

MODELING COPPER MOBILIZATION FROM LOW-GRADE ORE CONTROLLED BY MINERAL SURFACE REACTIONS

Ralf R. Haese , Apoorv Jyoti 

School of Geography, Earth and Atmospheric Sciences, The University of Melbourne, Parkville, Victoria 3010, Australia

Correspondence to:

Ralf R. Haese,
ralf.haese@unimelb.edu.au

How to Cite:

Haese, R. R. ., & Jyoti, A.
(2026). Modelling copper mobilization from low-grade ore controlled by mineral surface reactions. *InterPore Journal*, IPJ150526-3.
<https://doi.org/10.69631/q237yd92>

RECEIVED: 12 Sept. 2025

ACCEPTED: 21 Feb. 2026

AVAILABLE ONLINE: 18 Mar. 2026 (accepted version)

VERSION OF RECORD: 15 May 2026

ABSTRACT

Many metals of economic value are commonly recovered from low grade ores through heap leaching at mine sites. The recovery of metals in heaps is often limited for multiple reasons including mineral overgrowth of targeted minerals resulting in suboptimal mineral dissolution rates. Chalcopyrite is a major copper iron sulfide mineral found in copper sulfide ores and its dissolution is controlled by multiple dissolution reaction mechanisms and potential mineral overgrowth. Traditional continuum scale reactive-transport models, including those applied to simulate heap leaching, do not account for local, mineral surface-controlled processes which may have implications for large-systems such as copper recovery in heaps. A new finite element, multicomponent reactive-transport model was developed and enabled the simulation of concurrent reactions at the discrete chalcopyrite surface and its surrounding gangue mineral and the fluid phase. The model predicts the rate of chalcopyrite dissolution controlled by different reaction mechanisms (proton- and ferric-iron promoted) as well as the rate of secondary mineral formation (jarosite) at the mineral surface. The latter may increasingly inhibit copper mobilization over time through surface passivation. The onset and growth of the surface passivation layer is largely controlled by the surrounding fluid composition and ion transport through the gangue mineral. The reduction in porosity of the surface passivation layer leads to the breakdown of ionic transport to the chalcopyrite surface and associated copper mobilization. Maximum copper recovery is achieved by high ferric iron concentrations and low pH and by preventing the formation of a passivation layer by keeping the sulfate concentration low.

KEYWORDS

Coupled dissolution and reprecipitation, Copper leaching, Pore scale, Reactive-transport model



@2026 The Authors

This is an open access article published by InterPore under the terms of the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License (CC BY-NC-ND 4.0) (<https://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. INTRODUCTION

As the world transitions to a low CO₂ emission economy, the demand for copper has surged to an all-time high level because copper is the most widely used metal in renewable energy technologies including batteries and electric vehicles. The global copper demand is predicted to gradually increase by up to a factor of three by 2050 (10). With increasing copper production, the quality of the copper ore, also referred to as the ore grade, declines (17, 28). Consequently, improving copper recovery from low-grade ore will become increasingly important. Ensuring a sufficient supply of copper is a key concern for the energy transition, as demand is projected to exceed available resources in the second half of this century (36). These predictions highlight the need to increase copper recycling and enhance recovery from low-grade ore.

One process limiting copper recovery from low-grade ore is mineral overgrowth on the surface of the copper-containing mineral, which is often the mineral chalcopyrite (13). The mineral overgrowth is also referred to as passivation or coupled dissolution and reprecipitation (CDR). The widespread occurrence and significance of CDR across a wide range of geological systems, along with its thermodynamic and kinetic constraints, were established in landmark studies by Putnis (31, 32). As explained by Ruiz-Agudo and colleagues (35): *“the dissolution of a mineral by an aqueous solution results in an interfacial fluid film that may become supersaturated with respect to a new mineral phase, and that this phase may nucleate within this interfacial region. The common observation in both nature and experiment that one solid phase can be replaced by another via coupled dissolution–precipitation suggests that this is a universal mechanism of re-equilibration during fluid–mineral interaction.”* A large diversity and complexity of mineral textures (grain size and shape, porosity, thickness of secondary layer) at mineral boundaries was related to the diversity of mechanisms responsible for CDR (1). While observational data from natural rocks are abundant (see (1)) and some experimental studies (e.g., (14, 21)) have been published on CDR, numeric models simulating concurrent dissolution and reprecipitation reactions at mineral surfaces have only been developed in recent years (8, 12, 43).

Heap leaching is a key technology that is used to recover metals from low grade ores. A heap is a large pile of poorly sorted low-grade ore in which a reagent, referred to as a lixiviant, continuously infiltrates and leaches target metals from the rocks. The metal-enriched fluid is collected at the base of the heap. A heap is spatially complex and dynamic in time in terms of the thermal, hydrodynamic and mechanical conditions and the chemical reactions. This makes numerical modeling of such systems challenging, even though heap leaching has been studied mathematically over the past 20 years (4, 7, 23, 24, 27). HEAPSIM is one of the most comprehensive heap models used extensively to simulate a variety of processes in different ores (4, 9). In copper recovery via heap leaching, chalcopyrite (CuFeS₂) is the primary target mineral, and an acid lixiviant—typically with a pH of 1 to 2 and enriched in ferric iron (Fe³⁺)—is used. Oxygen is injected into the heap to keep most of it oxygenated. Proton-promoted and ferric iron promoted dissolution of chalcopyrite are the principal reaction mechanisms for the mobilization of copper (18, 20). The rate of chalcopyrite dissolution is often slow, which is typically due to mineral overgrowth of the chalcopyrite surface (19, 25). Secondary minerals in the form of jarosite (KFe₃(SO₄)₂(OH)₆), covellite (CuS), and hematite (Fe₂O₃) are potential secondary minerals which can form at the chalcopyrite surface.

By combining COMSOL and Phreeqc (29), we obtain iCP, which is a user-friendly reactive transport model that was used to model the coupling of transport and reactions in copper heaps to overcome the lack of specific mineral–water reactions in previous models (38). More recently, iCP was used for reactive-transport modeling at pore scale where, for example, reaction rates are predicted at discrete mineral boundaries (16).

Complementary to the existing models simulating coupled dissolution and precipitation at mineral surfaces and processes in heap systems at continuum scale, iCP was used in this study to develop a multi-component reactive transport model combining continuum and discrete

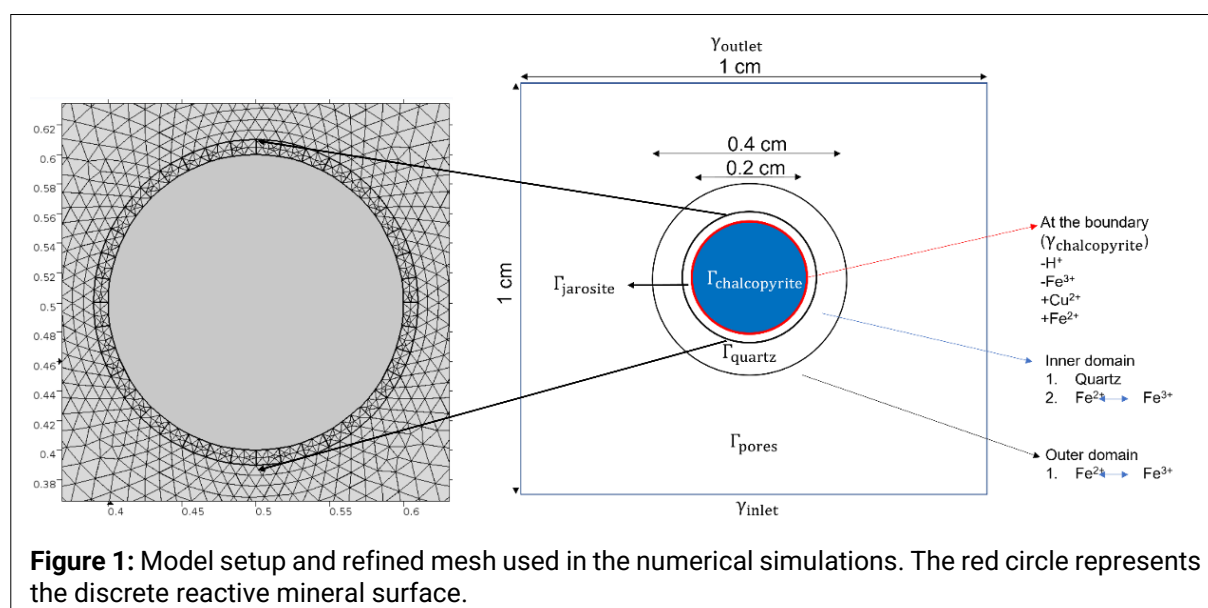
modeling techniques in order to simulate transport and reactions at the surface of a single grain composed of chalcopyrite surrounded by gangue mineral and lixiviant. The model allows the implementation of kinetically controlled dissolution and precipitation reactions at reactive mineral surfaces. A series of simulations with variable parameters (pH, dissolved Fe^{3+} and oxygen concentrations, flow velocity, volume ratio of chalcopyrite-to-gangue mineral) were run to investigate CDR processes at the surface of chalcopyrite and their consequences for copper recovery.

