

Modeling the Iodine-Assisted Chalcopyrite Leaching in Ferric Sulfate Media in Response to Operating Parameters in Heap Leaching

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Abstract

The iodine-assisted chalcopyrite leaching process involves the addition of iodine in ferric sulfate media to accelerate the dissolution of chalcopyrite at ambient temperature. This process is developed to mainly treat low-grade copper sulfide ores by heap leaching. To scale up the process from laboratory to industrial-scale heap leaching, it is essential to understand the fundamental processes that control the performance of the iodine-assisted chalcopyrite leaching in a heap leach environment. These fundamental processes include hydrodynamics, reaction kinetics, and heat transport, which can be controlled by manipulating various key design variables.

In this study, the effect of key design variables, including irrigation rate, ferric concentration, total iodide concentration, temperature, and heap height, on the copper extraction and the solution potential were investigated using the HeapSim 2D software. The HeapSim 2D model was calibrated using a kinetic equation developed for iodine-assisted chalcopyrite leaching and experimental data collected from the 1-m column leach tests. The sensitivity study shows that optimum copper extraction could be achieved by adjusting these key design parameters. The iodine-assisted leaching slowed down at potentials lower than 650 mV vs SHE, at which the predominant iodine species was iodide ions (I^-) and the leaching rate was similar to that of the conventional ferric sulfate leaching. Interestingly, passivation was not observed in the course of leaching and leaching was resumed with fast kinetics when the solution potential was sufficiently high (above 650 mV vs SHE).

Introduction

Heap leaching is considered to be an effective and economically viable technology for treating low-grade copper sulfide ores. Among all oxidants studied, ferric sulfate is the most commonly used lixiviant because

of process simplicity, proven downstream processes, and low capital and operating costs. However, the leaching process exhibits poor leaching performance when the dominant copper sulfide is chalcopyrite. The slow dissolution kinetics is related to a passivating layer, which has been reported to be metal-deficient sulfide ($M_{1-x}S_2$) (Buckley and Woods, 1984; Lu et al., 2000; Mikhlin et al., 2004), copper-rich, iron-deficient polysulfides (MS_n , $n > 2$) (Hackl et al., 1995), elemental sulfur (Dutrizac, 1989; Munoz et al., 1979), and iron precipitates (Antonijević et al., 2004; Córdoba et al., 2008).

JX Nippon Mining and Metals Corporation has developed a process called the iodine-assisted heap leaching of chalcopyrite ore to overcome the slow dissolution. This process involves the addition of 50 to 200 mg/L iodide to significantly enhance the dissolution of chalcopyrite in ferric sulfate media at ambient temperature (Manabe, 2012). The iodide ion is thought to be oxidized by ferric to diiodine (I_2), which can act as a strong oxidant (Eq. 1). Diiodine oxidizes chalcopyrite to release copper and iron and meanwhile is reduced to iodide (Eq. 2). Diiodine is continuously regenerated by ferric during leaching; hence, theoretically, the process does not require a continuous addition of iodine. Ferric ions are regenerated separately via ferrous oxidation assisted by iron-oxidizing bacteria (Kuwano et al., 2011).



The key factors that control the reaction rate and the mechanisms by which iodine accelerates the leaching kinetics have been investigated in previous studies by the authors (Winarko et al., 2022; 2020). Those studies reported that the solution potential was the primary factor affecting the process performance through influencing the iodine speciation. The dissolution rate was not hindered by the leaching product and iron precipitate. The dissolution rate of chalcopyrite in the process was described by Eq. 3.

$$X = 1 - \left(1 - 49.712 \exp\left(\frac{43,096}{R} \left(\frac{1}{298.15} - \frac{1}{T}\right)\right) \left(\frac{[Fe(III)]}{[Fe(II)]}\right)^{0.322} \left(\alpha[I_{total}] + \frac{2}{3}\beta(1 - \alpha)[I_{total}]\right)^{1.167} \cdot t(\text{day}) \right)^{3.236} \quad (\text{Eq. 3})$$

Where:

X is the fraction of the total copper dissolved,

t is the leaching time (in days),

R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$),

T is the leaching temperature in Kelvin,

$[Fe(III)]$, $[Fe(II)]$, and $[I_{total}]$ are the total concentration in mol/L of ferric, ferrous, and iodide, and

α and β are conversion factors of iodine ranging from 0 to 1.

This kinetic equation is essential to optimize the performance of the iodine-assisted leaching process in an industrial-scale heap leach pad.

