Effect of the Jetti Catalyst on the Dissolution of Chalcopyrite and Bornite – A Chemical and Electrochemical Analysis

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ABSTRACT

Using pulverized, pure mineral specimens, the Jetti leach catalyst is shown to increase leach kinetics of both chalcopyrite and bornite where after 24 hours, copper recovery increased from 10% to 39% on chalcopyrite and from 39% to 79% for the bornite sample studied. Under conventional acid-ferric sulfate leaching, bornite leaches in two stages, a rapid first stage kinetic where approximately 30% of the copper is leached until a passive Cu_2FeS_2 phase is formed. This passive condition is also seen in chalcopyrite leaching; however, second stage bornite remains more active than chalcopyrite as shown through lower rest potential and smaller potential difference (ΔOCP = OCP2-OCP1). Leach kinetics are independent of ORP within the range of 480 to 540 mV vs Saturated Ag/AgCl.

INTRODUCTION

Chalcopyrite ($CuFeS_2$), the most abundant copper-bearing mineral, accounts for approximately 70% of the world's known copper reserves (Zhao et al., 2019). Unlike bornite, chalcopyrite exhibits a highly stable tetragonal crystal structure with strong covalent bonding between copper, iron, and sulfur atoms, contributing to its well-documented refractory nature in hydrometallurgical processes. Its dissolution in acidic ferric sulfate solutions is notoriously slow, which has posed a major challenge for commercial heap leaching operations. Traditional explanations for chalcopyrite passivation involve the formation of surface layers rich in sulfur or copper, acting as diffusion barriers that hinder further reaction; however, more recent research suggests that an alternative mechanism involving semiconductor properties is responsible for its sluggish dissolution.

Specifically, electrochemical studies indicate that preferential iron dissolution during chalcopyrite leaching leads to the formation of a copper-rich, iron-deficient surface layer with p-type semiconductor behavior. This p-type layer, when formed on the n-type bulk chalcopyrite, creates a

p-n junction, which significantly alters the electrochemical properties of the mineral (Ren et al., 2022). The depletion region of this junction inhibits charge transfer, effectively slowing oxidation and dissolution processes. Understanding this semiconductor effect is crucial for developing strategies to enhance chalcopyrite leaching efficiency.

Bornite (Cu_5FeS_4), commonly known as "peacock ore" due to its characteristic iridescent tarnish, is an important copper-iron sulfide mineral in the global copper industry. With a high copper content of approximately 63% by weight, bornite is a valuable ore for copper extraction. The first report on the bornite leaching dates back to 1931 (Sullivan, 1931). Previous studies have suggested that bornite dissolution is generally faster than that of chalcopyrite, particularly in ferric sulfate and chloride media, but the mechanisms governing its leaching kinetics remain incompletely understood (Price & Chilton, 1981; Zhao et al., 2015). Previous studies suggest that bornite exhibits a more rapid initial dissolution due to its higher reactivity, but its multi-stage transformation introduces complexities that have not been fully characterized (Yang et al., 2018). While some research has indicated that bornite leaching may also be influenced by surface passivation effects, the role of semiconductor properties and electrochemical factors has not been extensively explored.

Jetti has been evaluating a leach catalyst which is known to increase leach kinetics of chalcopyrite under conventional acid-ferric sulfate leaching conditions, and in this study, we investigate and compare the leaching behaviours of pure bornite and chalcopyrite under control conditions and in the presence of the Jetti catalyst using electrochemical analysis and leaching tests. By examining their dissolution mechanisms in detail, we aim to provide new insights into the factors governing copper extraction from these minerals and contribute to the optimization of hydrometallurgical processes.

METHODOLOGY

For leaching tests, pure natural chalcopyrite and bornite samples were used. The minerals were pulverized and sieved to particle size between 75 and 106 μm. The lixiviant used in leaching contains 1.7 g/L Fe^{3+} from ferric sulfate at pH 1.7 adjusted by sulfuric acid. The lixiviant used in bioleaching experiments also contained *Acidithiobacillus ferrooxidans* for the regeneration of ferric ion. Leaching tests were conducted in a 1-L bioreactor under ambient conditions at a stirring speed of 500 rpm. A pulp density of 5 g/L was used. Use of low pulp density in leaching tests ensures minimal change to the solution matrix during the experiment. Copper and iron concentrations were analyzed with ICP-AES.

