Synchrotron-Based XRD and XANES Study of Bornite Leached by Mesophilic Mixed Bacteria

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Abstract In this study, bioleaching experiments, synchrotron X-ray Diffraction (SR-XRD), X-ray absorption near edge structure (XANES) and X-ray Photoelectron Spectroscopy (XPS) were conducted to investigate the intermediates and surface species of bornite leached by mesophilic mixed bacteria of *Leptospirillum ferriphilum*, *Acidithiobacillus caldus* and *Sulfobacillus thermosulfidooxidans*. CuS, $Cu_9Fe_9S_{16}$ and S_8 were the main intermediate species during bornite bioleaching by mesophilic mixed bacteria, and $CuFeS_2$ was also detected. The surface species of S^{2-} and $S_2{}^{2-}$ would be polymerized to S_n^{2-} during bioleaching. The formation of element sulfur and the increase of its content were confirmed by the fitted results of XPS spectra. The presence of polysulfide and element sulfur did not inhibit the bornite bioleaching. The formations of CuS and $CuFeS_2$ were confirmed by the results of Cu *K*-edge XANES spectra.

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B. Li et al. (eds.), *Characterization of Minerals, Metals, and Materials 2018*, The Minerals, Metals & Materials Series,
https://doi.org/10.1007/978-3-319-72484-3_35

Keywords Bornite · Bioleaching · Mesophilic mixed bacteria
Chemical speciation · Synchrotron · XRD · XANES · XPS

Introduction

Bornite is an important source of copper [1, 2], following chalcopyrite and chalcocite in economic importance [3], so the development of bornite processing can bring huge economic benefits. Bioleaching is a simple, lower cost and eco-friendly technology, which has been widely used in leaching low grade copper and complex ores [4, 5]. The dissolution mechanism during bornite leaching is still ambiguous. Some researchers have investigated the dissolution process during bornite leaching with different conditions [6–8]. Dutrizac found that the dissolution of synthetic bornite in acidified ferric sulfate solution in the temperature range 40–90 °C obeys a linear rate law. Nature and synthetic bornite dissolve by the same process and at essentially the same rate. Nonstoichiometric bornite ($Cu_{5-x}FeS_4$), chalcopyrite ($CuFeS_2$) and covellite (CuS) were formed during the leaching of bornite in either ferric chloride or ferric sulfate media, and then nonstoichiometric bornite converted to Cu_3FeS_4. Pesic also found the formation of covellite and chalcopyrite during the dissolution of bornite in sulfuric acid using oxygen as oxidant, but without the X-ray data of Cu_3FeS_4. Buckley et al. [9] investigated the anodic oxidation of bornite and found that an iron-free copper sulfide of Cu_5S_4 was formed.

The report about bornite bioleaching was relatively few, particularly in respect of intermediates evolutions during bornite bioleaching by bacteria. Zhao et al. [10] investigated the electrochemical dissolution of bornite in acid culture medium and found that covellite was the main intermediate specie during the bornite bioleaching. Covellite was detected as a secondary phase during bornite bioleaching by *A. ferrooxidans* with or without ferrous iron. Sulfur and jarosite were also found in the process [11]. For the ambiguous dissolution process of bornite bioleaching, this study aims to investigate the intermediates transformation during bornite bioleaching by mesophilic mixed bacteria of *L. ferriphilum*, *A. caldus* and *S. thermosulfidooxidans*.

Materials and Methods

Minerals

Bornite samples were obtained from Meizhou, Guangdong Province, China. Chemical analysis showed that the bornite sample contained (w/w) 61.81% Cu, 9.70% Fe, 21.18% S. Synchrotron-XRD result indicated that bornite used in the study were of high purity.

Microorganisms and Bioleaching Experiments

Domesticated cultivation of mixed bacteria of *L. ferriphilum*, *A. caldus* and *L. ferriphilum*, *A. caldus* and *S. thermosulfidooxidans* was conducted in an aeration beaker include 40 g mineral and 2 L 9 K basic salt medium, which did not include $FeSO_4 \cdot 7H_2O$ and S. Planktonic cells were collected from bacteria solution in logarithmic phase by centrifugation, then the collected bacteria used for bioleaching experiments. Bioleaching were conducted in 250 mL flasks containing 100 mL sterilized basal medium. 2 mL bacteria cultures and 2 g minerals were added in each flask, then which incubated at 45 °C and 170 rpm on a rotary shaker. The initial cell concentration was higher than 1.0×10^7 cells/mL. The pH was adjusted daily to 1.70 ± 0.03 with sulfuric acid. Evaporation losses was compensated periodically by adding distilled water. During the bioleaching process, the variation of pH values, redox potentials, and the concentration of ferric, ferrous and copper were measured.