2. MATERIALS AND METHODS

2.1. Conceptual model

A 2-dimensional (2D) model was developed to simulate dissolution reactions at the surface of chalcopyrite, secondary mineral precipitation within a thin layer surrounding the chalcopyrite and a number of reactions in the gangue mineral with microporosity outside of the precipitation layer and in the free fluid. The model combines continuum scale concepts, in which averaged properties such as porosity and permeability are used, with discrete modeling approaches, in which phases are spatially separated, for example in pore networks where fluid-filled pores are spatially separate from grains. The modeling approach is similar to that of Mollins and colleagues (26) and Soulaire (40 and references therein). The model development and its implementation in iCP is an extension of an earlier study by the authors (16) which modelled mineral surface reaction rates and dynamic changes to the grain shape and were validated against experimental results.

At the center of the model is a 2D circular, solid phase chalcopyrite grain ($\Gamma_{\text{chalcopyrite}}$) where no fluid or ionic transport is allowed (Fig. 1). The boundary of the solid chalcopyrite grain is explicitly defined ($\gamma_{\text{chalcopyrite}}$), and chemical reactions are allowed to take place at this boundary. The solid chalcopyrite domain is completely enclosed by a thin layer where jarosite can precipitate (Γ_{jarosite}). Adjacent to the thin precipitation layer is a layer of gangue mineral in the form of quartz (Γ_{quartz}). Figure 1 shows the chalcopyrite and gangue mineral grains with a diameter of 0.2 and 0.4 cm, respectively, resulting in a grain ratio of 1:2. The jarosite precipitation layer and the gangue mineral layer are treated as a porous media, where a porosity and permeability are defined and govern fluid flow and transport. The outer free fluid domain (Γ_{pores}) surrounds the gangue mineral layer. The free fluid enters from the inlet (γ_{inlet}) and exits the model from the outlet (γ_{outlet}) boundary.



2.2. Model set-up

The solid chalcopyrite grain ($\Gamma_{\text{chalcopyrite}}$) has a radius of 1 mm. The thin porous layer surrounding the solid chalcopyrite grain (Γ_{jarosite}) has a thickness of 0.1 mm and consists of 480 grid cells of equal size. In case of a chalcopyrite-to-gangue mineral grain ratio of 1:2 (Fig. 1), the thickness of the porous gangue mineral layer (Γ_{quartz}) is 1 mm and the quartz surface area is $22.64 \text{ m}^2 \text{ Kg}^{-1}$ (see Eq. S10 in the **Supplementary Material**, [available online](#)). The gangue mineral layer consists of 1654 grid cells, which increase exponentially in size from the inside out. For the porous media (Γ_{jarosite} , Γ_{quartz}) the permeability was defined as $1e^{-13} \text{ m}^2$ and the porosity as 0.1.

A fluid flow equation is used which connects the free flow domain to the porous media. To achieve this, the Brinkman equation for the porous media part and the Navier Stokes equation for the free flow part are used (27). The same fields, velocity $\mathbf{u}$ (m s^{-1}) and pressure p (Pa) were solved in the free flow domain (Γ_{pores}) and the porous domain ($\Gamma_{\text{quartz}} + \Gamma_{\text{jarosite}}$). This enforces a continuity between the fluid velocity in the free flow and the Darcy velocity in the porous domain. Details of the Navier-Stokes equation and the Brinkman equation are given in Section 1 in the **Supplementary Material** ([available online](#)).

Once the velocity and the pressure fields for the free and porous media domains are resolved, the transport and reaction of species can be solved using the standard advection-diffusion-reaction equation for each of the components in the aqueous phase (3). Details of the advection-diffusion-reaction equation are given in Section 2 of the **Supplementary Material** ([available online](#)).

The boundary conditions at the inlet and outlet were defined as follows: the left and the right boundaries (Fig. 1) were assigned no-flow conditions, the inflow velocity was set to $1.25e^{-6} \text{ m s}^{-1}$, and the outlet pressure to 101325 Pa.

For the jarosite domain, Γ_{jarosite} , the change in porosity due to the precipitation of jarosite alters the diffusive flux, which is calculated as (Eq. 1; 37):

$$\frac{\partial c_i}{\partial t} = -\phi'_{\Gamma_{\text{jarosite}}} \nabla \cdot (\nabla D_{\text{eff}} c_i) \Big|_{\Gamma_{\text{jarosite}}} \quad (1)$$

with $\phi'_{\Gamma_{\text{jarosite}}}$ being the porosity in the jarosite domain, D_{eff} is the effective diffusion coefficient and ∇c_i is the concentration gradient.

The effective diffusion coefficient is calculated as $D_{\text{eff}} = \frac{D_{\text{Diff}}}{\theta^2}$, where D_{Diff} is the diffusion coefficient in water ($1e^{-9} \text{ m}^2 \text{ s}^{-1}$) and tortuosity, θ is calculated as $\theta = 1 - \ln(\phi'_{\Gamma_{\text{jarosite}}})^2$.

For calculating the dynamic changes in porosity in the jarosite domain ($\phi'_{\Gamma_{\text{jarosite}}}$), the moles of jarosite precipitated ($\text{mole}_{\text{jaro}}$) is calculated for each time step. The volume of the precipitated jarosite (Vol_{jaro}) is calculated as (Eq. 2):

$$\text{Vol}_{\text{jaro}} = \frac{M_{\text{jaro}}}{\rho_{\text{jaro}}} \quad (2)$$

Here $\rho_{\text{jaro}} = 3.9 (\text{g cm}^{-3})$, M_{jaro} is the mass of jarosite and is calculated as (Eq. 3):

$$M_{\text{jaro}} = W_{\text{jaro}} * \text{mole}_{\text{jaro}} \quad (3)$$

Here, molecular weight of jarosite $W_{\text{jaro}} = 500.8 (\text{g mol}^{-1})$ and $\text{mole}_{\text{jaro}}$ is the amount of jarosite moles precipitating calculated from the model.

Next, the new porosity $\phi'_{\Gamma_{\text{jarosite}}}$ is calculated as (Eq. 4):

$$\phi'_{\Gamma_{\text{jarosite}}} = \frac{(\text{Vol}_{\Gamma_{\text{jarosite}}} - \text{Vol}_{\text{mineral}})}{\text{Vol}_{\Gamma_{\text{jarosite}}}} \quad (4)$$

Here $Vol_{\Gamma_{jarosite}}$ is the volume of the jarosite domain, $Vol_{mineral}$ is the total volume of the solid phase in the jarosite domain which is calculated as (Eq. 5):

$$Vol_{mineral} = Vol_{\Gamma_{jarosite}} * (1 - \phi'_{\Gamma_{jarosite}}) + Vol_{jaro} \quad (5)$$

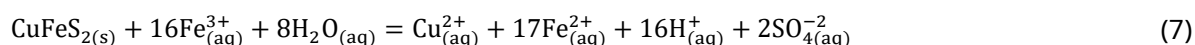
The calculated new porosity ($\phi'_{\Gamma_{jarosite}}$) from Equation 4 is used in the diffusive flux equation (Eq. 1) to calculate the change in concentrations of the aqueous species due to the altered porosity at each time step. Note, chemical reactions are written and referred to as equations.

Two reaction mechanisms lead to the dissolution of chalcopyrite at its surface, ($\gamma_{chalcopyrite}$), (18):

1) The proton-promoted reaction (Eq. 6):



2) The Fe^{3+} - promoted dissolution (Eq. 7):

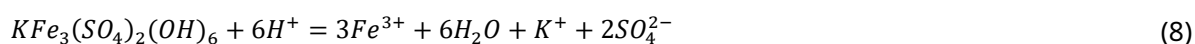


Rates of the two reactions are calculated as a function of the proton (H^+) and Fe^{3+} activities; details of the rate equations are given in Section 3 in the **Supplementary Material** (available online).

Reactions at the mineral surface can be explicitly defined without the need to define the mineral reactive surface area as an input to the model (16). Instead, the mineral surface area is calculated by integrating the local surface area of each boundary cell over the actual reactive boundary. The rate is integrated on the reactive boundary ($\gamma_{chalcopyrite}$) and a molar flux of the aqueous phase, $J_i = \int_{S_{chalcopyrite}} \dot{R}_a \cdot dS$ (mol s^{-1}), is computed for each species i , $\dot{R}_a$ is the reactions rate of the chalcopyrite using Equation S7 and Equation S8, which can be found in the **Supplementary Material** in Section 3 (available online), $S_{chalcopyrite}$ is the surface area of the mineral grain which is directly calculated from the model. This flux controls the molar mass of the species in or out of the aqueous phase due to surface reactions and is calculated in COMSOL. A constant equilibrium phase of atmospheric oxygen pressure is imposed on the system except for simulations 11 and 12 (Table 1).

There are kinetically-controlled reactions taking place in the two porous media domains, the chalcopyrite precipitation domain, $\Gamma_{chalcopyrite}$, and the quartz domain, Γ_{quartz} , (Fig. 1). The dissolution of quartz, $SiO_2(s) + 2H_2O = H_4SiO_4$, within the quartz domain is calculated as a function of the state of saturation according to Marty et al. (22). Details of the rate equation for quartz dissolution are given in the **Supplementary Material** in Section 3 (available online).

The precipitation of jarosite within the jarosite precipitation domain, $\Gamma_{chalcopyrite}$, is defined as show in Equation 8,



and is thermodynamically controlled with a $\log k = -9.21$. The mass of precipitated jarosite (M_{jaro}) (Eq. 3) is calculated at each time step in PhreeqC and transferred to COMSOL for determining its effect on the porosity.

The following two oxidation reactions are implemented in the free fluid domain, Γ_{pores} :

The oxidation of ferrous iron (Fe^{2+}) with oxygen (O_2) is defined as (Eq. 9):



The rate of the reaction is a function of the pH and the O_2 and Fe^{2+} concentrations according to (39) and is detailed in the **Supplementary Material** in Section 3 (available online).