For electrochemical analysis, pure bulk chalcopyrite mineral specimen was used. The minerals were mounted in epoxy resin with electrical contact provided on the unexposed side via conductive epoxy bonding of the mineral with a copper wire. All bulk mineral electrodes were prepared in an identical

manner. All electrochemical experiments were performed at room temperature using a VersaSTAT 4 potentiostat/galvanostat controlled by VersaStudio software. A conventional three-electrode electrolytic cell was used for electrochemical analysis. All electrode potential in this study is reported with respect to the Ag/AgCl reference electrode.

Cyclic voltammetry (CV) was used to reveal the *I-V* characteristics of chalcopyrite samples. The electrolyte used in the tests was DI water acidified by hydrochloric or sulfuric acid to pH 1.7. The CV test was conducted at a scan rate of 0.05 V per second.

X-ray powder diffraction analysis was carried out using Bruker D8 diffractometer with the Co x-ray source from 5 to 80 degree. The diffraction patterns were analyzed using Match3 software with mineral composition calculated using Pawley refinement for peak fitting.

RESULTS AND DISCUSSION

XRD analysis on chalcopyrite mineral and bornite mineral used in this work are shown in Figure 1 and Figure 2 respectively. Mineral specimen from Morocco shows high purity with 98.1% chalcopyrite. And the bornite specimen from Congo shows 84.4 % bornite.

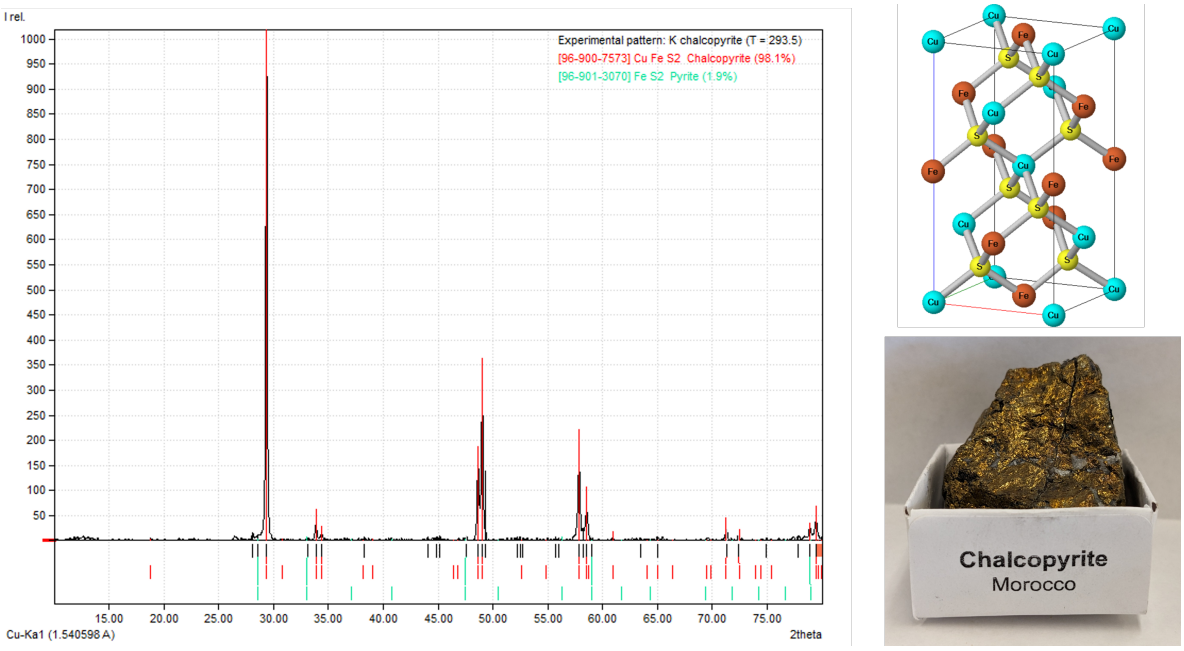


Figure 1 XRD pattern of chalcopyrite mineral, with its image and structure included

