MODELING COPPER LEACHING IN HEAP SYSTEMS CONSIDERING COMPETING REACTION MECHANISMS AND COUPLED DISSOLUTION WITH REPRECIPITATION (CDR) PROCESSES

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Heap leaching and its low recovery challenge



Coupled dissolution with reprecipitation (CDR)

 $AB_{(solid)} = A^+_{(aq)} + B^-_{(aq)}$

 $A^+_{(aq)} + C^-_{(aq)} = AC_{(solid)}$



$$CuFeS_{2(s)} + 4O_{2(aq)} + K_{(aq)}^{+} + 6H_2O + 2Fe_{(aq)}^{3+} = Cu_{(aq)}^{+} + KFe_3(SO_4)_2(OH)_{6(s)} + 6H_{(aq)}^{+}$$

Passivation mechanism(s)



Source: Ansah et al., 2023

5. Partial coating by thick insoluble product

Heap leaching and its low recovery challenge



Source: Jex Technologies





- 1. Mineral surface area controls CDR
- 2. Growth of a secondary mineral influences the reactive surface of the primary mineral

reacted

Kfs – k-feldspar Ccp – chalcopyrite Bn – bornite Cv – covellite Jrs - jarosite



3. How to model?

Introducing a surfacepassivate model to handle surface area variation

Objectives

- 1. How to best model various chalcopyrite reaction mechanisms and rate laws?
- 2. What effect do distinct types of gangue minerals (e.g., silicates, oxides, sulphates, etc.) have on Cu liberation from chalcopyrite?
- 3. What is the influence of precipitate (such as jarosite and gypsum) formation on
 - ✓ Surface area
 - ✓ Element (copper) mobilization?



Materials & Methods

Model conditions



- The initial fluid for proton-promoted simulations was 0.0316 M HCl with no Fe³⁺.
- 2. 0.1 M FeCl₃ solution was used in the ferric-iron promoted and combined ferric-iron-proton promoted cases.
- 3. The model is simulated at Eh of 650 mV SHE and pH 1.5 under ambient conditions.
- 4. The solution master species and solution species of Al, Ca, Cu, Cl, Fe, H, K, Mg, Na, O, S, and Si from the IInl.dat were used.
- 5. The models were run to simulate 1 to 5000 days of reaction.
- 6. The equilibrium rate constants for the aqueous species and mineral phases were taken from the Lawrence Livermore National Laboratory (LLNL) thermodynamic database (IInI.dat) with a few supplementary phases added (e.g., anhydrite, bornite and muscovite) from the wateq4f.dat database of PHREEQC
- 7. Initial chalcopyrite surface area = 0.94 m^2

Redox constraints

 $Fe_{(aq)}^{3+} + e^{-} = Fe_{(aq)}^{2+}$

 $0_{2(aq)} + 4H_{(aq)}^{+} + 4e^{-} = 2H_20$

 $Cu_{(aq)}^{2+} + e^{-} = Cu_{(aq)}^{+}$

$$SO_{4(aq)}^{-2} + 9H_{(aq)}^{+} + 8e^{-} = HS_{(aq)}^{-} + 4H_2O_{(aq)}^{-1}$$

Large kinetic rate constant (1E10) was assumed for the redox reactions, thereby behaving as equilibrium reactions

Case 1 – comparison of different rates and reactions of chalcopyrite dissolution

Proton-promoted (non-oxidative) dissolution of chalcopyrite (Lazaro and Nicol, 2003): $CuFeS_{2(s)} + 2H^{+}_{(aq)} = Cu^{2+}_{(aq)} + Fe^{2+}_{(aq)} + 2HS^{-}_{(aq)}$

The rate law for proton-promoted chalcopyrite dissolution (Kimball et al., 2010):

 $r = 10^{-1.52} e^{-28200/RT} [H^+]^{1.68}$

Ferric-iron promoted (oxidative) dissolution of chalcopyrite (Lu et al., 2000):

$$CuFeS_{2(s)} + 4Fe_{(aq)}^{3+} = Cu_{(aq)}^{2+} + 5Fe_{(aq)}^{2+} + 2S_{(s)}^{0}$$