The oxidation of sulfide (H_2S) with O_2 is defined as (Eq. 10):



And the respective rate equation is given in the **Supplementary Material** in Section 3 ([available online](#)).

All of the reaction rates are calculated for each time step and used in the standard advection-diffusion-reaction equation (**Eq. S5, Supplementary Material**, [available online](#)).

In order to account for all aqueous species in solution, primary aqueous species were defined and their relationship with other aqueous species in the solution was calculated by their equilibrium constants, K_{eq} . The model uses the PhreeqC database phreeqc.dat which comprises all log K_{eq} data to calculate the aqueous speciation (see also the **Supplementary Material**, Section 3, **Table S2**, [available online](#)).

The above-described model conditions were implemented as a pore-scale model with a discrete reactive mineral surface in iCP (16).

2.3. Set of simulations and their aims

A set of simulations with variable input parameters were run in this study to better understand the importance of variable processes and conditions controlling CDR and copper recovery. **Table 1** lists the simulation number and the parameters used. Simulations 1-6 study the effect of pH and Fe^{3+} by varying their concentrations. Simulations 7 and 8 study the effect of SO_4^{2-} concentration on copper recovery by tracking the porosity change and the volume of secondary mineral overgrowth. Simulations 9 and 10 study the effect of gangue mineral thickness surrounding the chalcopyrite grain, simulations 11 and 12 study the effects of oxygen concentrations and simulations 13 and 14 study the effects of changing inlet velocities on the copper recovery.

Table 1: Description of the models and the parameters used. Potassium (K^+) had a concentration of 0.01 M in all simulations. The chosen fluid flow velocities are based on previous studies (2, 5, 34).

Aim	Sim. no.	pH	Fe^{3+}	SO_4^{2-}	O_2	Grain ratio	Velocity
Dominant reaction at the chalcopyrite boundary	1	1	0.01M	1×10^{-13} M	Saturated	1:2	$1e-6$ m/s
	2	1	0.005M	1×10^{-13} M	Saturated	1:2	$1e-6$ m/s
	3	1	0.001M	1×10^{-13} M	Saturated	1:2	$1e-6$ m/s
	4	2	0.01M	1×10^{-13} M	Saturated	1:2	$1e-6$ m/s
	5	2	0.005M	1×10^{-13} M	Saturated	1:2	$1e-6$ m/s
	6	2	0.001M	1×10^{-13} M	Saturated	1:2	$1e-6$ m/s
Rate of jarosite precipitation, dynamic growth in the passivation layer and its effect on Cu^{2+} recovery	7	2	0.01M	5×10^{-5} M	Saturated	1:2	$1e-6$ m/s
	8	2	0.01M	9×10^{-5} M	Saturated	1:2	$1e-6$ m/s
Grain Ratio ($\approx$ surface area of gangue mineral) and its effect on Cu^{2+} recovery	9	2	0.01M	1×10^{-13} M	Saturated	1:3	$1e-6$ m/s
	10	2	0.01M	1×10^{-13} M	Saturated	1:4	$1e-6$ m/s
Effect of O_2 on Cu^{2+} recovery and rate of jarosite precipitation	11	2	0.01M	1×10^{-13} M	Half-sat.	1:2	$1e-6$ m/s
	12	2	0.01M	1×10^{-13} M	Zero sat.	1:2	$1e-6$ m/s
Effect of changing velocities on the outlet Cu^{2+} concentration	13	2	0.01M	1×10^{-13} M	Saturated	1:2	$1e-5$ m/s
	14	2	0.01M	1×10^{-13} M	Saturated	1:2	$1e-4$ m/s

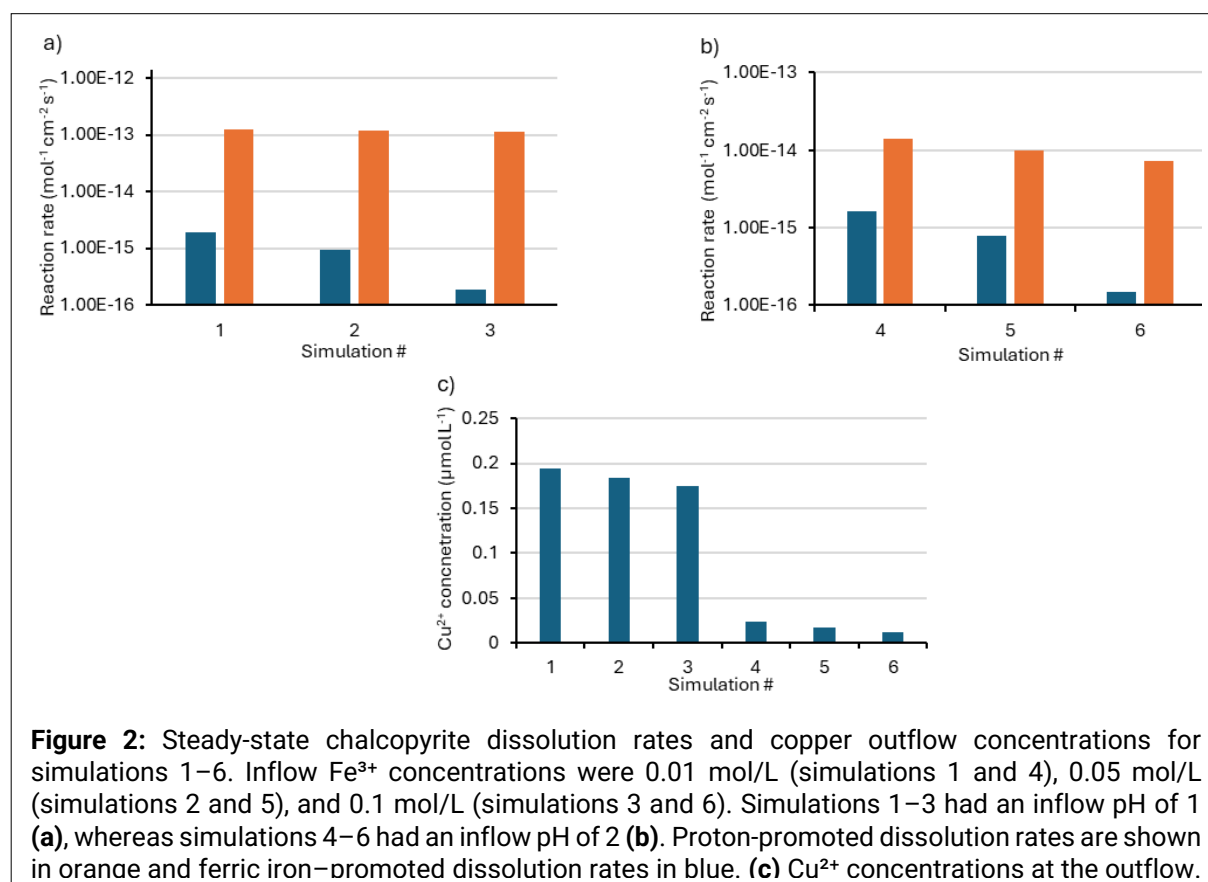
Sim. No. = simulation number.

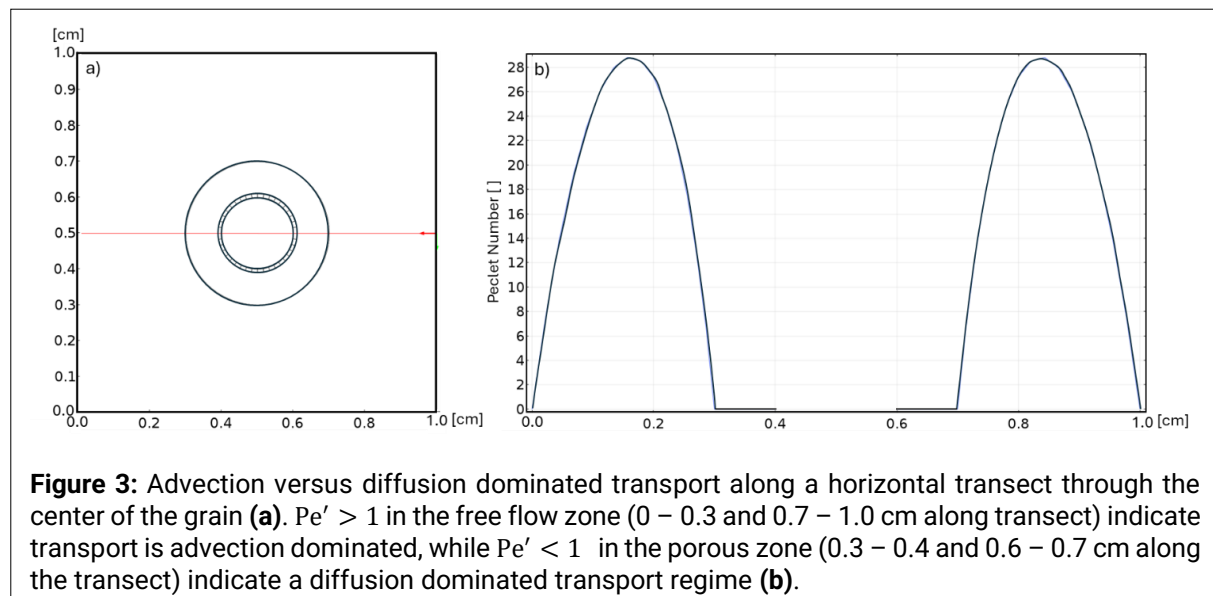
3. RESULTS

3.1. Simulations 1 – 6

Simulations 1 to 6 were run to investigate the importance of proton-promoted as opposed to ferric iron-promoted chalcopyrite dissolution and respective copper recovery. The sulfate concentration was kept low, the O_2 concentration was continuously high (saturated), and the grain radius ratio between the chalcopyrite grain and the gangue mineral of was chosen to be 1:2 (Table 1). The change in outflow concentrations and reactions rate over time follows the trend of a breakthrough curve, where initial values are zero followed by a rapid increase before constant values are reached. The short period of rapid increase in values occurs approximately when the system is flushed the first time and marks the breakthrough time or flushing time. In the study the flushing time is approximately 10,000 seconds (2.8 hours) based on tracer simulations (data not shown). The last phase of the breakthrough curve shows constant values representing steady-state conditions in terms of chemical reaction rates and respective fluid composition at the outflow.

