

Raman and Mössbauer analysis of the intermediate products formed during gold-bearing pyrite biooxidation by moderately thermophilic bacteria

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Abstract In the present study, intermediate products formed during gold-bearing pyrite biooxidation by moderately thermophilic bacteria at 42°C were studied by combined using XRD, Mössbauer and Raman spectroscopy. Biooxidation slowdown since 8th day showed that some intermediate products might hampered the further oxidation of gold-bearing pyrite. XRD and Mössbauer analysis confirmed there was no jarosite formed in the biooxidation. Raman analysis confirmed the accumulation of elemental sulfur on the gold-bearing pyrite surface led to the slowdown of the biooxidation.

Introduction

Refractory gold ores account for about 60% gold resource in the world, and the submicroscopic gold was incorporated in the sulfides minerals is one of primary reasons result from gold ore difficult for extraction. Biooxidation pre-treatment process has been approved to be more economical and eco-friendly than other pre-treatment methods, and it has been applied in many gold mines [1].

Oxidation slow is the most disadvantage of biooxidation process [2]. The amount of pyrite is common far higher than arsenopyrite in the gold-bearing sulfide ores, and the oxidation of the former is far slower than the latter [3]. Therefore, the key to improve the biooxidation rate of gold-bearing sulfide ores is to improve the oxidation rate of gold-bearing pyrite.

The oxidation dissolution of pyrite under the action of oxidant (biological or chemical) is a complex process, and many intermediate products such as elemental sulfur, thiosulfate, polysulfide and jarosite [3-5] were detected during pyrite bioleaching/biooxidation. Therefore, study the intermediate products formed on the surface of pyrite during bioleaching/biooxidation is the

precondition for the aim of to promote the biooxidation rate of refractory gold ores.

In the present study, intermediate products formed during the gold-bearing pyrite biooxidation by moderately thermophilic bacteria at 42°C was studied by combined using XRD, Mössbauer and Raman spectroscopy.

Materials and methods

Minerals

Gold-bearing pyrite concentrate was mainly composed by Fe 43.68%, S 51.60%, As 3.06%, and the concentrate contain gold is 54.79g/t. Gold-bearing pyrite (-200 mesh) samples were washed twice with 0.1 mol/L sulfuric acid for 24h to remove the surface oxidation products before experiments.

Strain and culture medium

Moderately thermophilic bacteria used in the present study were provided by state Key Laboratory of Comprehensive Utilization of Low-grade Refractory gold ores (Zijin Mining Group Co., Ltd). 9K medium was used to cultivate the moderately thermophilic bacteria.

Biooxidation experiments

All the oxidation experiments were carried out in the 250 mL Erlenmeyer flasks on suspensions consisting of 3 grams gold-bearing pyrite and 150 mL sterilized 9K medium. The initial pH of suspensions was adjusted to 2.0 with 0.1M sulphuric acid. The initial cell number was 2×10^7 cells mL⁻¹. Oxidation experiments were conducted in an air heating rotary shaker at 125 rpm and a constant temperature of 42°C. Each abiotic control was not inoculated, and 2 mL of ethanol solution with 2% thymol was added to inhibit the growth of bacteria. Triplicate experiments were carried out.

Cell numbers was determined with a blood cell counting chamber. The concentration of total iron ions was determined with atomic absorption spectrophotometer (AAS). The vary trend of pH and redox potential during leaching solution was measured with pH and redox potential meter.

Mineral composition analysis

The composition changes of gold-bearing pyrite during biooxidation were characterized by XRD and Raman spectroscopy.

Mössbauer spectra were measured with a constant acceleration transmission mode with a ⁵⁷Co/Rh source room temperature. The velocity was calibrated by 25 µm α-Fe foil, and the Isomer Shift (I.S.) was relative to the center of α-Fe at room temperature. The spectra were fitted using MossWinn [4].

Results and discussion

Oxidation characteristic of gold-bearing pyrite

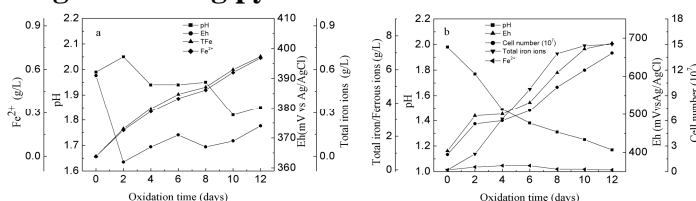


Fig.1. Oxidation characteristics of gold-bearing pyrite in the (a): abiotic control and (b): biooxidation.

Oxidation characteristics in abiotic control and biooxidation of gold-bearing pyrite by moderately thermophilic bacteria are shown in Fig.1a and 1b, respectively. Total iron ions

concentration in abiotic control and biooxidation both increased with the proceeding of oxidation, and it reached 0.69 and 7.5 g/L at 12th days, respectively. The results showed that the presence of moderately thermophilic bacteria effectively promoted the oxidation dissolution of gold-bearing pyrite. It clearly that rapid biooxidation took place in the range of day 2 to day 8, and then the biooxidation slowdown in the latter of the biooxidation. The result indicated that there might be some intermediate products formed on the surface of gold-bearing pyrite, which hampered the further oxidation.

It is clear that the vary of ferrous ions is similar with that of total iron ions in abiotic control. Maximum concentration of ferrous ions 0.66 g/L was reached at 12th days, which was almost equal to the maximum concentration of total iron ions (0.67 g/L). The result indicated the dissolved iron ions are mostly existed as ferrous ions in the abiotic control.