The rate law for ferric-iron promoted chalcopyrite dissolution (Rimstidt et al., 1994):

 $r = -1.78 \times 10^{-7} [Fe^{3+}]^{0.43}$

Combined ferric-iron-proton promoted dissolution of chalcopyrite (Kimball et al., 2010):

$$CuFeS_{2(s)} + 16Fe_{(aq)}^{3+} + 8H_2O_{(aq)} = Cu_{(aq)}^{2+} + 17Fe_{(aq)}^{2+} + 16H_{(aq)}^{+} + 2SO_{4(aq)}^{-2}$$

The rate law for combined feric-iron-proton promoted chalcopyrite dissolution (Kimball et al., (2010):

 $r = 10^{1.88} e^{-\frac{48100}{RT}} [H^+]^{0.8} [Fe^{3+}]^{0.52}$

a

Case 2 - Influence of gangue minerals on combined ferric-proton chalcopyrite dissolution

Quartz: $SiO_{2(s)} + 2H_2O_{(aq)} = H_4SiO_{4(ss)}$

k-Feldspar: KAlSi₃O_{8(s)} + $4H_{(aq)}^{+} = Al_{(aq)}^{3+} + K_{(aq)}^{+} + 2H_2O + 3SiO_{2(ss)}$

Anhydrite: $CaSO_{4(s)} = Ca^{+}_{(aq)} + SO^{2-}_{4(aq)}$

Albite: NaAlSi₃O_{8(s)} + 8H₂O = Na⁺_(aq) + Al(OH)⁻_{4(aq)} + 3H₄SiO_{4(aq)}

Muscovite:KMg₃AlSi₃O₁₀(OH)_{2(s)} + 10H⁺_(aq) = K⁺_(aq) + 3Mg²⁺_(aq) + Al³⁺_(aq) + 3H₄SiO_{4(aq)} Hematite: Fe₂O_{3(s)} + 6H⁺_(aq) = 2Fe³⁺_(aq) + 3H₂O

The rate expression for k-feldspar, albite, muscovite, hematite, gypsum/anhydrite in pure H₂O (neutral pH), acid (promoted by H⁺) and base (promoted by OH⁻) (Palandri and Kharaka, 2004 and references therein).

$$r = k_{\text{acid}}^{298.15K} e^{\frac{-E}{acid} \left(\frac{1}{T} - \frac{1}{298.15}\right)} a_{H^+}^{n_1} (1 - \Omega^{p_1})^{q_1} + k_{\text{neutral}}^{298.15} e^{\frac{-E}{R} \frac{1}{T} - \frac{1}{298.15}} a_{H^+}^{n_2} (1 - \Omega^{p_2})^{q_2} + k_{\text{base}}^{298.15} e^{\frac{-E}{R} \frac{1}{T} - \frac{1}{298.15K}} a_{H^+}^{n_3} (1 - \Omega^{p_3})^{q_3} + k_{\text{base}}^{298.15} e^{\frac{-E}{R} \frac{1}{T} - \frac{1}{298.15K}} a_{H^+}^{n_3} (1 - \Omega^{p_3})^{q_3} + k_{\text{base}}^{298.15K} e^{\frac{-E}{R} \frac{1}{T} - \frac{1}{298.15K}} a_{H^+}^{n_3} (1 - \Omega^{p_3})^{q_3} + k_{\text{base}}^{298.15K} e^{\frac{1}{T} - \frac{1}{298.15K}} a_{H^+}^{n_3} (1 - \Omega^{p_3})^{q_3} + k_{\text{base}}^{298.15K} e^{\frac{1}{T} - \frac{1}{298.15K}} a_{H^+}^{n_3} (1 - \Omega^{p_3})^{q_3} + k_{\text{base}}^{298.15K} e^{\frac{1}{T} - \frac{1}{298.15K}} a_{H^+}^{n_3} (1 - \Omega^{p_3})^{q_3} + k_{\text{base}}^{298.15K} e^{\frac{1}{T} - \frac{1}{298.15K}} a_{H^+}^{n_3} (1 - \Omega^{p_3})^{q_3} + k_{\text{base}}^{298.15K} e^{\frac{1}{T} - \frac{1}{298.15K}} a_{H^+}^{n_3} (1 - \Omega^{p_3})^{q_3} + k_{\text{base}}^{298.15K} e^{\frac{1}{T} - \frac{1}{298.15K}} a_{H^+}^{n_3} (1 - \Omega^{p_3})^{q_3} + k_{\text{base}}^{298.15K} e^{\frac{1}{T} - \frac{1}{298.15K}} a_{H^+}^{n_3} (1 - \Omega^{p_3})^{q_3} + k_{\text{base}}^{298.15K} a_{H^+}^$$