Analysis Methods

The mineralogical components of bornite samples and leaching residues were analyzed by synchrotron-XRD at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) with a wavelength of 0.6887 Å. All XPS spectra were calibrated by C 1 s peak at 284.8 eV. XPS PEAK 4.1 software was used for fitted the XPS peaks. Sulfur *2p* peaks occur as doublets (S $2p_{3/2}$ and S $2p_{1/2}$) because of spin orbit splitting. Only the S $2p_{3/2}$ peaks are displayed in the figures for clarity. The Cu and Fe *K*-edge XANES data were conducted in transmission mode at beamline 1W1B of Beijing Synchrotron Radiation Facility (BSRF), Beijing, China. The near edge part of the Cu or Fe *K*-edge X-ray absorption spectra was collected with a step of 1 eV and dwell time of 1 s in appropriate energy range.

Results and Discussion

Figure 1 shows the variations of solution ORP and copper extractions during bioleaching of bornite. It indicated that the solution ORP increased slowly in the first two days, and then successively increased from 303.6 to 405.9 mV. The variation of copper extractions presented a similar pattern. The copper extractions increased rapidly in the last two days.

SR-XRD analysis (Fig. 2) indicates that before copper extractions reached 11.25%, the bornite was the main species of leached residue. The results showed that only small amount bornite dissolved in the first two days, and the crystal structure of bornite has not changed. The results were consistent with the lower

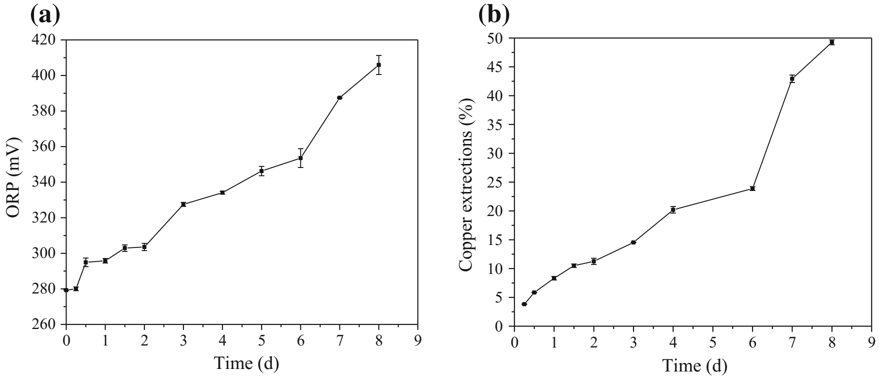
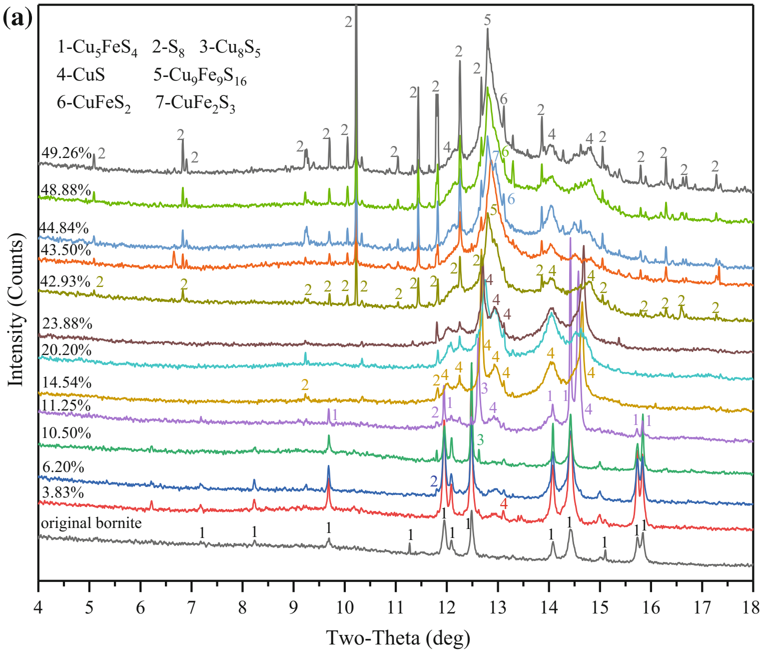