However, the maximum ferrous ions concentration was just 0.26 g/L in biooxidation (Fig.1b), which was far lower than the concentration of total iron ions (7.5g/L). The result indicated the dissolved iron ions are mostly existed as ferric ions in biooxidation, which is consistent with the results of LIU et al.[5]. The different fate of dissolved iron ions in abiotic control and biooxidation was mainly due to there was no microbes oxidize ferrous ions to ferric ions in the former.

The pH in abiotic control was kept slightly fluctuated in the abiotic control. However, the pH in biooxidation constantly dropped from 1.98 to 1.17 after 12 days biooxidation. The production of sulfuric acid by sulfur oxidation microbes from the oxidation of reduced sulfur compounds should accountable for the decrease of pH in the biooxidation.

XRD analysis

XRD spectroscopy of the bio-oxidized residue are shown in the Fig.2. Similar with the peaks of original gold-bearing pyrite, just characterized peaks of pyrite and quartz were observed in the XRD patterns of bio-oxidized residues. No special signals of elemental sulfur and jarosite were found in the XRD patterns. Our results are in agreement with the report of [6].

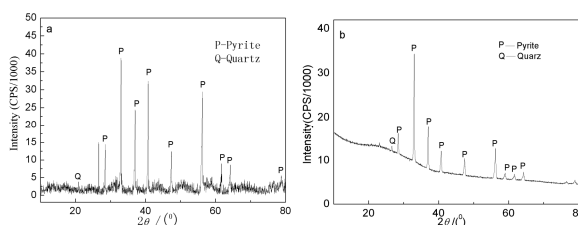


Fig.2. XRD spectra of (a) :original gold-bearing pyrite and (b):bio-oxidized residues.

Mössbauer analysis

Mössbauer spectra of pyrite, original gold-bearing pyrite, jarosite, bio-oxidized residues at 6th day and 10th day are shown in Fig.3, and the parameters of mössbauer spectroscopy are list in Table 1.

Fig.3 shows that the spectrum of pyrite and gold-bearing pyrite both exhibited a Fe^{2+} doublet peak. However, the isomer shift of pyrite and gold-bearing pyrite is different, 0.310 mm/s is for the former and 0.282 mm/s is for the latter (Table 1). The result is consistent with Jia [7], the author found the isomer shift values decreasing with the increasing of the gold content in the gold-bearing pyrite. One Fe^{3+} doublet peak was observed in the spectrum of jarosite, and its isomer shift is 0.353 mm/s and the quadrupole splitting is 1.114 mm/s (Table 1), which is consistent with the result of Leclerc [8]. It is clear that there were no characteristics peaks of jarosite appeared in the spectra of gold-bearing pyrite bio-oxidize residues at 6th and 10th days (Fig.4). The result of mössbauer further confirmed there was no jarosite form during biooxidation. Our results are agreement with [6,

9].

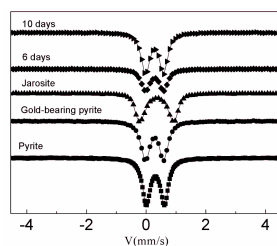


Fig.3. Mössbauer spectra of pyrite, gold-bearing pyrite, jarosite and biooxidized residues.

Table 1. Mössbauer results (the isomer shift is given with respect to metallic iron).

Samples	Isomer shift (mm/s)	Quadrupole splitting (mm/s)	Average line width (mm/s)
Pyrite	0.310	0.611	0.310
Gold-bearing pyrite	0.282	0.612	0.336
Jarosite	0.353	1.114	0.358
Biooxidation 6th days	0.280	0.605	0.330
Biooxidation 10th days	0.280	0.603	0.315

Raman analysis

To further confirm whether elemental sulfur form or not in the gold-containing pyrite biooxidation, the bio-oxidize residues were analyzed by Raman spectroscopy, and the results are shown in the Fig.4.

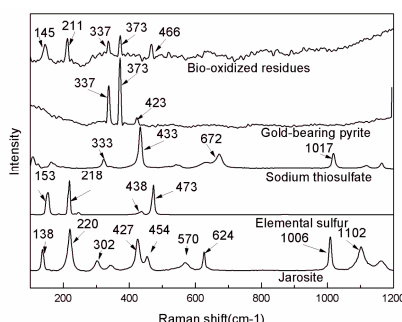


Fig.4. Raman spectra of gold-bearing pyrite, elemental sulfur and bio-oxidized residues.

It is clear that besides the characterized peaks (337cm^{-1} , 373cm^{-1} and 423cm^{-1}) belong to gold-bearing pyrite were observed, three additional peaks were observed at $\sim 145\text{cm}^{-1}$, $\sim 211\text{cm}^{-1}$ and $\sim 466\text{cm}^{-1}$ in the Raman spectroscopy of bio-oxidized residues, respectively. The three additional Raman peaks should be assigned to elemental sulfur based on the comparison with the characterized peaks of elemental sulfur. The result confirmed the accumulation of elemental sulfur on the surface of gold-bearing pyrite during biooxidation.

Elemental sulfur is the common intermediate product of metal sulfide ores biooxidize dissolution, and elemental sulfur might accumulate and form a barrier layer on the surface of metal sulfide which hamper the diffusion of oxygen or Fe^{3+} ions and make the metal sulfide passivation. Therefore, we consider the accumulation of elemental sulfur on the gold-containing surface should responsible for the slowdown of the biooxidation.

Conclusions

The biooxidation of gold-bearing pyrite by moderately thermophilic bacteria at 42°C showed that the oxidation rate is slowdown since 8th day, which means there are some products formed on the mineral surface which might hamper the further dissolution of gold-bearing pyrite. XRD and Mössbauer spectroscopy analysis of the bio-oxidized residues confirmed there were no jarosite formed in the biooxidation. Elemental sulfur were detected by Raman spectroscopy analysis the bio-oxidized residues, which should responsible for the slowdown of the biooxidation.

Acknowledgements

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