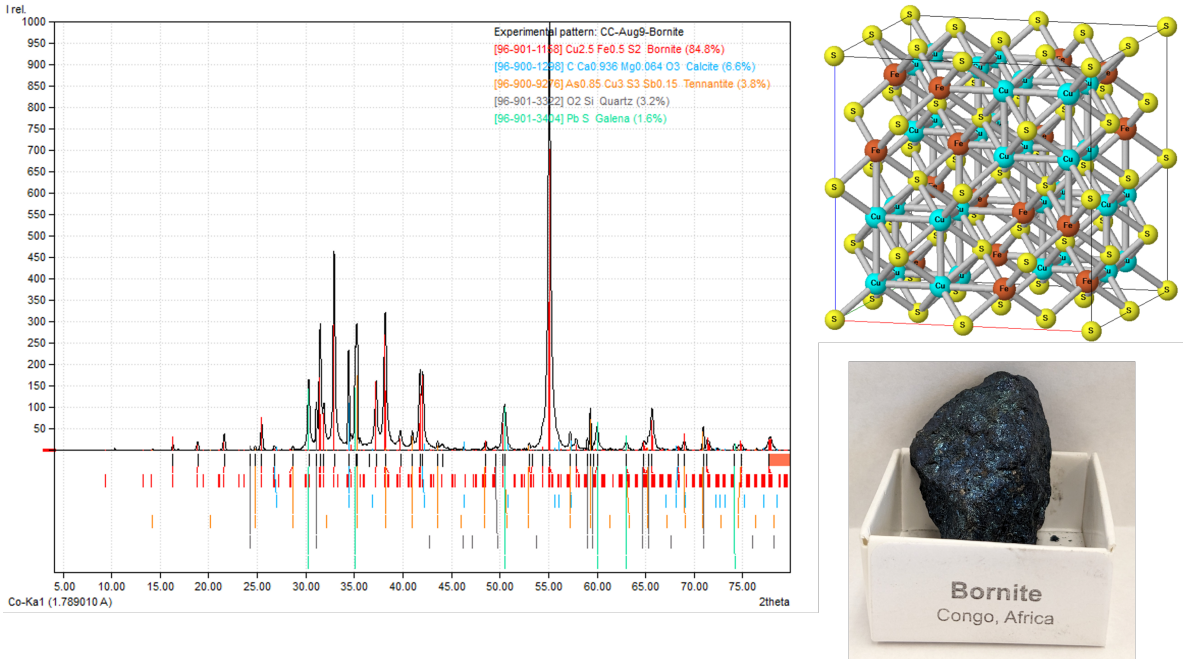


Figure 2 XRD pattern of bornite mineral, with its image and structure included

Cyclic voltammetry (CV) was performed on the bulk minerals configured as electrodes, and the resulting voltammograms for chalcopyrite and bornite are presented in Figure 3. For chalcopyrite, the open-circuit potential measured during the forward scan (OCP_1, from −0.1 to 0.6 V vs. Ag/AgCl) is approximately 0.20 V, which is lower than the open-circuit potential measured during the reverse scan (OCP_2, from 0.6 to −0.1 V) at about 0.35 V. A similar trend is observed for bornite, where OCP_1 (0.13 V) is lower than OCP_2 (0.20 V). This behavior is typical of passivation in metals and alloys (Tait, 2018) with the higher OCP_2 indicating that, after anodic polarization, the electrode surface becomes more stable than in its original state.

It is also noteworthy that, within the same electrolyte, both OCP_1 and OCP_2 for chalcopyrite are higher than those for bornite. This suggests that chalcopyrite is more refractory than bornite under oxidative dissolution conditions, consistent with its known slower dissolution kinetics.