Case 3 - Influence of passivate (jarosite and gypsum) on combined ferric-proton chalcopyrite dissolution taking account into gangue minerals

The precipitation of secondary minerals requires

- 1. aqueous speciation
- 2. the calculation of the state of mineral saturation for each computational iteration
- 3. the implementation of either thermodynamic or kinetic control of the precipitation process

Jarosite: $2SO_{4(aq)} + K_{(aq)}^{+} + 6H_2O + 3Fe_{(aq)}^{3+} = KFe_3(SO_4)_2(OH)_{6(s)} + 6H_{(aq)}^{+}$ Gypsum: $Ca_{(aq)}^{+} + SO_{4(aq)}^{2-} + 2H_2O_{(aq)} = CaSO_4 \cdot 2H_2O_{(s)}$

The reaction rate expression for jarosite (Elwood Madden et al., 2012):

 $r = 10^{-6.487} [\text{H}^+]^{0.899} + 10^{-1} .964 [\text{OH}^-]^{0.392}$

Limitations of the Model

- 1. Focussed only on the kinetic rate-dependent process of chalcopyrite dissolution in stagnant or very slow-moving liquid coupling dissolution of gangue minerals and precipitation of secondary phases.
- 2. Heap hydrodynamics was not considered despite having the potential to affect this rate-dependent process.
- 3. For the sake of simplicity, a microbe-free model of a solely chemical heap system under ambient conditions was used.
- 4. An open system that was equilibrated with oxygen, where the oxygen was modelled to be constant during the simulation period.
- 5. Surface tension and gravity were not considered



Results & Discussion

Case 1 – comparison of different rates and reactions of chalcopyrite dissolution



Ferric- promoted > Combined ferric-proton > Proton-promoted

Case 1 – comparison of different rates and reactions of chalcopyrite dissolution



- Fe consumption/release controls chalcopyrite dissolution
- Sulphate release controls pH but H2S appears not to influence pH

Case 2 - Influence of gangue minerals on combined ferric-proton chalcopyrite dissolution



Hematite (Hem) > Silicate (Sil) > Anhydrite (Anh)

Hematite (Hem) > Anhydrite (Anh) > Silicate (Sil)

Case 2 - Influence of gangue minerals on combined ferric-proton chalcopyrite dissolution



- Hematite dissolution releases Fe and hematite reprecipitation leads to pH decline

- Sulphate release increases pH. Possible occlusion of Cu by anhydrite
- Silicate dissolution consume protons.

History Matching of Experimental Data (Role of surface area)



BET = EXTERNAL + INTERNAL SURFACE AREA



Rate, $R_{(CP-D)t} = (r * A_{CP-D})$ Coloured is copper mineral and grey is siliclastic gangue.

Where, $A_{CP-D}\left[\frac{m^2}{g}\right]$ is the reactive grain surface area of a specific mineral, $S_{A_i} = S_{A_BET}\left[\frac{m^2}{g}\right]$ is the overall BET specific surface area that was experimentally determined, r is the dissolution rate constant, n_i is the mole fraction of a specific mineral individual mineral phase in the total rock ore, $M_{wi}\left[\frac{mol}{g}\right]$ is the molecular weight of a specific mineral

Ansah et al 2022

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History Matching of Experimental Data



