The effect of anodic potential on bornite dissolution: A key button of copper pollution

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Abstract. The relationship between anodic potential and sulfur film of bornite in acidic electrolyte was investigated by electrochemical experiments and surface analytical techniques. The formation of sulfur film decreased the conductivity of bornite, and the initial current density of bornite was positively correlated with subjected potential due to thermodynamic energy. The higher potential hindered the formation of sulfur precipitates Sn2-/S0 and forced products of bornite diffuse into electrolyte. The S 2p\(^{3/2}\) spectrum proved that S\(^{-2}\) has been converted to S\(^{2-}\), Sn2-/S0 and SO\(_4\)^{2-} during bornite dissolution. Combined with the composition of sulfur film formed on the bornite surface, the passive effect of sulfur film was mainly caused by formed Sn2-/S0. The solution potential was the primary factor in the bornite dissolution under acidic environment.

1. Introduction
The development of mining industry acts as the Damocles Sword to human society— On the one hand, it does contribute to economy; on the other hand, mine wastes cause acidic mine drainage (AMD) when exposed to atmospheric conditions— A severe acidification and accumulation of toxic metals [1]. Metal sulfide is the main resource of AMD [2, 3]. And copper-bearing sulfides should be regarded as a key point— Copper takes essential part in cell growth such as enzyme synthesis [4], but excessive intake forces human being to suffer from neoplastic disease [5], Alzheimer’s diseases [6] and childhood cirrhosis [7]. Besides, copper ions also promote other sulfides to dissolve and release toxic metals such as Zn [8], Pb [9] and As [10]. In this way, the copper-bearing mine wastes have been attracted plenty of attention, especially that of chalcopyrite due to its abundance [11, 12]. In contrast, few attention has been paid on bornite: The widely distributed copper resource with economic value after chalcopyrite [13]. Given that bornite and chalcopyrite are the intermediates of each other during dissolution [14], it is no surprise that the dissolution of bornite has been targeted as the break point of AMD control. Since the dissolution of bornite mainly occurs in high potential region via redox reaction, the high-potential conditions of AMD environment further promote its dissolution [15]. However, sulfur film was formed at same time, hinder dissolution [16, 17]. These findings came up with a question: how the high potential affects the surface property of bornite in AMD? To fill up this knowledge gap, we conducted chronoamperometry, electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS) to obtain a further understanding of the surface property of bornite at constant high potential.
2. Experiments & discussion

2.1. Bornite samples and experiments flow
The bornite samples contained (w/w) 60.72% Cu, 11.74% Fe and 23.83% S with high purity (Figure 1). They were cut into cylinders with a diameter of about 1.2 cm and a thickness of 0.5 cm, then polished before electrochemical experiments. We conducted chronoamperometry and electrochemical impedance spectroscopy (EIS) in a conventional three-electrode cell [18]. The pH 1.5 of deionized water was adjusted to pH 1.50 by sulfuric acid as electrolyte. Bornite was subjected at the potentials of 0.50, 0.60, 0.70 and 0.80 V and maintained for 6 hours in chronoamperometry. Then we performed EIS with amplitude of 50 mV in the frequency range of 0.1–10⁵ Hz and used the software of ZSimpwin 3.20 (2004) to fit EIS data. Afterwards, samples were investigated by S 2p XPS analysis. Only the S 2p3/2 peak is shown to simplify the graph.

![Figure 1. XRD analysis of bornite.](image)

2.2. Electrochemical experiments
The bornite electrodes were subjected different potentials for 6 hours during chronoamperometry (Figure 2). The formed sulfur film hindered product H⁺ ions to diffuse into the bulk solution, causing the current density dropped [16, 19], then entered to a quasi-steady state with value of 1.91, 2.0, 2.00 and 2.24 mA cm⁻² at 0.50, 0.60, 0.70 and 0.80 V’s respectively. In the first 200 sec, the initial current density was proportional to the voltage. At 0.50 V, the current density kept steadily. It differed at 0.60 V, the value kept dropping and changed rate at about 30 sec. The thermodynamic potential energy caused the differences of initial current density [20]. The solution potential was the primary factor in the bornite dissolution under acidic environment.