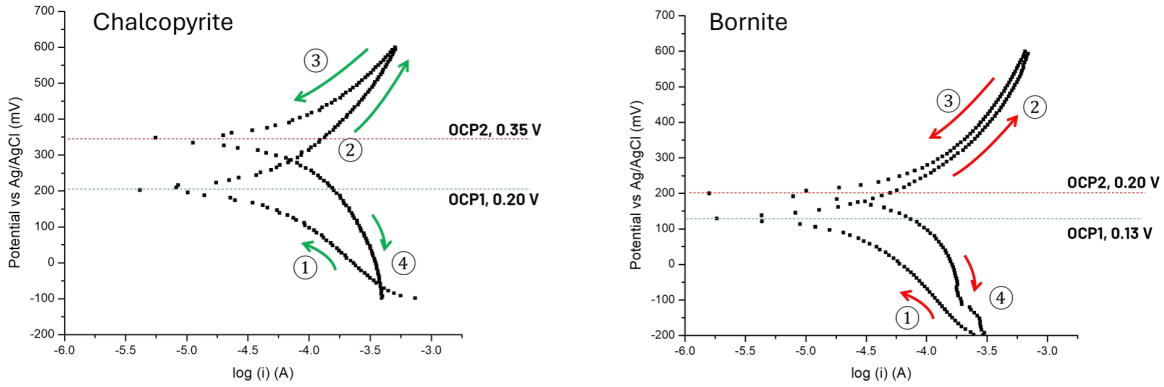


Figure 3 Cyclic voltammetry of the chalcopyrite mineral in acidic chloride and acidic sulfate media

Leaching tests using pulverized chalcopyrite and bornite minerals were performed, and the results are presented in Figure 4. Both minerals were crushed in a ring mill and sieved to achieve a particle size range of 75–106 μm. The tests were carried out in the same acidic ferric sulfate lixiviant for comparative purposes. After 24 hours, chalcopyrite under the control condition achieved only 10% copper recovery, and the leaching profile appeared to reach a near-plateau. In contrast, bornite under the same control condition exhibited a much higher initial dissolution rate, achieving 27% copper extraction within the first hour; however, its dissolution rate also declined significantly afterward, reaching 39% at 24 hours.

The effect of the Jetti catalyst was then evaluated. For both chalcopyrite and bornite, the addition of the catalyst substantially enhanced the leaching rate. After 24 hours, the copper recovery increased to 49% for chalcopyrite and 79% for bornite, highlighting the catalyst's significant impact on both minerals.