Reaction mechanism-specific steady-state chalcopyrite dissolution rates vary over two orders of magnitude. The lowest rates occur for the ferric-promoted dissolution mechanism at pH 2 ($\sim 1.4 \times 10^{-16} \text{ mol cm}^{-2} \text{ sec}^{-1}$ simulation 6), while the highest rates occur for the proton-promoted dissolution at a pH of 1 and the highest Fe^{3+} concentration ($\sim 1.25 \times 10^{-13} \text{ mol cm}^{-2} \text{ sec}^{-1}$ simulation 1) (Fig. 2). Proton-promoted dissolution rates are not affected by variable Fe^{3+} concentrations whereas the ferric iron-promoted dissolution rates are increased at higher proton concentrations (simulations 1 to 3) relative to lower proton concentrations (simulations 4 to 6). Copper (Cu^{2+}) outflow concentrations reflect the chalcopyrite dissolution rates, with the highest concentrations observed at pH 1 (simulations 1 to 3) and concentrations approximately one order of magnitude lower at pH 2 (simulations 4 to 6).

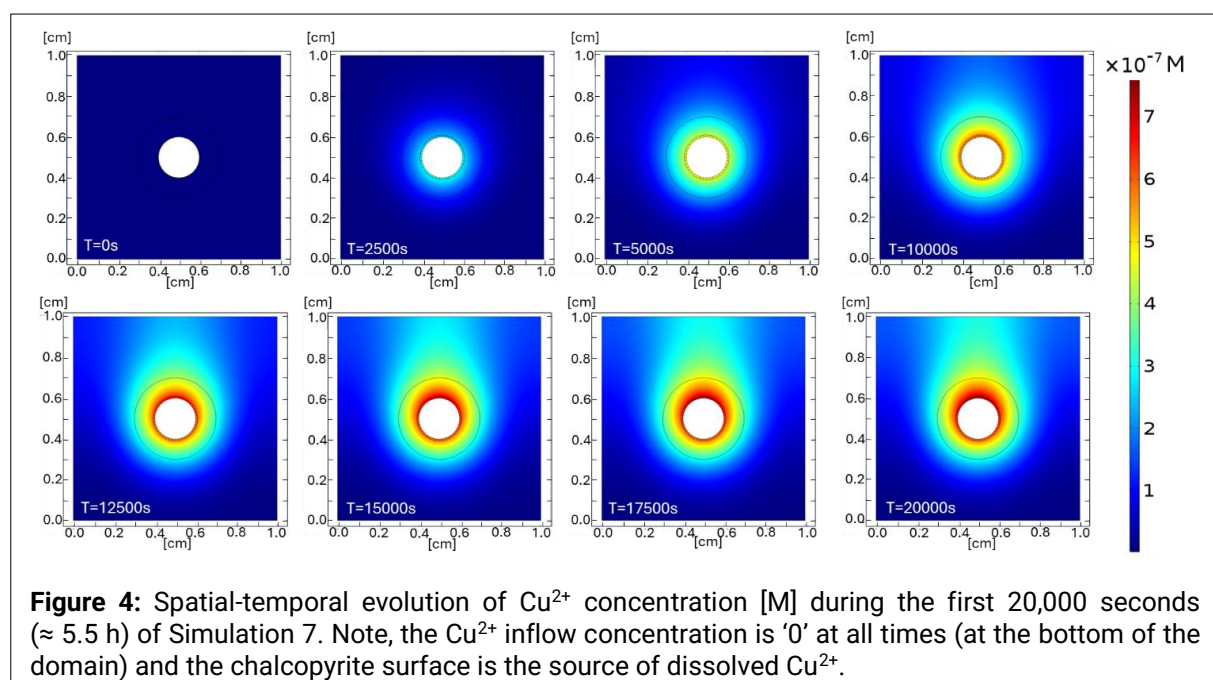




3.2. Simulations 7 and 8

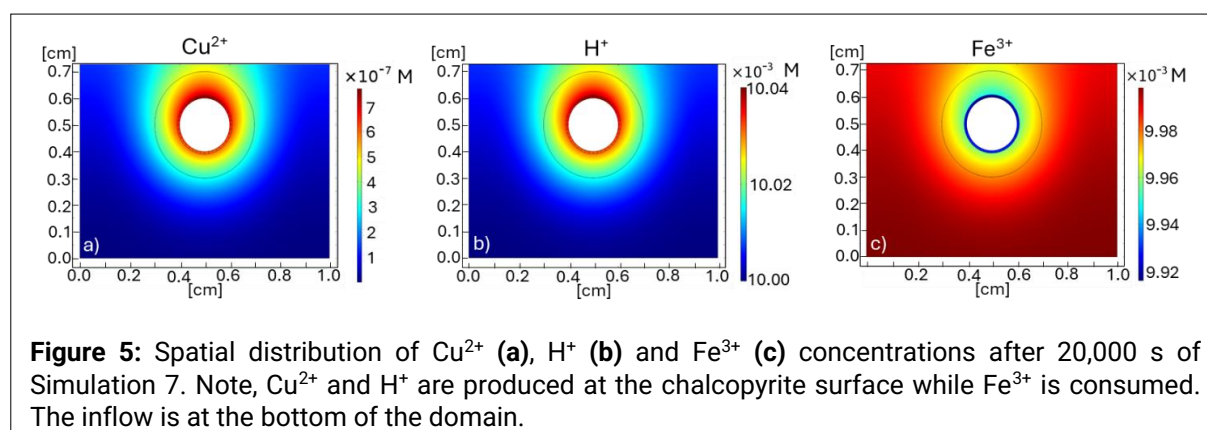
Simulation 7 was used for the following investigations:

1. The dominant transport regime (advection vs. diffusion) was determined along a transect through the center of the grain in order to reveal differences in transport between the free flow and the porous domains (Fig. 3a). The Péclet number (Pe') was calculated, $Pe' = u_{in} * w * D_{diff}^{-1}$, with u_{in} as the inflow velocity, w is the domain width (0.01m) and D_{diff} is the diffusion coefficient ($10^{-9} m^2 s^{-1}$). A $Pe' > 1$ and a $Pe' < 1$ indicate advection and diffusion dominated regimes, respectively. As can be seen in Figure 3b, the free flow domain is advection dominated, while the porous domain is diffusion dominated.
2. The spatial-temporal evolution of the Cu^{2+} concentration distribution was followed from the beginning of the simulation (0 sec) until 20,000 sec (≈ 5.5 h). The Cu^{2+} inflow concentration was '0' at all times, but the Cu^{2+} concentration increased to over $7 * 10^{-7} M$ within the jarosite domain adjacent to the chalcopyrite surface (Fig. 4). A steep Cu^{2+} concentration gradient occurs from the mineral surface to the outer boundary of the porous domain. Given the porous domain is diffusion dominated, see above, the Cu^{2+} flux to the free flow domain is



diffusion controlled. In contrast, once the Cu^{2+} reaches the free flow domain, its transport is advection dominated as illustrated by the pear-shaped Cu^{2+} plume.

- Concentration distributions for Cu^{2+} , Fe^{3+} and H^+ are shown to reveal concentration gradients controlled by the coupled dissolution and reprecipitation (Fig. 5). As shown above (Fig. 4), the chalcopyrite surface is the source of dissolved Cu^{2+} and the porous domain is characterized by a distinct concentration gradient from the mineral surface to the outer bound (Fig. 5a). Together with a $\text{Pe}' > 1$ in the porous domain, see above, Cu^{2+} transport through the porous domain to the free flow domain is diffusion controlled. The pattern of the H^+ concentration distribution (Fig. 5b) is similar to Cu^{2+} distribution (Fig. 5a) suggesting the chalcopyrite surface is a source of H^+ . This can be reconciled through the balance of reactions occurring in the jarosite domain adjacent to the chalcopyrite surface: Ferric iron – promoted chalcopyrite dissolution (Eq. 7) and jarosite precipitation (Eq. 8) produce H^+ while proton-promote chalcopyrite dissolution (Eq. 6) consumes H^+ . Here, the H^+ production outcompetes the H^+ consumption. The Fe^{3+} inflow concentration is 0.01 M (Table 1) and its concentration drops to a minimum of about 0.001M in the jarosite domain (Fig. 5c) due to the precipitation of jarosite (Eq. 8) and the ferric iron reduction during the ferric iron-promoted chalcopyrite dissolution (Eq. 7). The rate of ferrous iron oxidation by oxygen (Eq. 9) is apparently too slow to compensate for the rate of ferric iron consumption.



