); ref. disp. = dispersivity set to 2.5 m (1% of the domain length) and low disp. = dispersivity set to 0.25 m (0.1% of the domain length).

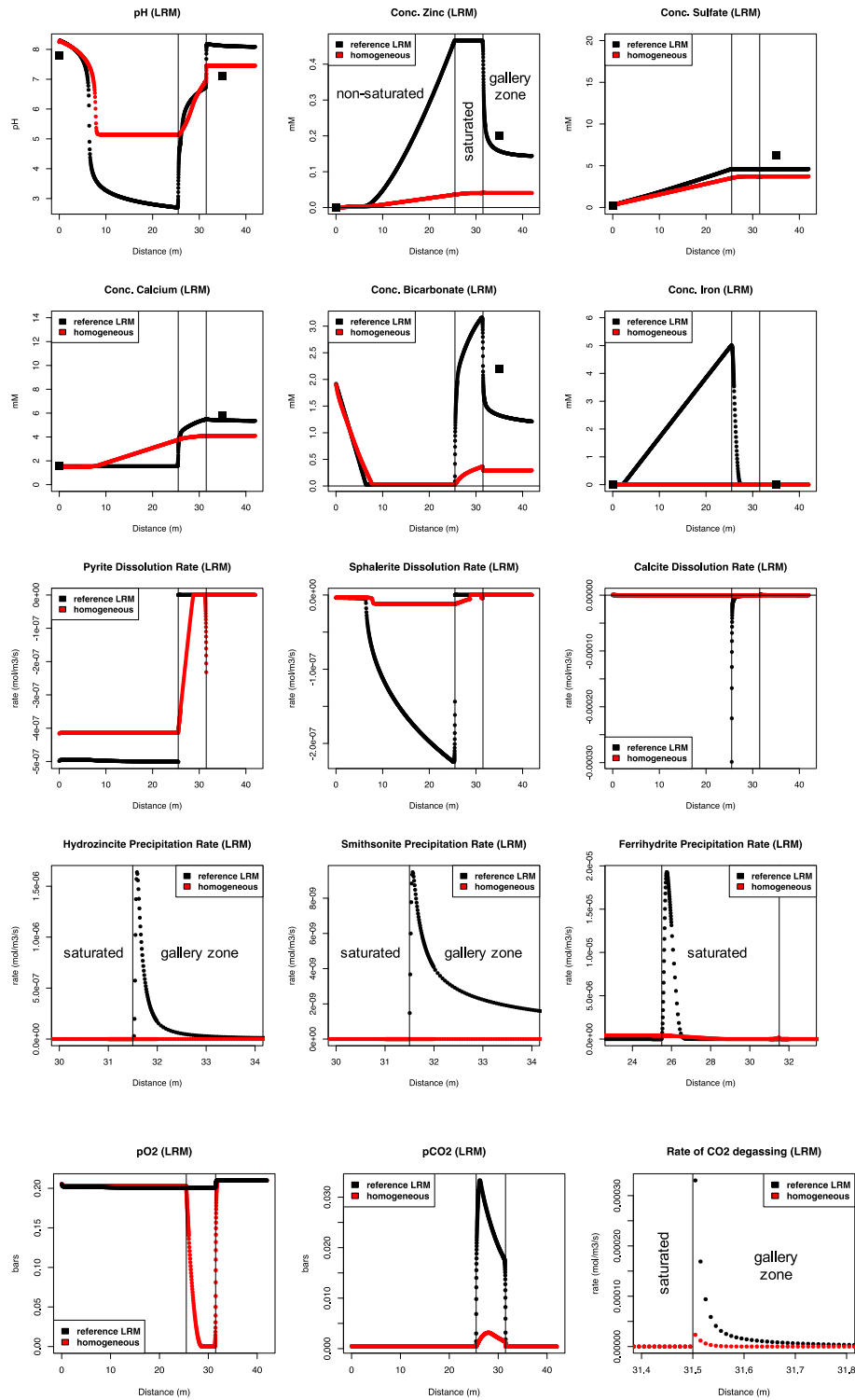


FIGURE VII. CrunchFlow simulation results from the low reactivity host rock model (LRM) comparing the homogeneous host rock case and the layered host rock (reference) case. Results are plotted as a function of distance at $t = 60$ d. The vertical black lines represent zones of saturated and non-saturated conditions rather than mineralogical composition. The gallery zone was not changed in this simulation, such that it is still effectively a non-saturated zone where flowing water is in contact with the atmosphere. The plots for calcite, hydrozincite, smithsonite and CO₂ degassing rates have been scaled on the x-axis to more clearly visualize the model behavior. These five rates remain at zero outside of the visible range, except for smithsonite, which is slightly above zero ($\sim 5.0 \cdot 10^{-9}$ mol m⁻³ s⁻¹) in the reference model. The ferrihydrite precipitation rate is $4.10 \cdot 10^{-7}$ mol m⁻³ s⁻¹ from 0 to 27 m and then drops to zero.