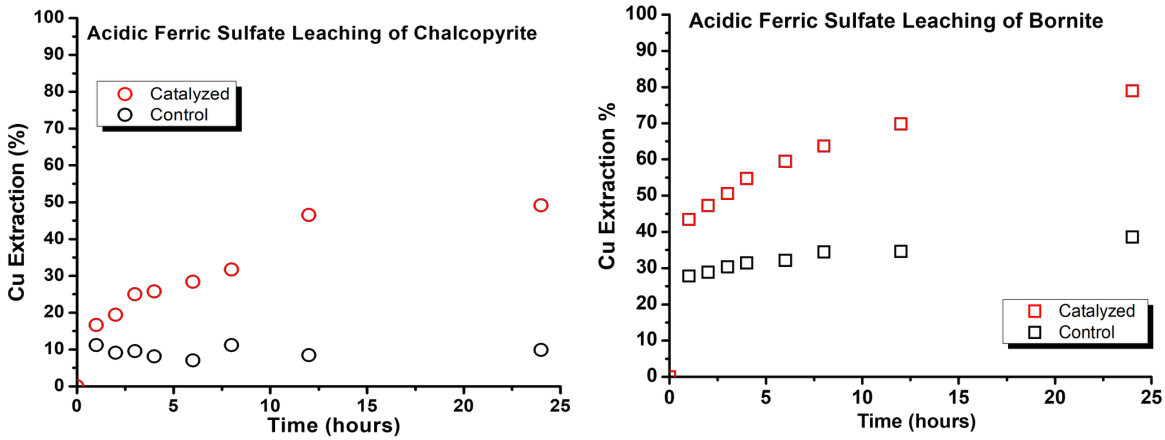
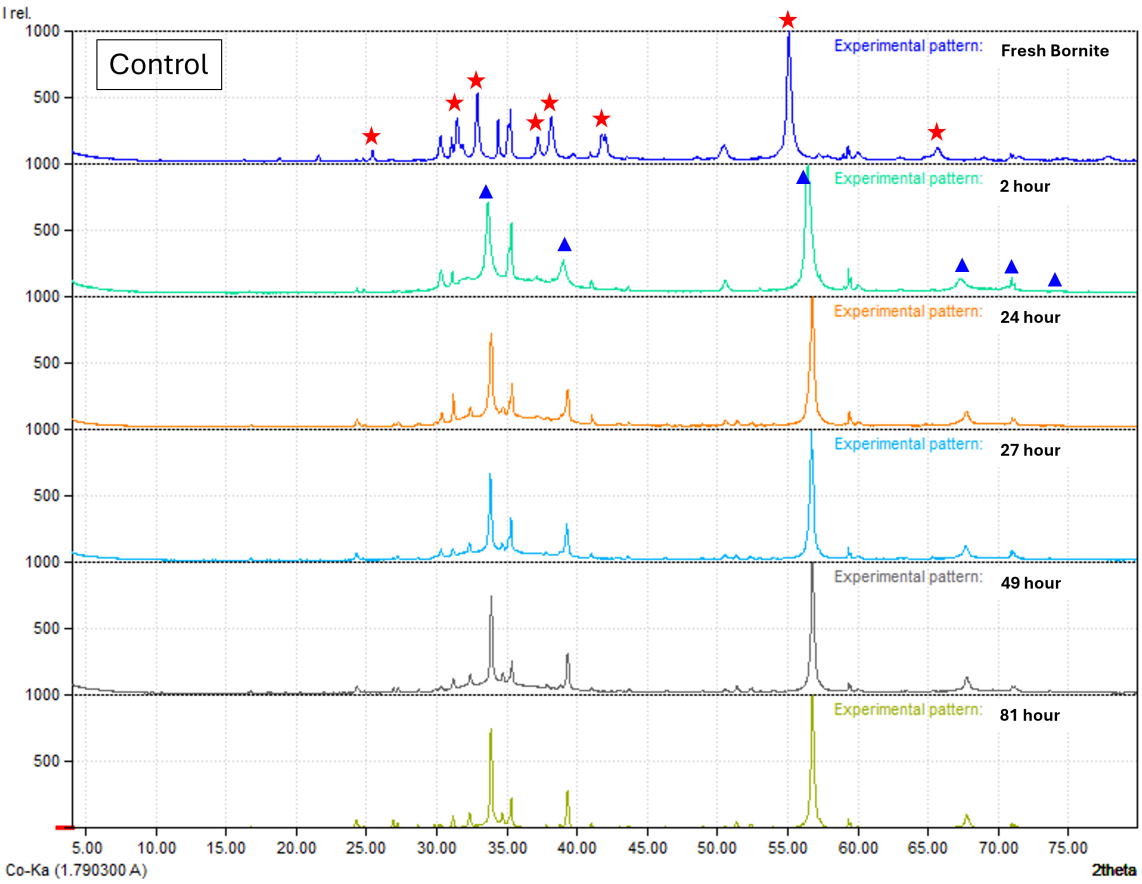


Figure 4 Leaching chalcopyrite and bornite mineral with acidic ferric sulfate media under catalyzed and uncatalyzed conditions

To further reveal the reaction mechanism of bornite in acidic ferric sulfate media, a replicate test identical to the one shown in Figure 4 (right) was conducted where the solid was collected during the leaching and analysed by X-ray powder diffraction.

Figure 5 A shows the transition of bornite from fresh mineral to the residue. It can be clearly observed that the mineral transitioned from Cu_5FeS_4 to Cu_2FeS_2 rapidly within 2 hours of leaching. The Cu_2FeS_2 phase is actually the $Cu_8Fe_4S_8$ phase as previously identified by Ding (Ding et al., 2005). This transition is also highly thorough with no sign of the original Cu_5FeS_4 remaining in the residue after 2 hours of leaching. In addition, although under catalyzed conditions, Jetti catalysed reaction reached 44% Cu recovery compared with 29 % for control in the first 2 hours.

Between 2 hours and 81 hours of leaching, the XRD pattern of the solid residue from either control or Jetti-catalyzed reactors did not show significant variation despite the significantly higher extraction in Jetti-catalyzed test. All the residue shows Cu_2FeS_2 being the dominant phase with > 80% content. No other copper containing species were generated through this leaching period. This result suggests that the dissolution of Cu_2FeS_2 may not involve multiple steps, or intermediate species.


