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A novel bio-oxidation and two-step thiourea leaching method applied to a refractory gold concentrate

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ABSTRACT

Biooxidation-thiourea (TU) leaching is considered to be a more environmentally friendly and efficient method than cyanidation to recover gold from refractory sulfide gold-bearing ores/concentrates. However, high consumption of the TU reagent and additional oxidants hinders its commercial adoption. In this work, single TU leaching and novel two-step TU leaching processes were designed and performed after the biooxidation of refractory sulfide gold-bearing concentrate from Axi, China. The novel method contained an additional six-hour bioprocess and a six-hour lixiviant leaching. During the two-step TU leaching, the microbes remaining on the residue from biooxidation regenerated Fe^{3+} as oxidant. Compared with the highest gold recovery rate of the single TU leaching (92.2 ± 1.54%), which had additional Fe^{3+} and Na_2SO_3 supplied after prewashing, the rate reached 95.0 ± 0.73% in the two-step TU leaching process without additional oxidant and reductant. A microbial community analysis by 16S rRNA gene amplicon sequencing indicated that the genera *Acidithiobacillus* and *Leptospirillum* greatly contributed to the regeneration of ferric ions during the two-step TU leaching process and further improved the recovery of gold. As a non-cyanide method, combining the two-step TU leaching process with biooxidation takes full advantage of the microorganisms and is worthy for industrial application.

1. Introduction

The biooxidation pretreatment of refractory gold ores and concentrates prior to cyanidation has been widely used for the past two decades, mainly because of its environmental friendliness and applicability to low-grade ores (Harvey et al., 2002; Donati and Sand, 2007; Corkhill and Vaughan, 2009; Fantauzzi et al., 2011; Vera et al., 2013; Kaksonen et al., 2014). However, the combination of biooxidation and cyanidation results in many problems (La Brooy et al., 1994; Ciftci and Akcil, 2010; Karthikeyan et al., 2015). For example, the high toxicity of cyanide causes an increasing pressure on the environment. More importantly, the neutralization between the acidic biooxidation and the alkaline cyanidation is a major contributor to its operating cost (van Aswegen et al., 2007). Because of these challenges, indigenous groups and representatives of the NGO community have done many studies to develop less toxic leaching reagents with acceptable recovery rates (La Brooy et al., 1994; Vukcevic, 1996; Grosse et al., 2003; Hilson and Monhemius, 2006; Zheng et al., 2006; Li et al., 2012).

Thiourea (TU) has been considered as an alternative to cyanide for gold recovery due to its faster kinetics and lower toxicity (Yang et al., 2011; Jing-ying et al., 2012; Altansukh et al., 2014). Moreover, acidic TU leaching is more suitable for the treatment of refractory sulfide gold ores and does not need neutralization after biooxidation pretreatment. For example, Murthy (1990) reported the increase of the gold recovery rate from 23 to 92% after TU leaching of the bacterial residue. However, the utilization of acidic TU is not economically efficient in industrial application due to its high reagent consumption (Hilson and Monhemius, 2006). New processes with oxidants (such as ferric iron) and reductants related to gold extraction by TU remain of great interest in hydrometallurgical research (Li and Miller, 2006; Örgül and Atalay, 2002; Poisot Díaz et al., 2012). However, the large amounts of additional reagents that are consumed in these processes are undesirable.

The iron-oxidizing microorganisms in biooxidation processes accumulate large amounts of ferric iron (Brierley and Brierley, 2001; Canales et al., 2002; Sand et al., 2001), which can theoretically act as an oxidant during the TU leaching. However, previous studies showed that the excessive ferric iron and other impurities left from the biooxidation system consume TU (Deng and Liao, 2002; Deng et al., 2001). Actually, microorganisms remain in the residue after biooxida-

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tion (Harneit et al., 2006; Afzal Ghauri et al., 2007; Donati and Sand, 2007) and still have the ability to regenerate ferric iron ions during the TU leaching. In addition, some studies have already been conducted to investigate the effect of TU reagents on microbial activity (Murthy, 1990; Díaz and Roldán, 1999). Very recently, researchers started to pay attention to biological gold solubilization (Kaksonen et al., 2014). Attempting to make full use of these biological reactions while keeping a balance between the improvement of the gold recovery rate and the consumption of reagents during the TU leaching process are the questions that remain to be addressed.

This study is a part of an investigation aimed at designing a new biooxidation-TU leaching process that will recover gold from refractory gold ores and concentrates. To improve the biooxidation efficiency, several conditions including adding a high temperature chemical oxidation before the biooxidation, controlling the pH during the biooxidation and acclimating the microflora were tested in our previous study (Wang et al., 2015; Liu et al., 2015; Wang et al., 2016). In this paper, a normal biooxidation-TU leaching process was carried out on Axi refractory gold-bearing concentrate to examine the effect of some factors such as treatment methods for bio-residue and the presence of Fe^{3+} and sodium sulfite on the recovery of gold. Because microbes benefit the gold extraction by renewing the ferric ions, a newly designed two-step TU leaching process was carried out on bio-residue from the semi-continuous biooxidation. Furthermore, the microbial compositions before and after the leaching process were analyzed by 16S rRNA gene amplicon sequencing.