Simulations 7 and 8 investigate the effects of variable sulfate concentrations on the potential formation of the passivation layer and the associated decline in the chalcopyrite dissolution rate and copper mobilization. The Fe^{3+} concentration (0.01 mol/L) and the pH (pH of) were kept the same in both simulations, but the sulfate concentration was varied between 5×10^{-5} (simulation 7) and 9×10^{-5} (simulation 8) mol/L. The simulations were run for about 14 hours (50,000 s). The jarosite saturation index varied from a very small value to 0.49 and 1.003 for sulfate inflow concentrations of 5×10^{-5} (simulation 7) and 9×10^{-5} (simulation 8) mol/L, respectively (Fig. 6a). Even though the pH (= 2) and the Fe^{3+} inflow concentration (0.01 M) were the same in simulations 4, 7 and 8, the maximum copper mobilization and outflow concentration is only about half in simulations 7 and 8 (1.18×10^{-8} mol/L) compared to the maximum (steady state) concentration in simulation 4 (2.33×10^{-8} mol/L) (Fig. 6d). The onset of jarosite precipitation and the associated reduction in porosity (Fig. 6c) occurs while jarosite is still undersaturated in the outflow (Fig. 6a). The Cu^{2+} outflow concentration starts to decline when the porosity in the jarosite precipitation domain decreased from 0.1 to about 0.05 (Fig. 6d). Figure 6e shows the change in porosity along a transect across the jarosite precipitation domain. The initial porosity in the whole domain was 0.1, which changed to a porosity gradient across the domain and with time.

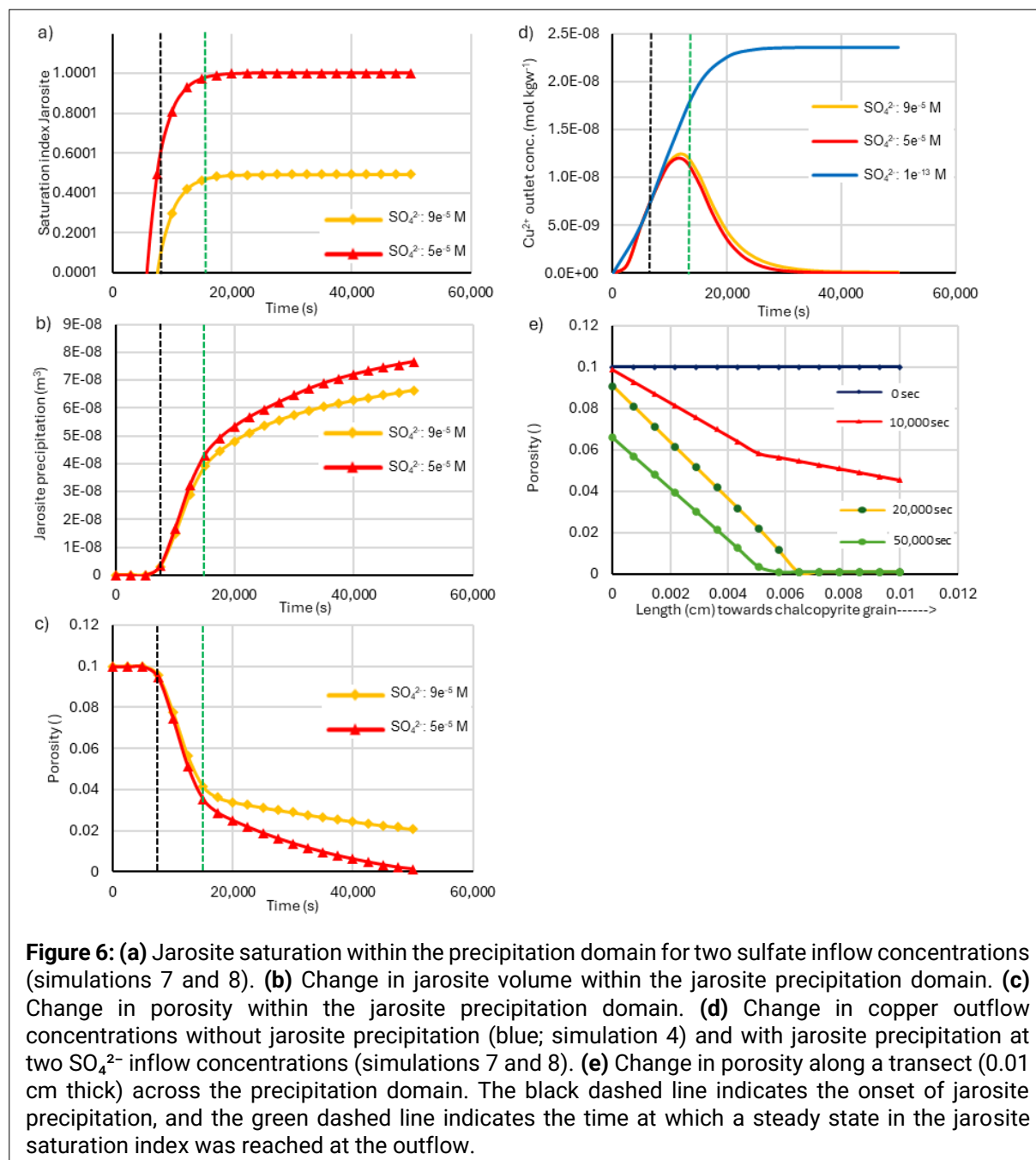


Figure 6: (a) Jarosite saturation within the precipitation domain for two sulfate inflow concentrations (simulations 7 and 8). (b) Change in jarosite volume within the jarosite precipitation domain. (c) Change in porosity within the jarosite precipitation domain. (d) Change in copper outflow concentrations without jarosite precipitation (blue; simulation 4) and with jarosite precipitation at two SO_4^{2-} inflow concentrations (simulations 7 and 8). (e) Change in porosity along a transect (0.01 cm thick) across the precipitation domain. The black dashed line indicates the onset of jarosite precipitation, and the green dashed line indicates the time at which a steady state in the jarosite saturation index was reached at the outflow.

3.3. Simulations 9 to 12

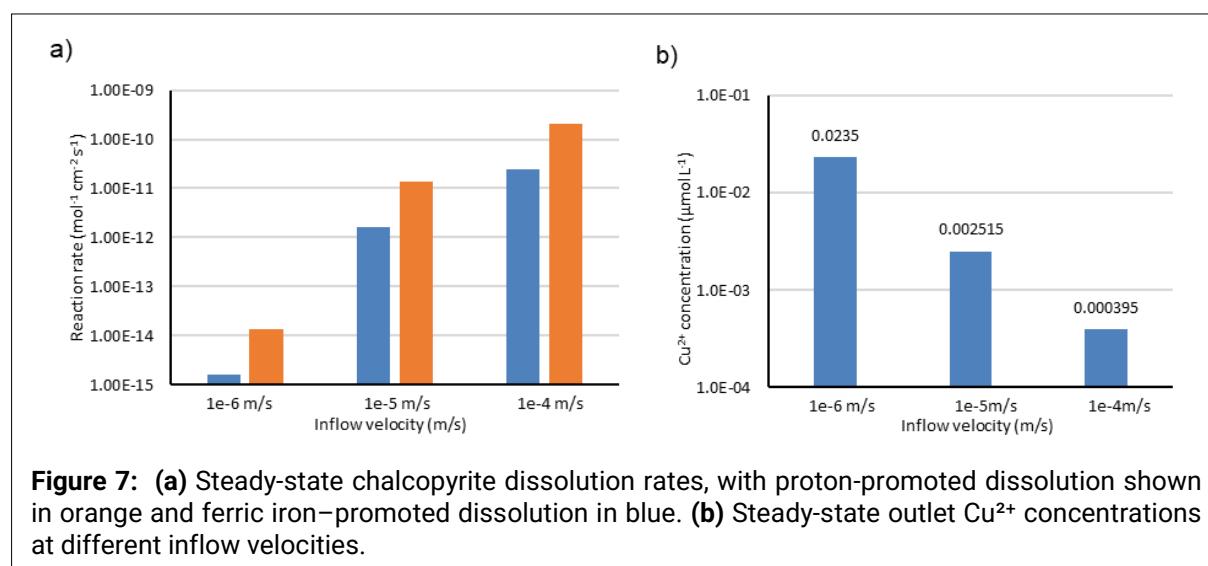
Simulations 9 and 10 investigated the potential influence of variable gangue mineral (quartz) to chalcopyrite ratio. An injection fluid with pH 2 and a 0.01 M Fe^{3+} was used and the ratio of the chalcopyrite to quartz mineral was varied between 1:2 (simulation 4), 1:3 (simulation 9) and 1:4 (simulation 10). Steady state Cu^{2+} outflow concentrations varied for different ratios. A Cu^{2+} outflow concentration of $1.8 \times 10^{-7} \text{ mol/L}$ for a ratio of 1:2, a concentration of $1.9 \times 10^{-7} \text{ mol/L}$ for a ratio of 1:3 and a concentration of $2.2 \times 10^{-7} \text{ mol/L}$ for a ratio of 1:4 were observed. These variations in copper outflow concentration are minor compared to the range observed in simulations 1 to 6, which spans more than one order of magnitude (Fig. 1).

Simulations 11 and 12 investigated the potential influence of variable oxygen concentrations in the inflow. All variables remained the same, however the oxygen concentration varied from fully saturated (simulation 4) to half-saturated (simulation 11) and oxygen-depleted (simulation 12). No

variations in the Cu^{2+} outflow concentrations were observed, which can be explained by the very slow rate of ferrous iron oxidation using oxygen at a low pH (see also section 4.3).