To assist the simulation and prediction of heap leaching performance, the HeapSim 2D model has been developed, which incorporates solution transport, heat transport, and kinetics of reactions occurring inside a heap (Bouffard and Dixon, 2009). In the current study, the HeapSim 2D model was used to simulate the iodine-assisted chalcopyrite leaching. Two sets of 1-m column leaching tests were performed: one for calibration and the other for validation of the HeapSim 2D model. The calibrated model was then used to understand the effect of various heap leach design parameters, i.e., irrigation rate, solute concentration, temperature, and heap height on the leaching performance. The findings of this study will assist the optimization of the iodine-assisted heap leaching of chalcopyrite ore by manipulating the key design factors that determine the process performance.

Methodology

Column leaching tests for model calibration

Sample preparation

The copper ore used for the test had the following particle size distribution: 46% > 11.2 mm, 25% – 11.2 + 4.75 mm, and 29% < 4.75 mm. The copper content was analyzed using the sequential leaching method to obtain the acid soluble copper, the secondary copper sulfides or cyanide-soluble copper, and the primary copper sulfides or insoluble copper. The chemical analysis was performed using inductively coupled plasma-optical emission spectrometry (ICP-OES). The percentage distribution of copper is shown in Table 1.

Table 1: The distribution of copper minerals in the ore used for the column tests for model calibration

	Total Cu	Acid soluble Cu	Secondary Cu sulfides	Primary Cu sulfides
Grade (%)	0.616	0.026	0.026	0.564
Cu (%)	100	4.22	4.22	91.56

Column leaching test procedure

The column leaching tests were carried out in polypropylene columns of 10 cm in diameter and 1 m in height. The inner surface was coated with a PTFE film to prevent iodine loss by adsorption onto the plastic material. Each column contained 12 kg of primary copper sulfide ore.

The column leach tests were performed at two total iodide concentrations, i.e., 100 and 200 mg/L. For comparison, a control test similar to conventional ferric sulfate leaching in the absence of iodine was also performed. All column leach tests were conducted at the atmospheric pressure and the room temperature (~25 °C) and at an initial ferric concentration of 5 g/L. The conditions under which the column tests were carried out for the model calibration are shown in Table 2. For the tests with iodide addition, iodide and

ferric solutions were introduced separately to prevent loss of diiodine by evaporation before iodine came into contact with the ore. The total solution flowrate was set at 1 L/day.

Table 2: Experimental design of the column leaching tests used for the model calibration

Column leaching tests	[Fe(III)]	[I _{total}]	Solution flow rate, L/day	
	g/L	mg/L	KI	Fe ₂ (SO ₄) ₃
Control test	5	0	0	1
Total iodide concentration	5	100	0.5	0.5
	5	200	0.5	0.5

The column leaching tests were run in three sequential stages: acid leaching, ferric leaching, and iodine leaching.

1. Acid leaching stage: the columns were initially irrigated with sulfuric acid solution at pH 1.2 for 8 days. The ratio of the total volume of leaching solution to the mass of the ore was 0.7 m³/tonne ore for this stage.
2. Ferric leaching stage: the columns were then irrigated with a ferric sulfate solution at 5 g/L Fe(III) for 14 days. The ratio of the total volume of leaching solution to the mass of the ore was 1.9 m³/tonne ore for this stage.
3. Iodine leaching stage: all columns continued to be irrigated with a ferric sulfate solution, but two of the three columns (except the control test) were also irrigated with an iodide solution. Ferric sulfate and iodide were supplied to the columns via two separate feed solutions to prevent iodine loss via volatilization during solution preparation. The flow rate of the two feed solutions was fixed at 0.5 L/day, which gave a total solution flow rate of 1 L/day. The tests were completed when the ratio of the total volume of the leaching solution to the mass of the ore reached 10 m³/tonne ore (125 days).

Solution samples were collected weekly and analyzed by ICP-OES for concentrations of the total Cu and the total Fe. The solution pH and ORP and the total iodide concentration were measured weekly. At the end of the column leach tests, the residues were digested and analyzed for the copper and iron contents by ICP-OES.

Column leaching tests for model calibration

Sample preparation

A different copper ore was used in the column leaching tests for the model validation. The ore has a particle size (P₈₀) of 20 mm. The total copper content in this ore was 0.57% – 0.60%, of which 0.02% Cu was acid soluble, 0.01% – 0.02% Cu was secondary, and 0.53 – 0.57% was primary copper sulfides.