![Figure 2. Chronoamperometry curves of bornite electrodes (a: 0.50 and 0.60 V; b: 0.70 and 0.80 V; c: 0.50, 0.60, 0.70 and 0.80 V).](image)

We conducted electrochemical impedance spectroscopy (EIS) after chronoamperometry (Figure 3). Two incomplete semicircles in the high and intermediate frequency regions. The reduction of Fe(III) to Fe(II) related to the higher one, while the oxidation of bornite caused the other [21, 22]. The existence of a finite diffusion process related to the straight line with a typical Warburg impedance (W) in the low frequency region [23]. We proposed an equivalent circuit $R_s(Q_1(R_1))(Q_2(R_2W))$ (Figure 3e) to simulate
the impedance data. \( R_s \), \( R_1 \) and \( R_2 \) represented the resistance of electrolyte, the charge transfer and the sulfur film oxidation charge transfer respectively. \( Q_1 \) and \( Q_2 \) represent the double-film capacitances of electrode/electrolyte and sulfur film/electrolyte [24].

Table 1 showed the parameters of the equivalent circuit, the change of \( R_s \) and \( R_1 \) indicated the electrolyte conductivity increased and the oxidation rate of bornite decreased with the increase of potential. The increase of \( R_2 \) also suggested the sulfur film play a key role in bornite dissolution.

### Table 1. Parameters of the equivalent circuit.

| Applied potential (V) | 0.50  | 0.60  | 0.70  | 0.80  |
|-----------------------|-------|-------|-------|-------|
| \( R_s (\Omega \ cm^{-2}) \) | 3.277 | 1.594 | 1.231 | 1.531 |
| \( Y_0,1 \times 10^{-3} \ S \ s^{-1} \ cm^{-2} \) | 0.001 | 1.676 | 0.542 | 0.001 |
| \( n \) | 0.85  | 0.79  | 0.72  | 0.74  |
| \( R_1 (\Omega \ cm^{-2}) \) | 1.15  | 1.755 | 2.399 | 1.613 |
| \( Y_0,2 \times 10^{-3} \ S \ s^{-1} \ cm^{-2} \) | 5.483 | 3.108 | 119.1 | 0.1645 |
| \( n \) | 0.83  | 0.78  | 0.70  | 0.70  |
| \( R_2 (\Omega \ cm^{-2}) \) | 3.87  | 18.35 | 19.52 | 17.74 |
| \( W (10^{-1} S \ s^{0.5} \ cm^{-2}) \) | 1.254 | 2.845 | 1.654 | 0.309 |
| \( \chi^2 (10^{-4}) \) | 9.2   | 2.05  | 1.53  | 3.57  |

### 2.3. Surface analysis

Figure 4 shows the S 2p\(_{3/2}\) spectra of bornite before and after chronoamperometry, the strongest doublet at 161.3 eV was attributed to S\(^{2-}\) [18, 25], while that at 162.4 eV was assigned to S\(^{2-}\) [2, 26, 27]. Concerned about the range of the elemental sulfur(163.05–164.7 eV) crosses that of polysulfide (163.0–163.9 eV) [28] and multiple substances of polysulfide with different chain lengths is hard to achieve differential fit [18], the doublet in the range from 163.0 to 164.7 eV was attributed to S\(_{n2}/S^0\) in this study. The peak 168.8 eV represented to SO\(_4^{2-}\) [24, 29, 30]. The peaks of S\(_{n2}/S^0\) and SO\(_4^{2-}\) became broader, while the peak of S\(^{2-}\) became narrower after chronoamperometry— The S\(^{2-}\) was transformed into S\(_n^{2-}/S^0\) and SO\(_4^{2-}\), which aggravated with increase of potential. A considerable change at 0.80 V happened: The amount of S\(_{n2}/S^0\) and SO\(_4^{2-}\) were 5.47, 22.21 and 55.97 %, while they were 3.26, 58.51 and 24.63% at 0.70V. Combined with electrochemical experiments, the formation of sulfur film (S\(_{n2}/S^0\)) played the key role in blocking bornite dissolution.
3. Conclusion

The formed sulfur film decreased the conductivity of bornite, and the initial current density of bornite was positively correlated with subjected potential due to thermodynamic energy. The S 2p$_{3/2}$ spectrum proved that S$^2-$ has been converted to S$_2^{2-}$, S$_0^{2-}$/S$^0$ and SO$_4^{2-}$ during bornite dissolution. The higher potential hindered the formation of S$_0^{2-}$/S$^0$ and forced products of bornite diffuse into electrolyte. Combined with the composition of sulfur film formed on the bornite surface, the passive effect of sulfur film was mainly caused by formed S$_0^{2-}$/S$^0$. The solution potential was the primary factor in the bornite dissolution under acidic environment. These findings open the new door on copper pollution.

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