Fig. 1 Variations of solution ORP (**a**) and copper extractions (**b**) during bioleaching

copper extractions in the first two days as showed in Fig. 1(b). Small amount of covellite (CuS, PDF#78-0877) and element sulfur (S_8, PDF#85-0799) was formed in earlier bioleaching process. A peak represented geerite (Cu_8S_5, PDF#33-0491) was detected. When the copper extractions reached 11.25%, the higher intensity peak of Cu_8S_5 appeared with the disappearance of two bornite peak ($2\theta = 12.484$ and 20.468). The peaks of bornite and Cu_8S_5 all disappeared at the copper extractions of 14.54%, while CuS became the main specie. The change of the peak indicated that Cu_8S_5 may convert to CuS. The cooper extractions increased significantly from day 6 to day 7, meanwhile, the SR-XRD pattern has changed significantly. Large amount of element sulfur and mooihoekite ($Cu_9Fe_9S_{16}$, PDF#27-0164) formed and two CuS peak ($2\theta = 12.704$ and 20.833) disappeared. When the copper extractions reached 44.84%, a peak ($2\theta = 13.117$) represented chalcopyrite ($CuFeS_2$, PDF#33-0491) and a peak ($2\theta = 12.948$) represented isocubanite ($CuFe_2S_3$, PDF#81-1738) were detected (Fig. 3).

The results of copper extractions and SR-XRD analysis indicated that the dissolution of bornite bioleaching in this study occurs in three stages. Firstly, only small amount bornite dissolved in the first two days and small amount CuS and S_8 were formed. Secondary, crystal structure of bornite changed significantly. With the dissolution of bornite, a large amount of CuS was formed. Thirdly, with the dissolution of CuS a large amount of $Cu_9Fe_9S_{16}$ was formed (Fig. 4).

The fitted results of XPS spectra suggested that the amount of S^{2-} species of bornite bulk decreased with time. The amount of ${S_2}^{2-}$ species also decreased during bioleaching. The variation of the amount of S^{2-} and ${S_2}^{2-}$ is consistent with the dissolution of bornite. The amount of S_n^{2-}/S^0 species increased with time from 28.15 to 49.96%, which were consistent with the results of SR-XRD. These changes confirm that S^{2-} and ${S_2}^{2-}$ were polymerized to S_n^{2-} [12]. In combination with the results of copper extractions, indicated that the presence of polysulfide did not inhibit the bornite bioleaching. The amount of sulfate increased from 1.59 to



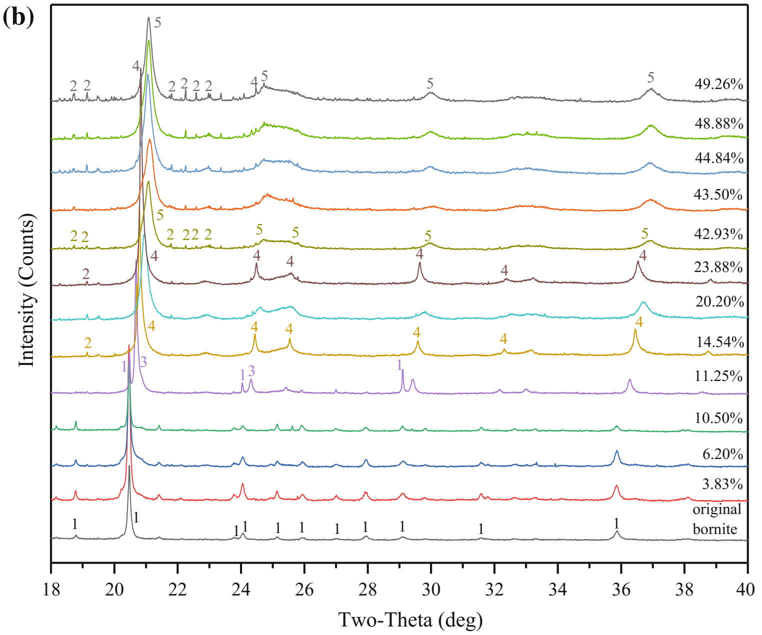


Fig. 2 SR-XRD analysis of bioleaching residue: **a** Two-Theta = 4°–18°, **b** Two-Theta = 18°–40°