Column leaching test procedure

Column leaching tests for the model validation were carried out in a column of a different dimension and at a flowrate and ferric and iodide concentrations different from the tests used for the model calibration. The column leaching tests for the model validation were carried out in columns of 1 m in height and 15 cm in diameter at the atmospheric pressure and the room temperature (~25 °C). The column contained around 25 kg of the ore sample and was irrigated at a solution flowrate of 1.9 L/day.

Two tests were performed: one without iodide addition similar to conventional ferric sulfate leaching as control and the other at 100 mg/L total iodide. The initial total iron concentration was set at 5 g/L. The column test with iodide addition was first irrigated with only ferric sulfate solution for 21 days to remove secondary copper sulfides. Then, ferric sulfate and iodide solutions were supplied separately to the column. The flowrate was adjusted to 1.7 L/day for the ferric sulfate solution and 0.2 L/day for the iodide solution.

Model calibration and validation

The HeapSim 2D model was used in this study to simulate the 1-m column leaching tests. The kinetic model developed in the stirred reactor tests (Eq. 3) was rearranged to (Eq. 4), which was then incorporated into the HeapSim 2D model.

$$r = \frac{dC_{cpy}}{dt} = \rho_b \frac{k_{cpy}}{C_{cpy,0}^{(\varphi-1)}} \exp \left[\frac{43,096}{R} \left(\frac{1}{298.15} - \frac{1}{T} \right) \right] \left(\frac{[Fe(III)]}{[Fe(II)]} \right)^{0.322} \left[\alpha [I_{total}] + \frac{2}{3} \beta (1 - \alpha) [I_{total}] \right]^{1.167} C_{cpy}^{\varphi} \quad (\text{Eq. 4})$$

Where:

r is the rate of chalcopyrite dissolution,

k_{cpy} is the rate constant at the reference temperature (25 °C),

ρ_b is the bed packed density (kg/m³_{heap}),

$C_{cpy,0}$ is the concentration of chalcopyrite in ore at $t = 0$ (kmol/kg),

C_{cpy} is the concentration of chalcopyrite in ore at time t (kmol/kg),

φ_{cpy} is the topological exponent corresponding to the degree of liberation.

In the model calibration, the intrinsic parameters controlling the leaching reaction, including the activation energy and the reaction orders, were maintained the same as derived from the reactor tests. Because the size fraction and the characteristics of the ore used in the column tests were different from those in the reactor tests, the topological exponent (φ_{cpy}) and the rate constant (k_{cpy}) that could represent these differences were adjusted in the model calibration. The model calibration was carried out using the first set of column leaching data. Then, the calibrated model was validated with the second set of column tests. During model validation, the rate constant (k_{cpy}) was the only parameter adjusted.

Sensitivity test

The calibrated model was used to simulate column leaching performance under different key design parameters, i.e., irrigation rate, solute concentration (including ferric and iodide concentration), temperature, and column height. The data obtained from the simulations included the percentage of copper extraction and the solution potential. The conditions under which the simulations were performed are shown in Table 3.

Table 3: The variations of key design parameters investigated in the sensitivity test

Parameters	Design parameters				
	Irrigation rate (L/m ² /h)	[Fe(III)] (g/L)	[I _{total}] (mg/L)	Temperature (°C)	Column height (m)
Irrigation rate	2.65	5.0	200	25	1.0
	5.30	5.0	200	25	1.0
	7.95	5.0	200	25	1.0
	10.60	5.0	200	25	1.0
Ferric concentration	5.30	2.5	200	25	1.0
	5.30	5.0	200	25	1.0
	5.30	10.0	200	25	1.0
	5.30	15.0	200	25	1.0
Iodide concentration	5.30	5.0	50	25	1.0
	5.30	5.0	100	25	1.0
	5.30	5.0	150	25	1.0
	5.30	5.0	200	25	1.0
	5.30	5.0	250	25	1.0
Temperature	5.30	5.0	200	15	1.0
	5.30	5.0	200	25	1.0
	5.30	5.0	200	35	1.0
	5.30	5.0	200	30	1.0
	5.30	5.0	200	35	1.0
Column height	5.30	5.0	200	25	0.5
	5.30	5.0	200	25	1.0
	5.30	5.0	200	25	2.0
	5.30	5.0	200	25	4.0

Results and discussion

Model calibration

Figure 1a shows the copper extraction over time at three different total iodide concentrations for the 1-m high column tests for the model calibration. For all three tests, the conventional ferric sulfate leaching was carried out for the initial 21 days to remove acid soluble copper minerals and secondary copper sulfides. From day 21 onwards, copper was dissolved very slowly in the absence of iodine, with a dissolution rate of $< 0.05\%$ copper per day. By contrast, the addition of iodide significantly accelerated the kinetics of the copper dissolution. The copper extraction reached 54.7% in the presence of 200 mg/L total iodide on day 125, whereas the conventional ferric sulfate leaching achieved only 6.5% copper extraction during the same leaching period.