3.4. Simulations 13 and 14

Simulations 13 and 14 investigated the effects of fluid inflow velocities on chalcopyrite dissolution rates and Cu^{2+} outflow concentrations as the injection velocities are changed. All variables remained the same as in simulation 4 except for the injection rate. The ferric-promoted dissolution rate changed from $1.62 \times 10^{-15} \text{ mol cm}^{-2} \text{ s}^{-1}$ at a flow velocity of 1e-6 m/s to a maximum rate of $2.4 \times 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$ at a flow velocity of 1e-4 m/s . The proton-promoted rate also increased from 1.39×10^{-14} to $2.06 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$ (Fig. 7a). In contrast, the Cu^{2+} outflow concentration decreased with increasing fluid inflow velocity from 0.0235 to $0.000395 \text{ } \mu\text{mol/L}$ (Fig. 7b) as the mobilized dissolved copper becomes increasingly diluted by the fluid not reacting with the chalcopyrite.



4. DISCUSSION

4.1. Temporal evolution of the geochemical system

It is important to recognize the temporal evolution of reaction rates and concentrations as well as changes in porosity and permeability within the jarosite domain as precipitation proceeds. At a flow rate of $1 \times 10^{-6} \text{ m s}^{-1}$ and a domain length of 1 cm, the fluid residence time between inflow and outflow in the free-flow domain is 10,000 s. However, ion transport through the porous domain is more variable as it is controlled by diffusion, and the diffusive flux is a function of the concentration gradient and porosity (Eq. 1). Given reactions at the chalcopyrite surface produce or consume ions, including H^+ , Fe^{3+} , SO_4^{2-} and Cu^{2+} , the rate of these concurrent reactions affect the concentration gradients and the respective fluxes. Furthermore, the precipitation of jarosite in the jarosite domain changes its porosity, which also affects the diffusion rate. The temporal evolution of the Cu^{2+} concentration distribution (Fig. 4) illustrates the gradual changes in the Cu^{2+} concentration gradients in the porous domain and in the free-flow domain during the first 20,000 s ($\approx 5.5 \text{ h}$). Similarly, it was demonstrated that jarosite precipitation and associated porosity reduction in the jarosite domain proceeded over 50,000 s at given conditions (Fig. 6d). From the above, it is evident that CDR at mineral surfaces involves a dynamic and complex interplay between ionic transport and concurrent reactions.

4.2. Ion transport in the free-flow domain surrounding the grain and within the porous domain adjacent to chalcopyrite

The dominant transport mechanism is either advection or diffusion and can be calculated using the Pe' Number (see Section 3.2). For the majority of the simulations, we chose a fluid inflow

velocity of $1 \times 10^{-6} \text{ m s}^{-1}$, which is within the range of previously published flow velocities in heaps (**Table 1**). It was further assumed that the chalcopryrite grain diameter is half of the full grain diameter and the chalcopryrite grain is surrounded by gangue mineral with a low porosity (0.1) and low permeability ($1 \times 10^{-13} \text{ m}^2$). In this case, it was determined that the free-flow domain is advection-dominated while the porous domain was diffusion-dominated (**Section 3.2**). The importance of diffusion-dominated transport adjacent to the chalcopryrite has consequences for the question whether chalcopryrite dissolution and associated Cu^{2+} mobilization is limited by the (diffusive) transport or by the reaction rate (**Section 4.4**)

4.3. Variability in the chalcopryrite dissolution rate in the absence of jarosite formation

Chalcopryrite dissolution rates varied by over two orders of magnitude within the range of conditions covered in this study (pH between 1 and 2; $\text{Fe}^{3+}_{(\text{aq})}$ between 0.01 and 0.001 mol/L). The proton-promoted dissolution rate always outcompeted the ferric iron-promoted dissolution rate (simulations 1 to 6, **Fig. 1**) leading to the highest dissolution rate at a pH of 1 and a $\text{Fe}^{3+}_{(\text{aq})}$ concentration of 0.01 mol/L. The proton-promoted dissolution rate was solely dependent on the proton concentration (pH), while the ferric iron-promoted dissolution rate was dependent on the proton and the $\text{Fe}^{3+}_{(\text{aq})}$ concentration. This observation can be explained with the rate laws for the two reactions where the proton and $\text{Fe}^{3+}_{(\text{aq})}$ concentrations are variables for the ferric iron-promoted dissolution reaction (**Eq. S7** in the **Supplementary Material**, [available online](#)) and only the proton concentration is an input to the proton-promoted reaction (**Eq. S8** in the **Supplementary Material**, [available online](#)).

The results of simulations with variable O_2 concentrations (simulations 12 to 14) showed no influence of O_2 on the dissolution rate, suggesting that a secondary reaction of $\text{Fe}^{2+}_{(\text{aq})}$ oxidation with O_2 is negligible. This can be attributed to the following two reasons. First, Fe^{2+} oxidation is limited to the free fluid domain. Second, the OH^- concentration at a pH of 2 is very low, having an inhibiting influence on the oxidation rate (**Eq. S11** in the **Supplementary Material**, [available online](#)).

The role of the fluid advection rate around the grain composed of chalcopryrite and the gangue (quartz) mineral on the rate of chalcopryrite dissolution was explored by varying the fluid flow rate by over two orders of magnitude (1.2×10^{-6} to $1.2 \times 10^{-4} \text{ m sec}^{-1}$ in simulations 4, 13 and 14). The results indicate that chalcopryrite dissolution rates increased by over four orders of magnitude for both reaction mechanisms in response to a two-order-of-magnitude increase in flow velocity (**Fig. 7a**). In contrast, the $\text{Cu}^{2+}_{(\text{aq})}$ outflow concentrations were negatively correlated with the fluid advection rate (**Fig. 7b**). The diffusive Damköhler number ($Da_{II} = k_a * \gamma_a * S * R^2 * D_{\text{Diff}}^{-1}$) was calculated. Here k_a is the rate constant, γ_a is the activity coefficient, S is the specific grain surface area, R is the grain radius, D_{Diff} is the diffusion coefficient. For the proton-promoted dissolution reaction, the $Da_{II}^{\text{H}^+}$ is calculated as 600 and for the ferric-iron promoted reaction $Da_{II}^{\text{Fe}^{3+}} \gg 1000$. This suggests that the reaction rate exceeds the diffusion rate, indicating that the system is diffusion limited. The inverse correlation between the fluid advection rate and the Cu^{2+} outflow concentration is the result of higher dilution of $\text{Cu}^{2+}_{(\text{aq})}$ -enriched fluid leaving the grain at higher advection rate, due to the increased transport of $\text{Cu}^{2+}_{(\text{aq})}$ -depleted fluid around the grain. The increase in the $\text{Cu}^{2+}_{(\text{aq})}$ outflow concentration with an increase in the chalcopryrite-to-gangue mineral radius ratio is initially counterintuitive as one might expect that the relative decrease in chalcopryrite surface area leads to lower reaction rates. However, the surface area of the gangue mineral controls the diffusive flux of ions to the chalcopryrite surface area. A larger gangue mineral surface area captures more ions, including protons and $\text{Fe}^{3+}_{(\text{aq})}$ required for the chalcopryrite dissolution from the ambient fluid into the grain. This result provides further evidence for the control of chalcopryrite dissolution rate by the diffusive flux through the gangue mineral.

4.4. Conditions and impact of coupled dissolution and reprecipitation (CDR)

Hypothetically, the rate of chalcopyrite dissolution and the potential of coupled chalcopyrite dissolution and reprecipitation of jarosite are controlled by three principal conditions:

Firstly, the composition of the inflow solution controls the availability of ions involved in the set of coupled reactions. For example, our results showed that low SO_4^{2-} inflow concentrations (10^{-13} M) inhibit jarosite precipitation, while high inflow SO_4^{2-} concentrations (10^{-5} M) resulted in jarosite supersaturation and precipitation at the chalcopyrite surface.

Secondly, the rates of the coupled reactions are important as certain aqueous species are concurrently consumed and produced. The coupling of species consumption and production can be summarized as follows: Fe^{2+} is produced by the proton-promoted (Eq. 6) and the ferric iron-promoted (Eq. 7) dissolution of chalcopyrite, and can be consumed by the oxidation with O_2 (Eq. 9). Fe^{3+} is consumed by the ferric iron-promoted dissolution of chalcopyrite (Eq. 7) and jarosite precipitation (Eq. 4) and produced by the Fe^{2+} oxidation reaction (Eq. 9). SO_4^{2-} is consumed by the jarosite precipitation reaction (Eq. 8) and produced by the ferric iron-promoted chalcopyrite dissolution reaction (Eq. 7) and H_2S oxidation reaction (Eq. 6). H^+ is consumed by the proton-promoted chalcopyrite dissolution mechanism (Eq. 2) and Fe^{2+} oxidation (Eq. 5), while it is produced by ferric iron-promoted chalcopyrite dissolution (Eq. 3) and sulfide oxidation (Eq. 10). The coupling of concurrent aqueous species production and consumption has been shown to control species concentrations and the development of a steady state balance between production and consumption rates (30). In our simulations we observed the concurrent production of Cu^{2+} and H^+ , while Fe^{3+} was consumed at the chalcopyrite surface when jarosite precipitated (Fig. 5). This could, however, change for a range of reasons. For example, as jarosite precipitation reduces porosity, the diffusion of H^+ and Fe^{3+} to the chalcopyrite surface reduces. Similarly, if the pH is too high for significant H^+ -promoted chalcopyrite dissolution and respective H^+ consumption (Eq. 6), more net production of H^+ will occur due to the Fe^{3+} -promoted dissolution (Eq. 7) and jarosite precipitation (Eq. 8).