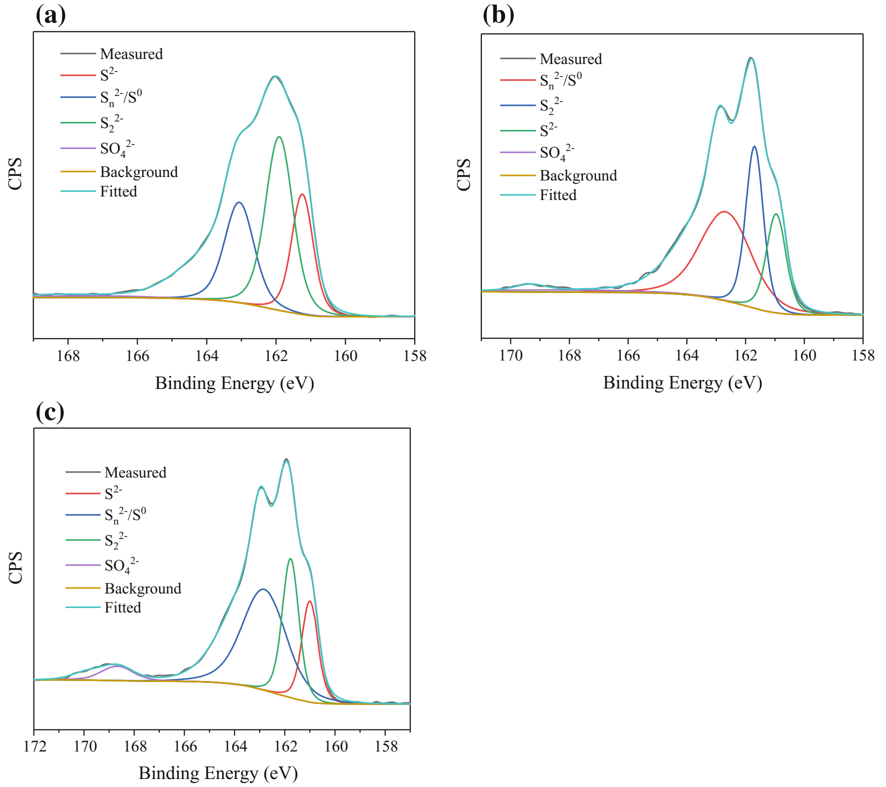


Fig. 3 S $2p_{3/2}$ XPS spectra of bioleaching residue: **a** copper extractions = 8.71%, **b** copper extractions = 14.37%, **c** copper extractions = 42.79%

5.20% during bioleaching, which may represent an increase of the amount of jarosite (Tables 1, 2).

The fitting results of Cu *K*-edge XANES spectra showed the presence of covellite and chalcopyrite, which indicated that bornite would convert to covellite and chalcopyrite during bioleaching. In the earlier period of bioleaching, covellite was the main intermediate species. With the bioleaching of bornite, the amount of covellite and chalcopyrite increased obviously. The Fe *K*-edge XANES spectra of sample with 49.26% copper extractions showed a very great difference with the other two samples, which indicated that the intermediate species had undergone massive changes. The appearance of the peak at 7130 eV represented the formation of jarosite.

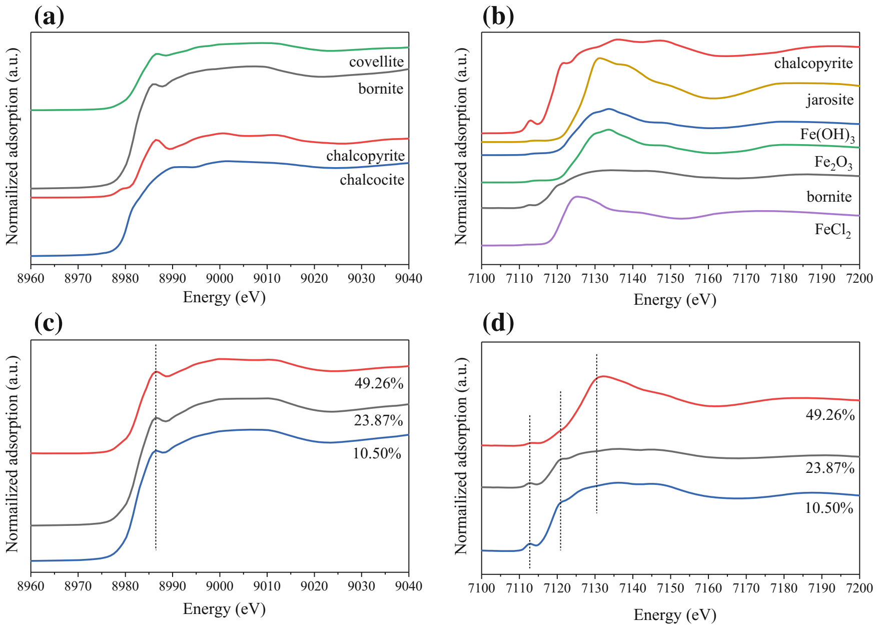


Fig. 4 Cu *K*-edge XANES spectra (**a**, **c**) and Fe *K*-edge XANES spectra (**b**, **d**) of reference samples (**a**, **b**) and bioleaching residue (**c**, **d**)