Figure 1b depicts the solution potential of the pregnant leach solution over time during leaching. The solution potential measured of the conventional ferric sulfate leaching test was the highest among the three tests, because the least amount of ferric was consumed by chalcopyrite oxidation. The potentials were similar in the presence of 100 mg/L and 200 mg/L total iodide. This was attributed to the existence of a potential window, within which the oxidized iodine species (diiodine and triiodide) are predominant and act as the oxidants for chalcopyrite dissolution. Once the solution potential decreased to below the lower limit of the potential window, ferric became the main oxidant and the conventional ferric leaching kicked in.

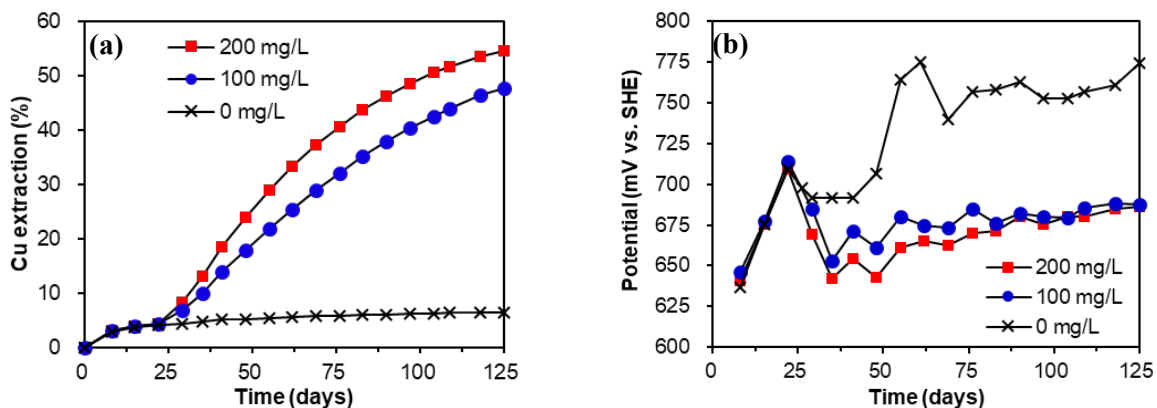


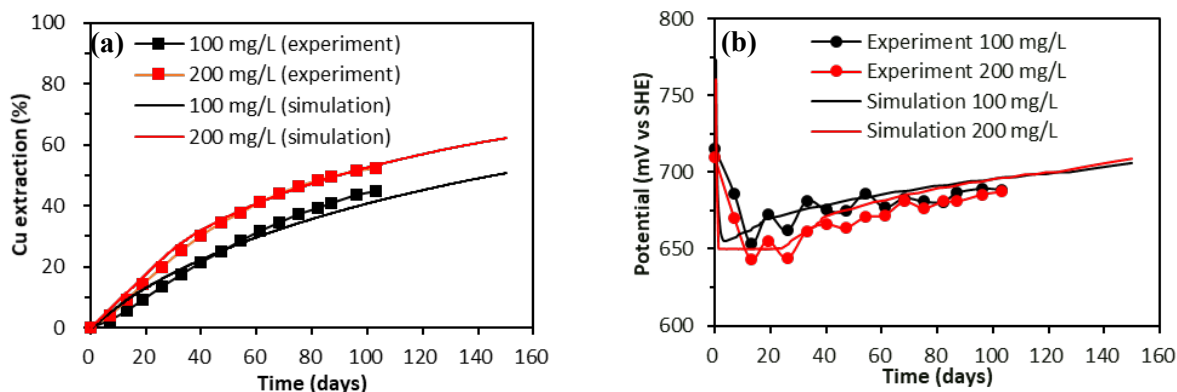
Figure 1: Experimental results of 1-m column leaching tests used for model calibration without and with the addition of 100 and 200 mg/L of iodide at room temperature ($\sim 25^\circ\text{C}$): (a) cumulative copper extraction; (b) solution potential during leaching

The model calibration used the column leaching data in the presence of iodine collected from day 22 onwards. The copper extraction was adjusted to account for the extraction from only chalcopyrite, which contained 0.564% of the total copper, because the acid soluble and secondary copper were removed in the first 21 days of leaching. The calibrated parameter values are presented in Table 4.