I rel.
Control
Experimental pattern: Fresh Bornite
Experimental pattern: 2 hour
Experimental pattern: 24 hour
Experimental pattern: 27 hour
Experimental pattern: 49 hour
Experimental pattern: 81 hour
1000
500
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
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Co-Ka (1.790300 A)
2theta

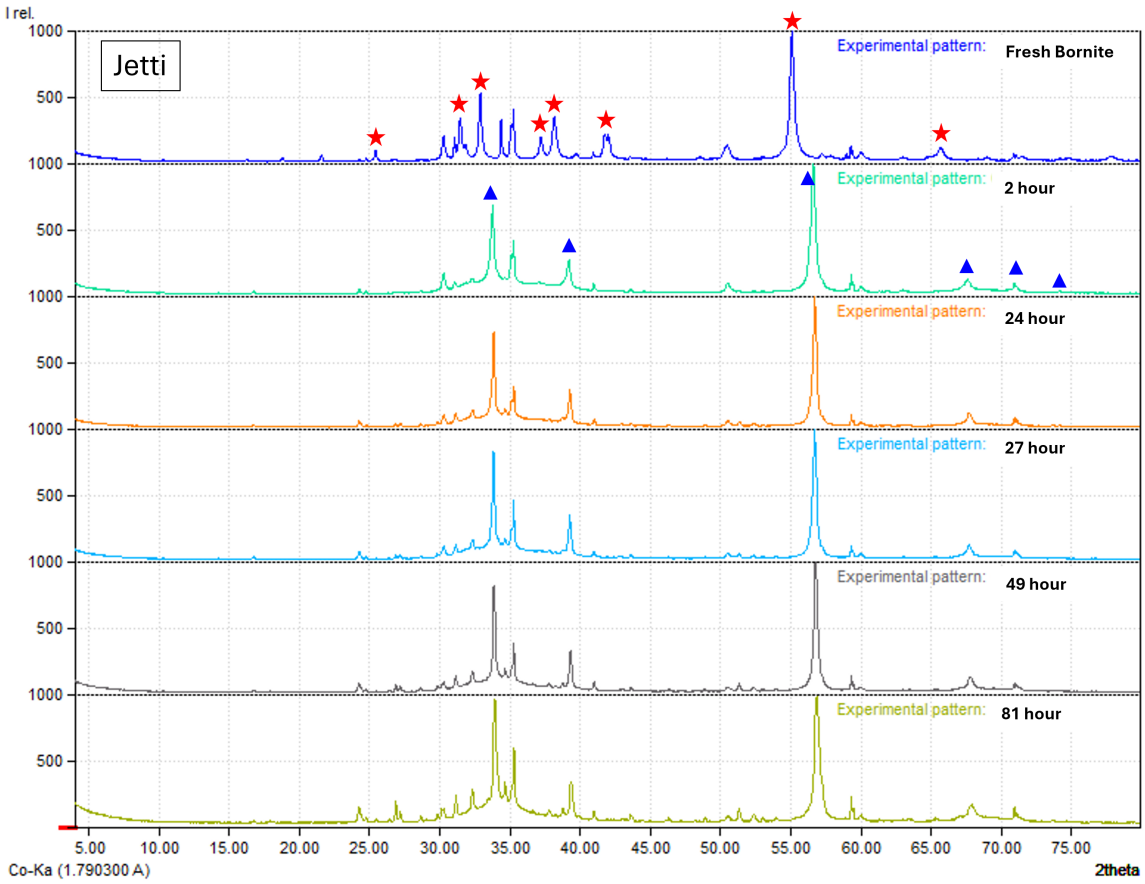

Figure 5 XRD diffraction pattern for the residue collected during different stage of leaching for control and catalyzed conditions. Red star marks the peaks from Cu5FeS4 phase and blue triangle marks the peaks from Cu2FeS2 phase.