Table 1 Proportion of different surface sulfur contents in bioleaching residue (%)

Samples (with different copper extractions)	S^{2-}	S_2^{2-}	S_n^{2-}/S^0	SO_4^{2-}
8.71%	24.87	45.39	28.15	1.59
14.37%	20.18	29.49	46.74	3.59
42.79%	18.63	26.20	49.96	5.20

Table 2 Fitted results of Cu *K*-edge XANES spectra of bioleaching residue (%)

Samples (with different copper extractions)	Bornite	Chalcopyrite	Covellite
10.50%	53.5	–	46.5
23.87%	29.8	13.0	57.2
49.26%	23.2	25.5	51.4

Conclusion

The intermediates and surface species of bornite leached by mesophilic mixed bacteria of *L. ferriphilum*, *A. caldus* and *S. thermosulfidooxidans* was investigated by bioleaching experiments, SR-XRD, Cu *K*-edge and Fe *K*-edge XANES and XPS. The SR-XRD results showed that CuS, $Cu_9Fe_9S_{16}$ and S_8 were the main intermediate species during bornite bioleaching by mesophilic mixed bacteria, and $CuFeS_2$ was also detected. The surface species of S^{2-} and ${S_2}^{2-}$ would be polymerized to S_n^{2-} during bioleaching. The formation of element sulfur and the increase of its content were confirmed by the fitted results of XPS spectra. The presence of polysulfide and element sulfur did not inhibit the bornite bioleaching. The formations of CuS and $CuFeS_2$ were confirmed by the results of Cu *K*-edge XANES spectra.

Acknowledgements This work was supported by the National Natural Science Foundation of China (project No. 51374248 and No. 51774332), the Program for New Century Excellent Talents in University (project No. NCET-13-0595), the Open Funds of SSRF (No. 2016-SSRF-PT-005985) and the Open Funds of BSRF (No. 2017-BEPC-PT-000653) and the Fundamental Research Funds for the Central Universities of Central South University.

References

1. Ferraz LFC, Verde LCL, Vicentini R et al (2011) Ferric iron uptake genes are differentially expressed in the presence of copper sulfides in *Acidithiobacillus ferrooxidans* strain Lr. Antonie Van Leeuwenhoek 99(3):609–617
2. Bevilaqua DI, Diéz-Perez C, Fugivara S et al (2003) Characterization of Bornite (Cu_5fes_4) electrodes in the presence of the bacterium *Acidithiobacillus ferrooxidans*. J Braz Chem Soc 14(4):637–644
3. Pesic B, Olson FA (1983) Leaching of bornite in acidified ferric chloride solutions. Metall Trans B 14(4):577–588
4. Brierley JA, Brierley CL (2001) Present and future commercial applications of biohydrometallurgy. Hydrometallurgy 59(2):233–239
5. Rawlings DE, Johnson DB (2007) Biomining. New York: Springer, Berlin
6. Dutrizac JE, Macdonald RJC, Ingraham TR (1970) The kinetics of dissolution of bornite in acidified ferric sulfate solutions. Metall Trans 1(1):225–231
7. Dutrizac JE, Chen TT, Jambor JL (1985) Mineralogical changes occurring during the ferric lon leaching of bornite. Metall Trans B 16(4):679–693
8. Pesic B, Olson FA (1984) Dissolution of bornite in sulfuric acid using oxygen as oxidant. Hydrometallurgy 12(2):195–215
9. Buckley AN, Hamilton IC, Woods R (1984) Investigation of the surface oxidation of bornite by linear potential sweep voltammetry and X-Ray photoelectron spectroscopy. J Appl Electrochem 14(1):63–74
10. Zhao H-B, Hu M-H, Li Y-N et al (2015) Comparison of electrochemical dissolution of chalcopyrite and bornite in acid culture medium. Trans Nonferrous Met Soc China 25(1):303–313
11. Bevilaqua D, Garcia O Jr, Tuovinen OH (2010) Oxidative dissolution of bornite by *Acidithiobacillus ferrooxidans*. Process Biochem 45(1):101–106
12. Harmer SL, Thomas JE, Fornasiero D et al (2006) The evolution of surface layers formed during chalcopyrite leaching. Geochim Cosmochim Acta 70(17):4392–4402