Table 4: The calibrated values of all leaching kinetic parameters

Parameters	Description	Value	Unit
φ_{cpy}	Topological exponent, corresponding to degree of liberation	3.6	–
k_{cpy}	The rate constant at reference temperature (25 °C)	34.56	1/day

The model with these calibrated parameters could satisfactorily simulate the copper extraction and the solution potential during leaching (Figure 2). The pregnant leach solution has lower potential values in the presence of iodine than the control test, because a higher amount of chalcopyrite was dissolved for the same period of time. With the addition of 200 mg/L iodide, the potential reached 650 mV vs SHE and remained stable at this value for the first 50 days of leaching. This suggests that there was not enough ferric in the column to maintain the potential in the range where the oxidized iodine species were predominant. When the potential was at 650 mV, conventional ferric leaching was responsible for chalcopyrite dissolution. As more ferric was provided to the column via irrigation and the leaching became slower, the potential eventually started to increase to around 688 mV vs SHE.

**Figure 2: The calibration of the kinetic parameters in the 1-m column leaching tests used in model calibration: (a) copper extraction; (b) solution potential****Table 4: The calibrated values of all leaching kinetic parameters**

Parameters	Description	Value	Unit
φ_{cpy}	Topological exponent, corresponding to degree of liberation	3.6	–
k_{cpy}	The rate constant at reference temperature (25 °C)	34.56	1/day

Model validation

Figure 3 shows the copper extraction and the solution potential during leaching without and with the addition of 100 mg/L total iodide for the model validation. The columns were initially irrigated with only ferric sulfate solution until day 25. The copper extractions achieved in both tests during this period were

MODELING THE IODINE-ASSISTED CHALCOPYRITE LEACHING IN FERRIC SULFATE MEDIA
IN RESPONSE TO OPERATING PARAMETERS IN HEAP LEACHING

similarly low (around 4% Cu). However, the copper extraction was significantly enhanced by the addition of 100 mg/L iodide (Figure 3a). In the presence of iodine, the rate of copper dissolution was faster (37.1% Cu extraction at the end of leaching) and the leaching reaction did not cease after 144 days (Figure 3b), while the control test (0 mg/L iodide) was very slow and only achieved 8.5% copper extraction in 144 days. It indicated that the chalcopyrite particles were not passivated in the course of leaching and iodine can significantly enhance the dissolution rate of chalcopyrite.

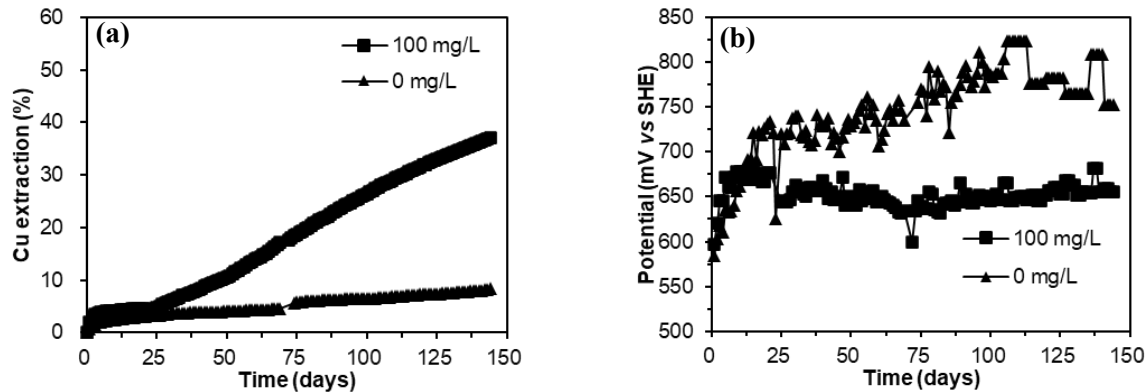


Figure 3: Experimental results of 1-m column leaching tests used in model validation without and with the addition of 100 mg/L of iodide at room temperature (~25 °C): (a) cumulative copper extraction; (b) solution potential during leaching

Note that the copper dissolution rates in this test were lower than those obtained from the 1-m column leaching tests for the model calibration. For example, on day 100, 28% copper extraction was achieved in this test as opposed to 42% in the test used for model calibration. This was attributed to the lower ratio of iodine to the mass of ore used in the test for model validation. Figure 3b shows that the solution potentials with the addition of 100 mg/L iodide were lower than those without iodide addition, because the former had higher levels of ferric consumption and ferrous generation from chalcopyrite oxidation.