Rate,
$$R_{(CP-D)t} = (r^* A_{CP-D})$$

 $A_{CP-D} = S_{A_i} \cdot M_{wi} \cdot n_i \cdot f$

Where, $A_{CP-D}\left[\frac{m^2}{g}\right]$ is the reactive grain surface area of

a specific mineral, $S_{A_i} = S_{A_BET} \left[\frac{m^2}{g}\right]$ is the overall BET specific surface area that was experimentally determined, r is the dissolution rate constant, n_i is the mole fraction of a specific mineral individual mineral phase in the total rock ore, $M_{wi} \left[\frac{mol}{g}\right]$ is the molecular weight of a specific mineral and f [-] is the surface reactivity factor

Ansah et al 2022

Case 3 - Modelling the growth of a secondary mineral related to the reactive surface of the primary mineral

Rate, $R_{(CP-D)t} = (r^*A_{CP-D})$

$$A_{CP-(t)} = A_{CP(0)} * [n_d - K_p(n_p)^{\rho}]^{T}$$

 $A_{CP-D(t)} \ge 0$

The overall precipitation rate coupled to the chalcopyrite dissolution rate

1. Surface-passivate modelling (SPM + TST)

The overall precipitation rate not coupled to the chalcopyrite dissolution rate

 $A_{CP-D(t)} = A_{CP(0)} * (n_d)^{\rho}$

2. No surface-passivate modelling (TST)

Here, $A_{CP(0)}$ [m²/mol] is the original chalcopyrite mineral specific surface, n_p [mol] is the amount of precipitated mineral, ρ [-] is a sphericity factor (assumed to be 0.67 for uniformly dissolving spheres, n_d [mol] is the amount of dissolving mineral remaining, and K_p [-] is a proportionality factor modifying the amount of precipitate in contact with dissolving mineral SPM – surface passivate model; TST – transition state theory 23

Case 3 - Modelling the growth of a secondary mineral related to the reactive surface of the primary mineral



1. With SPM, there is a further decline in the Cu release rate as the surface area of the chalcopyrite is further reduced by the precipitated jarosite.

2. Considering SPM, there is less copper release than a model where this was not accounted for.



SPM – surface passivate model; TST – transition state theory (Ansah et al., 2023,...Minerals Engineering)

Case 3 - Influence of passivate (jarosite and gypsum) on combined ferric-proton chalcopyrite dissolution taking account into gangue minerals



Gypsum > Jarosite



Limitation of the model: incongruent dissolution

Incongruent dissolution of chalcopyrite in acid-only





Afs – Alkaline feldspar (KAlSi3O8) Ccp – chalcopyrite (CuFeS2) Bn – bornite (Cu5FeS4) Cv –covellite (CuS)

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Leaching in acid-only





Afs – Alkaline feldspar (KAlSi3O8) Ccp – chalcopyrite (CuFeS2) Bn – bornite (Cu5FeS4) Cv –covellite (CuS)

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How to model Incongruent dissolution of chalcopyrite ???



- Why does covellite precipitate, if it is highly undersaturated (~ -110) throughout the simulation?

- Why is the copper flux from chalcopyrite dissolution the highest when covellite (CuS) passivates the surface?

- Shouldn't we expect copper mobilised by chalcopyrite dissolution to precipitate as covellite and thereby reducing the dissolved copper concentration?



2. Limitation of the model: role of thickness and porosity of passivate layer

Passivation mechanism(s)



Source: Ansah et al., 2023

How to tackle passivation, where to look?



Edited after Klauber, 2008 and references therein

So, what...,?

- 1. Accurate representation of different rate laws and reaction mechanisms is important during modelling of chalcopyrite and gangues in heap leaching.
- 2. The mineral surface area is critical for modelling and understanding chalcopyrite leaching.
- 3. Need to consider the role of secondary minerals on the original surface area of a chalcopyrite during heap leach modelling.
- 4. Incongruent dissolution of chalcopyrite leading to residual Cu-S rich phase (e.g., covellite) remains a mystery to model.
- 5. Future models should consider porosity and thickness of passivate on chalcopyrite dissolution.

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The importance of reaction mechanisms and coupled dissolution with reprecipitation (CDR) reactions when modelling copper leaching in heap systems

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