Thirdly, reaction rates can be controlled by the rate of ion transport to and away from the reaction site, or by the inherent kinetic control of the reaction (6). In case of a reaction rate controlled by transport, the reaction rate varies with the flow velocity or the diffusive flux, while kinetically controlled reactions do not vary with the transport rate.

We investigated CDR processes at the surface of chalcopyrite through a series of reactive-transport simulations. In order to study conditions of coupled chalcopyrite dissolution and jarosite reprecipitation at the chalcopyrite mineral surface, the sulfate inflow concentration was varied between 5×10^{-5} and 9×10^{-5} mol/L while all other conditions remained the same (simulations 7 and 8, Fig. 6). The mineral saturation state for jarosite was initially highly undersaturated at the outflow in both cases (Fig. 6e). Three temporal phases reflecting different process can be observed: The initial increase in the $\text{Cu}^{2+}_{(\text{aq})}$ outflow concentration was the same as in a comparable simulation with extremely low sulfate concentration (simulation 4); porosity remained constant and jarosite precipitation did not occur. During this phase, sulfide was mobilized and oxidized to sulfate according to the ferric iron-promoted chalcopyrite dissolution (Eq. 7) leading to a local enrichment in sulfate. The second phase commenced when the sulfate concentration in the jarosite precipitation zone was high enough to reach jarosite saturation (Fig. 4e). At this point jarosite started to precipitate and to accumulate and porosity started to decline in the jarosite precipitation zone. Consequently, ion transport to the chalcopyrite surface and the associated rate of chalcopyrite dissolution declined and the $\text{Cu}^{2+}_{(\text{aq})}$ outflow concentration decreased. The third phase was characterized by an exponential decline in **a)** the $\text{Cu}^{2+}_{(\text{aq})}$ outflow concentration, **b)** the porosity, and **c)** the rate of jarosite accumulation in the jarosite precipitation domain. This phase resulted in the shutdown of $\text{Cu}^{2+}_{(\text{aq})}$ mobilization due to the coupled dissolution and reprecipitation at the chalcopyrite surface. The two simulations with an inflow composition undersaturated with respect to jarosite (simulations 7 and 8) illustrate the importance of the inflow composition. Given

$\text{Fe}^{3+}_{(\text{aq})}$ contributes to chalcopyrite dissolution, one needs to keep the potassium and/or sulfate concentrations low to avoid jarosite precipitation. Previous experimental studies suggested using sulfuric acid with a sulfate concentration of 100×10^{-3} mol/L (37) or seawater with a sulfate concentration of 28×10^{-3} mol/L (15) as a lixiviant in areas with limited freshwater resources. However, such high sulfate concentrations would highly limit $\text{Fe}^{3+}_{(\text{aq})}$ concentrations and lead to abundant jarosite precipitation including precipitation at the surface of chalcopyrite where additional sulfate is formed. Given the critically important reaction of jarosite precipitation within a 10 μm zone at the chalcopyrite surface further suggests mesocosm experiments may show systemwide changes in the water composition, but may not reveal clues on mineral surface reactions causing surface passivation and respective decline in the dissolution rate of a primary mineral.

This study has successfully developed a reactive-transport model integrating reactions at a discrete mineral surface with continuum-scale domains enabling the prediction of coupled dissolution and replacement reactions (CDR) at a mineral surface. Specifically, jarosite precipitation at the chalcopyrite surface was predicted at given conditions. However, the formation of another secondary mineral in the form of covellite (42) and the potential transformation of jarosite to iron oxides (33) have been demonstrated under certain conditions, which have not been explored here. As pointed out earlier (1), variations in chemical and physical conditions from the micro- to macro-scale can lead to different CDRs at the mineral surface and warrant further investigations. Specifically, electrochemical conditions can impose redox-controlled mineral dissolution and surface passivation of metal sulfide minerals such as pyrite and chalcopyrite (41 and references herein), which has not been addressed in this study.

5. CONCLUSIONS

A reactive-transport model has been developed to predict coupled dissolution and reprecipitation reactions (CDR) at mineral surfaces and was applied to reveal reactions at the chalcopyrite mineral surface and the consequences for copper recovery in heap leaching systems. Proton-promoted chalcopyrite dissolution exceeded ferric iron-promoted dissolution of chalcopyrite under the given conditions. Reactions at the mineral surface were transport-limited where the diffusive flux of ions through the gangue mineral (quartz) surrounding chalcopyrite controlled the reaction rates. Ferrous iron oxidation is negligible under the very low pH conditions, whereas sulfide oxidation did occur near the chalcopyrite surface leading to elevated sulfate concentrations. Once the solution at the mineral surface reached thermodynamic equilibrium with jarosite, jarosite precipitation commenced leading to a reduction in porosity within the precipitation zone. As a consequence, ionic transport became increasingly restricted and ultimately terminated chalcopyrite dissolution and copper mobilization. It is recommended to keep sulfate concentrations low in the infiltrating solution to avoid jarosite precipitation. The study illustrates how processes at micro-meter scale can control systemwide changes in fluid composition, in this case copper recovery in low-grade ore heap leaching systems.

ORCID IDs

Ralf Haese



<https://orcid.org/0000-0002-3574-2819>

Apoorv Jyoti



<https://orcid.org/0000-0003-3316-0732>

STATEMENTS AND DECLARATIONS

Supplementary Material

Further information on the following topics can be found in the Supplementary Material, which is available for download online (<https://doi.org/10.69631/q237yd92>): Details of the fluid flow and transport modeling, details of the advection-diffusion-reaction equation, and the rate equations for reactions used in the study.

Acknowledgements

The authors wish to acknowledge earlier discussions with Dr. Eric Ansah and Dr. Jay Black from the University of Melbourne on copper dissolution in heap systems. The authors further wish to thank the three reviewers for their constructive comments.

Author Contributions

Ralf R. Haese contributed to the study by conceptualizing the study and modelling approach, provided the funding through a University of Melbourne account, contributed to the data analysis and interpretation and wrote most sections of the manuscript. **Apoorv Jyoti** contributed to the study through the model design and programming in COMSOL, he carried out the simulations, contributed to the data analysis and interpretation, he wrote parts of the manuscript and provided the figures.

Conflicts of Interest

Both authors do not have a conflict of interest in this study and its publication.

Data, Code & Protocol Availability

All modelling files are available at:

https://github.com/jyotiapoorv/Modelling_Copper_Mobilization_Using_iCP.

REFERENCES

1. Altree-Williams, A., Pring, A., Ngothai, Y., & Brugger, J. (2015). Textural and compositional complexities resulting from coupled dissolution-precipitation reactions in geomaterials. *Earth-Science Reviews*, 150, 628–651. <https://doi.org/10.1016/j.earscirev.2015.08.013>
2. Ansah, E. O., Black, J. R., & Haese, R. R. (2025). Impact of mineral dissolution-precipitation on pore geometry during copper sulphide heap leaching. *Minerals Engineering*, 230, Article 109379. <https://doi.org/10.1016/j.mineng.2025.109379>
3. Bear, J. (1972). *Dynamics of fluids in porous materials*. Society of Petroleum Engineers.
4. Bouffard, S. C., & Dixon, D. G. (2001). Investigative study into the hydrodynamics of heap leaching processes. *Metallurgical and Materials Transactions B*, 32(5), 763–776. <https://doi.org/10.1007/s11663-001-0063-1>
5. Bouffard, S. C., & West-Sells, P. G. (2009). Hydrodynamic behavior of heap leach piles: Influence of testing scale and material properties. *Hydrometallurgy*, 98(1–2), 136–142. <https://doi.org/10.1016/j.hydromet.2009.04.012>
6. Brantley, S. L. (2008). Kinetics of mineral dissolution. In S. L. Brantley, J. D. Kubicki, & A. F. White (Eds.), *Kinetics of water-rock interaction* (pp. 151–210). Springer. https://doi.org/10.1007/978-0-387-73563-4_5
7. Cariaga, E., Concha, F., & Sepúlveda, M. (2005). Flow through porous media with applications to heap leaching of copper ores. *Chemical Engineering Journal*, 111(2–3), 151–165. <https://doi.org/10.1016/j.cej.2005.02.019>
8. Deng, H., Poonosamy, J., & Molins, S. (2022). A reactive transport modeling perspective on the dynamics of interface-coupled dissolution-precipitation. *Applied Geochemistry*, 137, Article 105207. <https://doi.org/10.1016/j.apgeochem.2022.105207>
9. Dixon, D. G., & Hendrix, J. L. (1993). A mathematical model for heap leaching of one or more solid reactants from porous ore pellets. *Metallurgical Transactions. Part B*, 24(6), 1087–1102. <https://doi.org/10.1007/BF02661000>
10. Elshkaki, A., Graedel, T. E., Ciacci, L., & Reck, B. K. (2016). Copper demand, supply, and associated energy use to 2050. *Global Environmental Change*, 39, 305–315. <https://doi.org/10.1016/j.gloenvcha.2016.06.006>
11. Elwood Madden, M. E., Madden, A. S., Rimstidt, J. D., Zahrai, S., Kendall, M. R., & Miller, M. A. (2012). Jarosite dissolution rates and nanoscale mineralogy. *Geochimica et Cosmochimica Acta*, 91, 306–321. <https://doi.org/10.1016/j.gca.2012.05.001>
12. Emmanuel, S. (2022). Modeling the effect of mineral armoring on the rates of coupled dissolution-precipitation reactions: Implications for chemical weathering. *Chemical Geology*, 601, Article 120868. <https://doi.org/10.1016/j.chemgeo.2022.120868>