By using the same topological exponent, the model was validated using the experimental data of the 1-m column leaching test. To satisfactorily describe the leaching kinetics of this 1-m column test, the rate constant was reduced from 34.56/day (model calibration) to 10.37 /day (model validation) to account for the lower ratio of iodine to the ore mass for this column test. The simulation results of the copper extraction and the solution potential for this column test are shown in Figure 4.

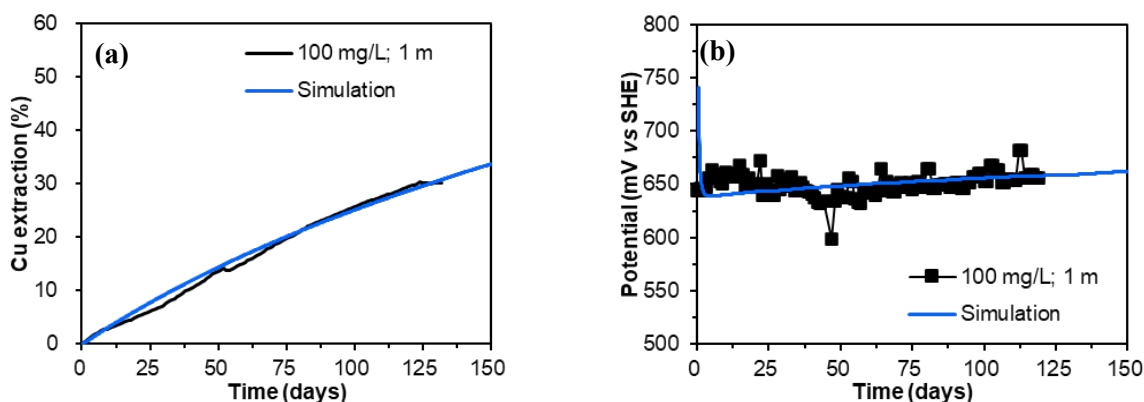


Figure 4: The calibration of the kinetic parameters in the 1-m column leaching test used in model validation: (a) copper extraction; (b) solution potential

Sensitivity tests

Sensitivity tests were performed to investigate the response of the leaching performance to variations in key design and operating parameters. The key parameters investigated were irrigation rate, ferric concentration, total iodide concentration, temperature, and column height.