TABLE I. Description of sampling locations that are referred to throughout the text. Samples 1-4 and 11 correspond to outdoor locations (Fig. 1). Samples 5-10 correspond to locations inside the Victoria Mine (Fig. 1). The distance labeled refers to the distance from the entrance of the 1330 Gallery. Sample 11 is an average of both Melics and Carné creeks. Dissolved Organic Carbon (DOC) concentrations from 2020 sampling campaign are listed. Samples were filtered through a 0.22 μm membrane. Analytical error is 0.05 ppm

Sample #	Location description	Additional information	DOC (ppm)
1	Lower Melics Creek	Subsequently flows into Garonne River	1.3
3	Combined Melics and mine effluent + DNA	Mix of samples 2 and 4	0.8
4	Sinçay Gallery effluent	Flux-weighted average of mine output	0.5
5	65 m + drip + DNA	First occurrence of hydrozincite	0.6
6	140 m + drip		0.6
7	162 m	Deep pool of blue water	0.6
8	190 m + drip	First occurrence of red precipitate	0.5
9	280 m + drip	Constant flow and main input into gallery	
10	310 m + DNA	Dark red seepage and pooling (red goo)	0.6
11	Melics and Carné average + DNA	Upper catchement/background water	1.0

TABLE II. The equilibrium constants ($\log K_{eq}$) at 7 °C for the equilibria of 86 secondary species in solution. Reactions are written as the destruction of 1 mole of the species using the following primary species: H^+ , Na^+ , K^+ , Mg^{++} , Fe^{++} , SO_4^{2-} , Ca^{++} , Zn^{++} , Cd^{++} , Sr^{++} , Ni^{++} , $SiO_{2(aq)}$, HCO_3^- , $O_{2(aq)}$

Species	$\log K_{eq}$	Species	$\log K_{eq}$	Species	$\log K_{eq}$
CO ₂ (aq)	-6.49E+00	Cd(OH) ₄ --	4.73E+01	SrCO ₃ (aq)	7.85E+00
CaHCO ₃ +	-1.06E+00	Cd ₂ OH+++	9.39E+00	SrOH+	1.33E+01
CaSO ₄ (aq)	-2.07E+00	CdCO ₃ (aq)	7.33E+00	Zn(OH) ₂ (aq)	1.73E+01
CdHCO ₃ +	-1.50E+00	CdOH+	1.01E+01	Zn(OH) ₃ -	2.88E+01
CdSO ₄ (aq)	-4.03E-03	Fe(OH) ₂ (aq)	2.06E+01	Zn(OH) ₄ --	4.16E+01
FeHCO ₃ +	-2.72E+00	Fe(OH) ₃ -	3.10E+01	ZnCO ₃ (aq)	6.43E+00
FeSO ₄ (aq)	-2.20E+00	Fe(OH) ₄ --	4.60E+01	ZnOH+	9.24E+00
KSO ₄ -	-8.70E-01	FeCO ₃ (aq)	5.60E+00	S ₂ --	2.60E+02
MgHCO ₃ +	-1.05E+00	FeOH+	9.50E+00	S ₂ O ₄ --	1.27E+02
MgSO ₄ (aq)	-2.21E+00	H ₂ SO ₄ (aq)	1.02E+00	S ₂ O ₆ --	5.54E+01
NaHCO ₃ (aq)	-3.09E-01	H ₂ SiO ₄ --	2.30E+01	S ₂ O ₈ --	2.46E+01
NaSO ₄ -	-8.20E-01	H ₄ (H ₂ SiO ₄) ₄ -	3.59E+01	S ₃ O ₆ --	1.57E+02
NiSO ₄ (aq)	-2.11E+00	H ₆ (H ₂ SiO ₄) ₄ -	1.36E+01	S ₄ O ₆ --	2.42E+02
SrSO ₄ (aq)	-2.30E+00	HO ₂ -	2.98E+01	Fe(OH) ₂ +	-3.90E+00
ZnHCO ₃ +	1.28E+00	HS ₂ O ₃ -	1.32E+02	Fe(OH) ₃ (aq)	2.43E+00
ZnSO ₄ (aq)	-2.16E+00	HSO ₄ -	-1.78E+00	Fe(OH) ₄ -	1.20E+01
HS-	1.48E+02	HSiO ₃ -	1.02E+01	Fe(SO ₄) ₂ -	-1.28E+01
S ₂ O ₃ --	1.43E+02	KHSO ₄ (aq)	-5.23E-01	Fe ₂ (OH) ₂ ++++	-1.62E+01
CO(aq)	4.48E+01	KOH(aq)	1.45E+01	Fe ₃ (OH) ₄ (5+)	-2.24E+01
Fe+++	-9.57E+00	Mg ₄ (OH) ₄ ++++	3.98E+01	FeCO ₃ +	-9.55E+00
H ₂ (aq)	4.92E+01	MgCO ₃ (aq)	7.63E+00	FeOH++	-7.38E+00
HSO ₅ -	1.88E+01	NaCO ₃ -	9.80E+00	FeSO ₄ +	-1.12E+01
SO ₃ --	4.96E+01	NaHSiO ₃ (aq)	8.39E+00	H ₂ S(aq)	1.41E+02
CO ₃ --	1.05E+01	NaOH(aq)	1.54E+01	H ₂ SO ₃ (aq)	4.04E+01
CaCO ₃ (aq)	7.35E+00	Ni(OH) ₂ (aq)	2.00E+01	HSO ₃ -	4.25E+01
CaOH+	1.29E+01	Ni(OH) ₃ -	3.10E+01	S--	1.62E+02
Cd(CO ₃) ₂ --	1.43E+01	Ni ₂ OH+++	1.07E+01	S ₂ O ₅ --	8.98E+01
Cd(OH) ₂ (aq)	2.03E+01	Ni ₄ (OH) ₄ ++++	2.77E+01	SO ₂ (aq)	4.08E+01
Cd(OH) ₃ -	3.33E+01	OH-	1.46E+01		