Further leaching tests employing lixiviants with varying ferric-to-ferrous ratios were conducted to gain additional insight into bornite's leaching behavior. The compositions of these solutions are summarized in Table 1. In all tests, the ferric ion concentration was maintained at 5 g/L to ensure that the chemical contribution to leaching remained constant across reactors. Tests 1 through 3 differed by their ferrous ion concentrations, ranging from 0.2 to 5 g/L. The presence of ferrous ions alters the solution's oxidation-reduction potential (ORP), thereby influencing the electrochemical contribution to the leaching process. The primary objective of these experiments was to determine whether solution potential affects the leaching of Cu_2FeS_2, which is considered the rate-determining stage in the dissolution of bornite.

As shown in Figure 6, although the initial addition of ferrous ions resulted in ORP values between 480 and 520 mV vs. Ag/AgCl, the bornite leaching rates remained unaffected. Tests 1, 2, and 3 produced nearly identical dissolution curves. This outcome indicates that the dissolution of Cu_2FeS_2 in acidic ferric sulfate media is potential-independent. These findings are consistent with electrochemical analyses, where bornite exhibits passivation when exposed to oxidative conditions.

Once passivated, the electrochemical activity on the mineral surface is significantly reduced, rendering variations in ORP inconsequential to the leaching rate.

Table 1 Solution composition for the bornite chemical leaching tests

#	Ferric (g/L)	Ferrous (g/L)	Sulfuric acid (g/L)	Catalyst
1	5	0.2	3	No
2	5	1	3	No
3	5	5	3	No
4	5	0.2	3	Yes

In this set of experiments, a Jetti-catalyzed test was conducted under conditions identical to Test 1 (5 g/L ferric, 0.2 g/L ferrous) except for the addition of catalyst. After achieving an initial copper extraction of approximately 18%, the Jetti catalyst successfully mitigated passivation, leading to a copper recovery of 69% at 140 hours—substantially higher than the 39% observed in the control. Due to the rapid leaching under catalyzed conditions, the solution ORP shifted from around 530 mV to 450 mV over the 140-hour period, overlapping the range covered by Tests 1 and 3. Despite this overlap in ORP, the leaching rate remained notably faster when the Jetti catalyst was present, confirming that ORP is not the primary factor governing Cu_2FeS_2 dissolution at least within the range tested in these experiment.

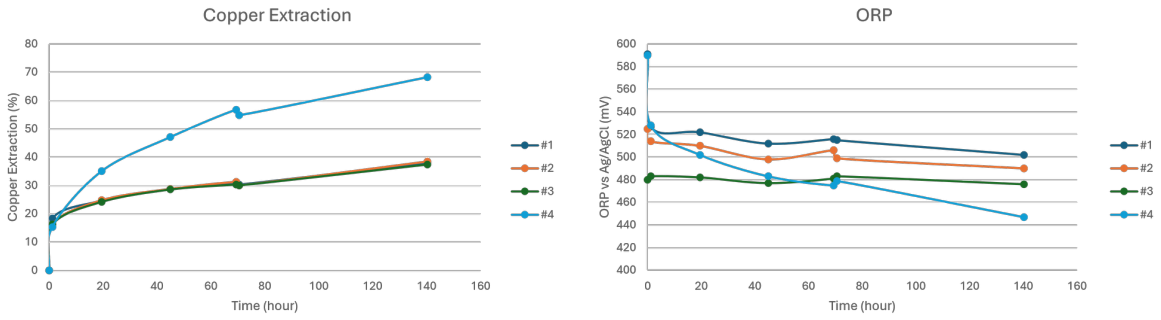

Figure 6 Chemical leaching of bornite under different ferric-ferrous ratio (ORP)

CONCLUSION

- Both chalcopyrite and bornite shows passivation behavior in electrochemical analysis

- Bornite is more reactive than chalcopyrite with lower rest potential (OCP1), and smaller potential difference (ΔOCP = OCP2 – OCP1)
- The chemical leaching tests show similar passivation behavior as electrochemical analysis where both minerals leach faster in the beginning of the test (< 1 hour) and slows afterwards.
- Bornite's first stage leaching involves a rapid conversion from Cu_5FeS_4 to Cu_2FeS_2.
- Ferrous ion and ORP has no significant impact on leaching rate within the range from 480 to 540 mV vs Ag/AgCl
- Use of Jetti catalyst significantly enhances the copper extraction for both chalcopyrite and bornite at ambient conditions, making it suitable for future bio-heap leaching

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