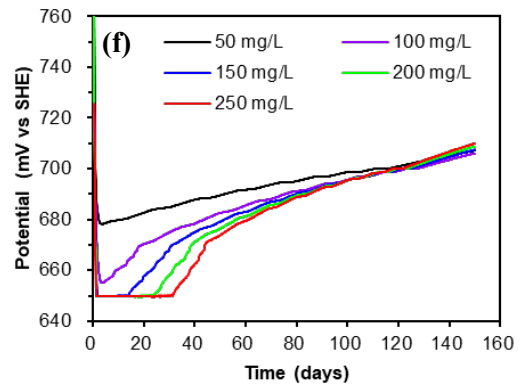
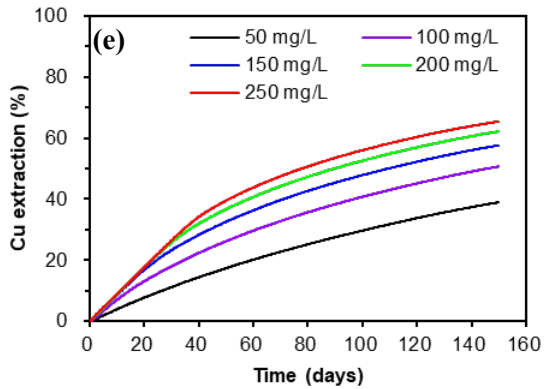
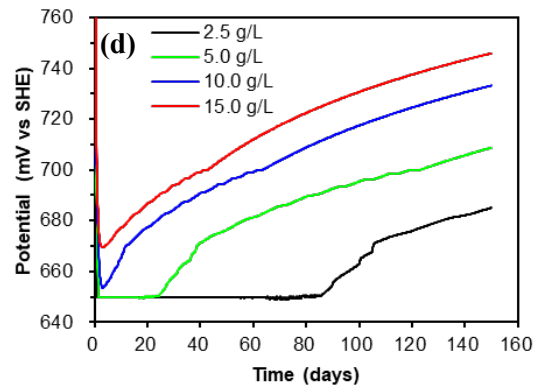
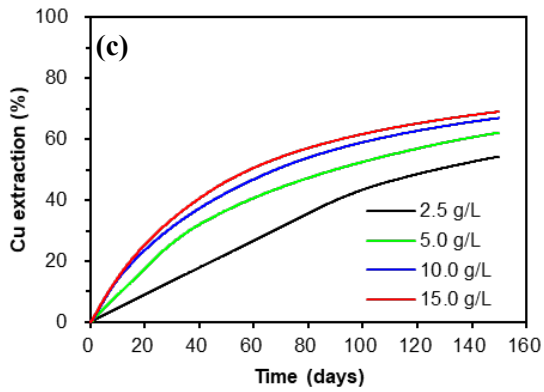
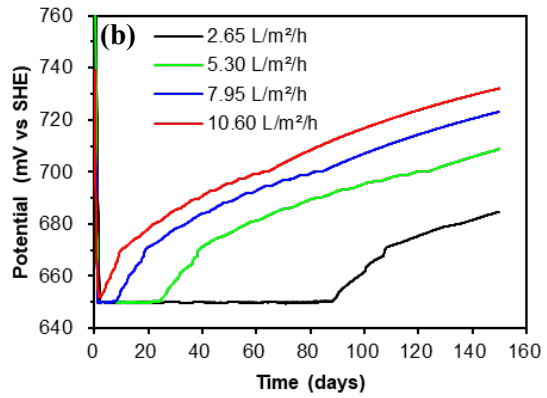
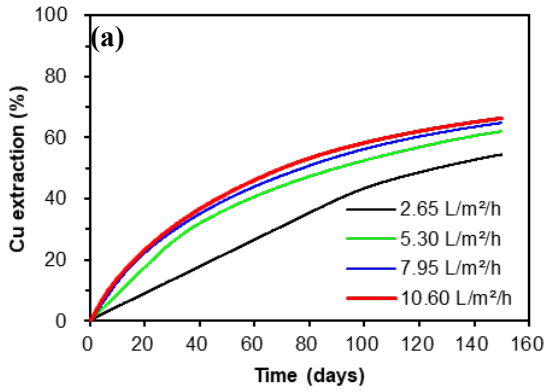
Figures 5 a and b show the leaching performance in response to changes in the irrigation rate. The results indicate the existence of an optimal irrigation rate, beyond which the leaching performance can no longer be improved. A similar conclusion can be drawn on the ferric concentration that the copper extraction increased with the ferric concentration up to a certain value, as shown in Figure 5c and d. This corresponds to the potential window within which the oxidized forms of the iodine species are predominant and act as the oxidants for chalcopyrite dissolution.

To further improve the leaching performance, a higher concentration of iodide must be added, along with sufficient ferric concentration or irrigation rate to maintain the potential value in the suitable range (Figure 5e and f). Raising temperature leads to an increase in the copper extraction, as shown in Figure 5g and h. The increase in the column height lowers the rate of copper extraction because of the decreasing amount of the oxidant available per unit mass of ore (Figure 5i and j). Reduction in the particle size is thought to increase the degree of liberation of chalcopyrite, thereby enhancing chalcopyrite dissolution (Winarko et al., 2022). However, the actual choice of these design and operating parameters must take into consideration the geotechnical stability of the heap and the possible occurrence of iron precipitation at higher ferric concentrations.

Figure 5b, d, f, h, and j show that the solution potential drops to 650 mV vs SHE when the ratio of ferric concentration to the mass of ore is low. Under these conditions, the column is segregated into two regions, the iodine leaching region and the conventional ferric leaching region. The former appears when the solution potential is above 650 mV vs SHE, whereas the latter occurs at potentials lower than 650 mV

MODELING THE IODINE-ASSISTED CHALCOPYRITE LEACHING IN FERRIC SULFATE MEDIA
IN RESPONSE TO OPERATING PARAMETERS IN HEAP LEACHING

vs SHE. The iodine leaching region expands as leaching progresses. When the dissolution becomes slower over time, the potential of the pregnant leach solution (PLS) gradually increases.