13. Hackl, R. P., Dreisinger, D. B., Peters, E., & King, J. A. (1995). Passivation of chalcopyrite during oxidative leaching in sulfate media. *Hydrometallurgy*, 39(1–3), 25–48. [https://doi.org/10.1016/0304-386X\(95\)00023-A](https://doi.org/10.1016/0304-386X(95)00023-A)
14. Harlov, D. E., Wirth, R., & Hetherington, C. J. (2011). Fluid-mediated partial alteration in monazite: The role of coupled dissolution–reprecipitation in element redistribution and mass transfer. *Contributions to Mineralogy and Petrology*, 162(2), 329–348. <https://doi.org/10.1007/s00410-010-0599-7>
15. Hiroyoshi, N., Hirota, M., Hirajima, T., & Tsunekawa, M. (1997). A case of ferrous sulfate addition enhancing chalcopyrite leaching. *Hydrometallurgy*, 47(1), 37–45. [https://doi.org/10.1016/S0304-386X\(97\)00032-7](https://doi.org/10.1016/S0304-386X(97)00032-7)
16. Jyoti, A., & Haese, R. R. (2021). Validation of a multicomponent reactive-transport model at pore scale based on the coupling of COMSOL and PhreeqC. *Computers and Geosciences*, 156, Article 104870. <https://doi.org/10.1016/j.cageo.2021.104870>
17. Kelly, T. D., & Matos, G. R. (2014). *Historical statistics for mineral and material commodities in the United States (2014)*, US Geological Survey Data, 140. Retrieved July 2025, <https://www.usgs.gov/centers/national-minerals-information-center/historical-statistics-mineral-and-material-commodities>
18. Kimball, B. E., Rimstidt, J. D., & Brantley, S. L. (2010). Chalcopyrite dissolution rate laws. *Applied Geochemistry*, 25(7), 972–983. <https://doi.org/10.1016/j.apgeochem.2010.03.010>
19. Leahy, M. J., & Schwarz, M. P. (2009). Modeling jarosite precipitation in isothermal chalcopyrite bioleaching columns. *Hydrometallurgy*, 98(1–2), 181–191. <https://doi.org/10.1016/j.hydromet.2009.04.017>
20. Li, Y., Kawashima, N., Li, J., Chandra, A. P., & Gerson, A. R. (2013). A review of the structure, and fundamental mechanisms and kinetics of the leaching of chalcopyrite. *Advances in Colloid and Interface Science*, 197–198, 1–32. <https://doi.org/10.1016/j.cis.2013.03.004>
21. Manecki, M., Kwaśniak-Kominek, M., Majka, J. M., & Rakovan, J. (2020). Model of interface-coupled dissolution-precipitation mechanism of pseudomorphic replacement reaction in aqueous solutions based on the system of cerussite PbCO_3 —Pyromorphite $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$. *Geochimica et Cosmochimica Acta*, 289, 1–13. <https://doi.org/10.1016/j.gca.2020.08.015>
22. Marty, N. C. M., Claret, F., Lassin, A., Tremosa, J., Blanc, P., Madé, B., Giffaut, E., Cochepin, B., & Tournassat, C. (2015). A database of dissolution and precipitation rates for clay-rocks minerals. *Applied Geochemistry*, 55, 108–118. <https://doi.org/10.1016/j.apgeochem.2014.10.012>
23. McBride, D., Croft, T. N., Cross, M., Bennett, C., & Gebhardt, J. E. (2014). Optimization of a CFD—Heap leach model and sensitivity analysis of process operation. *Minerals Engineering*, 63, 57–64. <https://doi.org/10.1016/j.mineng.2013.11.010>
24. McBride, D., Cross, M., & Gebhardt, J. E. (2012). Heap leach modeling employing CFD technology: A “process” heap model. *Minerals Engineering*, 33, 72–79. <https://doi.org/10.1016/j.mineng.2011.10.003>
25. McBride, D., Gebhardt, J., Croft, N., & Cross, M. (2018). Heap Leaching: Modeling and forecasting using CFD technology. *Minerals*, 8(1), 9. <https://doi.org/10.3390/min8010009>
26. Molins, S., Soulaire, C., Prasianakis, N. I., Abbasi, A., Poncet, P., Ladd, A. J. C., Starchenko, V., Roman, S., Trebotich, D., Tchelepi, H. A., & Steefel, C. I. (2021). Simulation of mineral dissolution at the pore scale with evolving fluid-solid interfaces: Review of approaches and benchmark problem set. *Computational Geosciences*, 25(4), 1285–1318. <https://doi.org/10.1007/s10596-019-09903-x>
27. Mostaghimi, P., Tollit, B. S., Neethling, S. J., Gorman, G. J., & Pain, C. C. (2014). A control volume finite element method for adaptive mesh simulation of flow in heap leaching. *Journal of Engineering Mathematics*, 87(1), 111–121. <https://doi.org/10.1007/s10665-013-9672-3>
28. Mudd, G. M., Weng, Z., & Jowitt, S. M. (2013). A detailed assessment of global Cu resource trends and endowments. *Economic Geology*, 108(5), 1163–1183. <https://doi.org/10.2113/econgeo.108.5.1163>
29. Nardi, A., Idiart, A., Trinchero, P., de Vries, L. M., & Molinero, J. (2014). Interface COMSOL-PHREEQC (iCP), an efficient numerical framework for the solution of coupled multiphysics and geochemistry. *Computers and Geosciences*, 69, 10–21. <https://doi.org/10.1016/j.cageo.2014.04.011>
30. Phukan, M., Vu, H. P., & Haese, R. R. (2021). Mineral dissolution and precipitation reactions and their net balance controlled by mineral surface area: An experimental study on the interactions between continental flood basalts and CO_2 -saturated water at 80 bars and 60 °C. *Chemical Geology*, 559, Article 119909. <https://doi.org/10.1016/j.chemgeo.2020.119909>
31. Putnis, A. (2002). Mineral replacement reactions: From macroscopic observations to microscopic mechanisms. *Mineralogical Magazine*, 66(5), 689–708. <https://doi.org/10.1180/0026461026650056>
32. Putnis, A. (2009). Mineral replacement reactions. In *Reviews in Mineralogy and Geochemistry* E. H. Oelkers & E. H. Schott (Eds.), Thermodynamics and kinetics of water-rock interactions, 70(1), 87–124. <https://doi.org/10.2138/rmg.2009.70.3>

33. Ren, Z., Chao, C., Krishnamoorthy, P., Asselin, E., Dixon, D. G., & Mora, N. (2022). The overlooked mechanism of chalcopyrite passivation. *Acta Materialia*, 236, Article 118111. <https://doi.org/10.1016/j.actamat.2022.118111>
34. Robertson, S. (2017). Development of an integrated heap leach solution flow and mineral leaching model. *Hydrometallurgy*, 169, 79–88. <https://doi.org/10.1016/j.hydromet.2016.12.010>
35. Ruiz-Agudo, E., Putnis, C. V., & Putnis, A. (2014). Coupled dissolution and precipitation at mineral-fluid interfaces. *Chemical Geology*, 383, 132–146. <https://doi.org/10.1016/j.chemgeo.2014.06.007>
36. Schipper, B. W., Lin, H.-C., Meloni, M. A., Wansleeben, K., Heijungs, R., & van der Voet, E. (2018). Estimating global copper demand until 2100 with regression and stock dynamics. *Resources, Conservation and Recycling*, 132, 28–36. <https://doi.org/10.1016/j.resconrec.2018.01.004>
37. Schulz, H. D. (2006). Quantification of early diagenesis: Dissolved constituents in pore water and signals in the solid phase. In H. D. Schulz, M. Zabel (Eds.), *Marine geochemistry* (pp. 73–124). Springer-Verlag. https://doi.org/10.1007/3-540-32144-6_3
38. Silva, O., Nardi, A., Román-Ross, G., Molinero, J., & Quesada, P. (2014). Hydro-mechanical-chemical coupled modeling of copper heap leaching with iCP. Iberian COMSOL Multiphysics Conference, 26–28. <https://www.comsol.com/paper/download/210581/IberianCOMSOLConference.pdf>
39. Singer, P. C., & Stumm, W. (1970). The solubility of ferrous iron in carbonate-bearing waters. *Journal AWWA*, 62(3), 198–202. <https://doi.org/10.1002/j.1551-8833.1970.tb03888.x>
40. Soulaire, C. (2024). Micro-continuum modeling: An hybrid-scale approach for solving coupled processes in porous media. *Water Resources Research*, 60(2). <https://doi.org/10.1029/2023WR035908>
41. Teimouri, S., Herman Potgieter, J. H., & Billing, C. (2025). A comparison of the electrochemical oxidative dissolution of pyrite and chalcopyrite in dilute nitric acid solution. *Chemistry Open*, 14(5), Article e202400053. <https://doi.org/10.1002/open.202400053>
42. Velásquez-Yévenes, L., & Quezada-Reyes, V. (2018). Influence of seawater and discard brine on the dissolution of copper ore and copper concentrate. *Hydrometallurgy*, 180, 88–95. <https://doi.org/10.1016/j.hydromet.2018.07.009>
43. Wang, Z., Hu, M., & Steefel, C. (2024). Pore-scale modeling of reactive transport with coupled mineral dissolution and precipitation. *Water Resources Research*, 60(6). <https://doi.org/10.1029/2023WR036122>