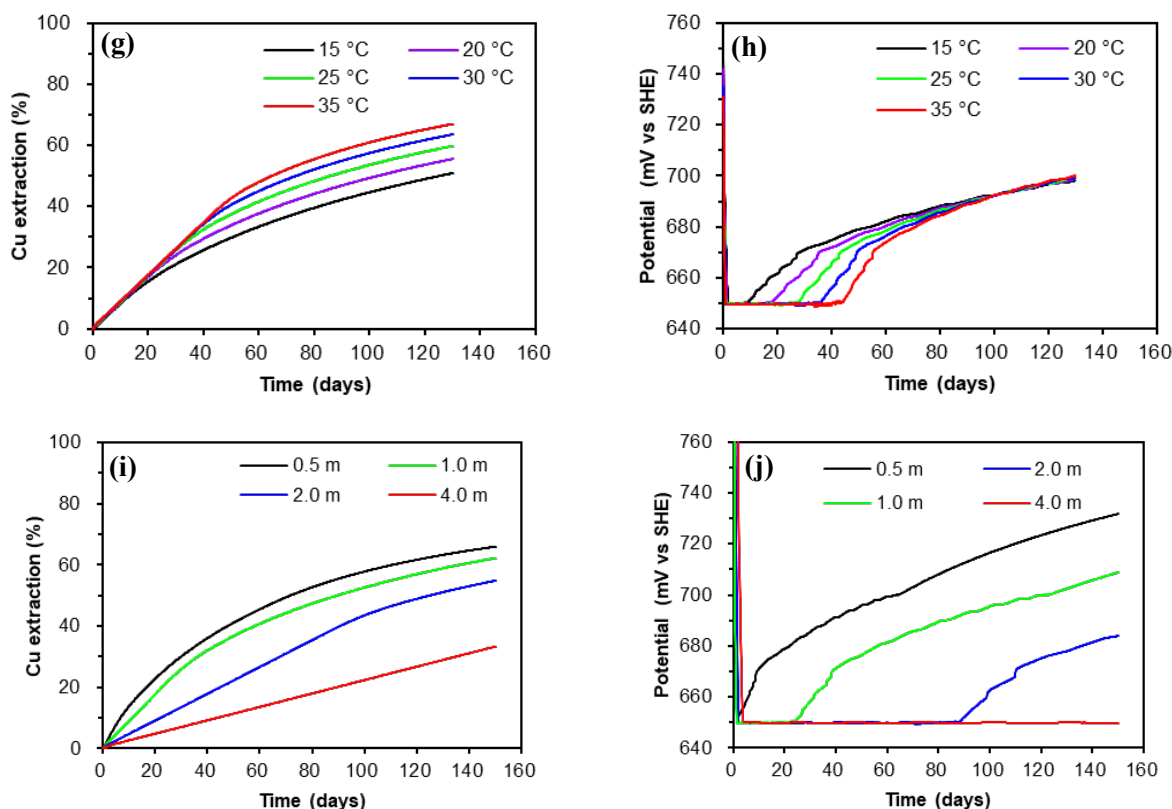


Figure 5: The simulation of copper extraction and solution potential trends for column leaching under the following conditions (5.30 L/m²/h of irrigation rate, 5 g/L of ferric concentration, 200 mg/L of total iodide concentration, 25°C, and 1 m in height), except the parameter under investigation: different irrigation rate (a-b), different ferric concentration (c-d), different total iodide concentration (e-f), different temperature (g-h), and different column height (i-j)

Conclusions

Chalcopyrite dissolution was enhanced in the presence of iodine in ferric sulfate media. The kinetic modeling of the column tests shows that the performance of the iodide-assisted chalcopyrite leaching is dependent on the solution potential. When ferric was insufficient, the potential measured in the PLS dropped and maintained stable at 650 mV vs SHE, at which the leaching kinetics was very slow. In this case, the predominant iodine species becomes iodide as the solution percolates towards the end of the column; thus, the leaching process becomes conventional ferric sulfate leaching. Therefore, it is important to supply sufficient ferric to maintain the potential in the entire column within the range where diiodine or triiodide are predominant. All copper extraction curves show that the leaching did not plateau, meaning that the leaching would proceed as long as a fresh ferric solution is continuously supplied.

The simulations indicate that there is an optimal value of irrigation rate and ferric concentration, beyond which further increases do not lead to significant improvements in the copper extraction. To further improve the leaching performance, a higher concentration of iodide must be added, along with sufficient

ferric concentration or irrigation rate to maintain the potential value in the suitable range. In general, the copper extraction increases with increasing temperature. The actual choices of these design and operating parameters must take into consideration the geotechnical stability of the heap and the possible occurrence of iron precipitation at higher ferric concentrations.

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