2. Materials and methods

2.1. Materials sample

The refractory gold-bearing concentrate tested in this experiment was obtained from the Axi gold mine, Xinjiang, P. R. China. The sample was finely ground, and 92% of the particle sizes were < 0.074 mm. A chemical component analysis showed that 55.52 g/t Au, 23.68% Fe, 24.53% S, and 2.25% As were in the concentrate. Mineralogical studies showed that half of the gold (Table 1) was deposited in sulfides in a very fine grain size as submicron particles. Gold recovery rates were 48.3% ± 0.88% by direct TU leaching (unpublished data, TU 2.75 g/L, $Fe_2(SO_4)_3$ 3 g/L, Na_2SO_3 1 g/L, 25 °C, pulp density 33%, 6 h) and 51.22% by directly cyanidation (Li and Guo, 2014). Pyrite and arsenopyrite were the main sulfide minerals based on X-ray Diffraction (XRD) analysis (Wang et al., 2015).

2.2. Microorganisms and culture medium

The mixed AX culture used in the biooxidation process was structured with acidophilic bacteria and archaea preserved in the Key Laboratory of Biometallurgy of the Ministry of Education, China, based on the information from industrial investigations using metagenomic technologies. The culture was maintained at 45 °C in 9K mineral salts medium containing $(NH_4)_2SO_4$ (3.0 g/L), KCl (0.1 g/L), K_2HPO_4 (0.5 g/L), $MgSO_4{\cdot}7H_2O$ (0.5 g/L), and $Ca(NO_3)_2{\cdot}4H_2O$ (0.01 g/L) and included 15% (w/v) Axi gold concentrate as the sole source of energy. The initial pH of the medium was adjusted to 1.6. All chemical reagents were of analytical grade and purchased from commercial sources. After the domestication with Axi concentrate for three consecutive years, *Acidithiobacillus* spp., *Sulfobacillus* sp., *Leptospirillum* spp. and *Ferroplasma* sp. were dominant in the AX consortium.

Table 1
Gold state in Axi refractory gold concentrate.
(Li and Guo, 2014)

Occurrence	Exposed gold	Gold contained in sulfide	Gold contained in other minerals	Total
Occupancy (%)	51.33	44.13	4.54	100

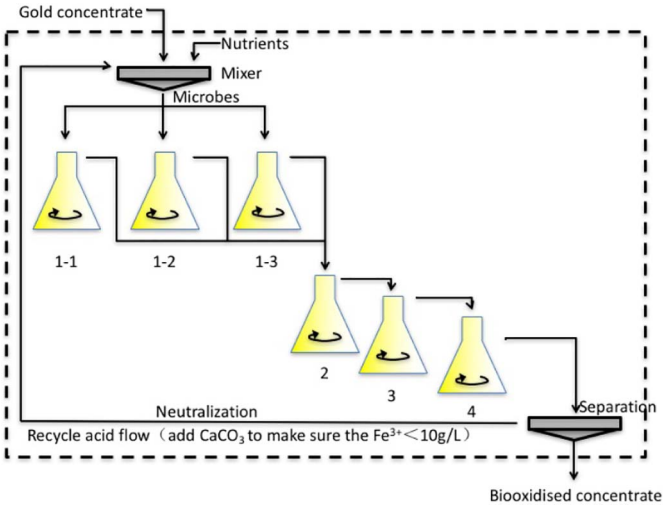

Fig. 1. A simple flowchart of the semi-continuous biooxidation reactor.

2.3. Biooxidation pretreatment

The batch biooxidation process was carried out in six 1-L shake flasks with 500 mL of 9K medium (initial pH 1.6), with 1 ± 0.2 × 10^8 cells/mL of microbial culture (using centrifuged cells as inoculum) and 75 g of gold concentrate as the only energy source. As shown in Fig. 1, the pilot flow was operated with the first three flasks in parallel and the three secondary flasks in series, giving a total of four stages (van Aswegen et al., 2007). The reaction flasks were incubated at 45 °C and 180 rpm on rotary shaker. The culture was adjusted to pH 1.6 at the start and manually maintained pH at 1.0–1.5 every 4 h during the biooxidation by the addition of $CaCO_3$ or H_2SO_4 to guarantee the activity of microbes. Overflow from the primary flasks to the next stage was manually diverted every 8 h, depending on the redox potentials. The vitality of the cells and the redox potential were checked to make sure that the processes were stable until the redox potential of each flask was in the range of 550–650 mV and the cell density was above 10^8 cells/mL. The whole residence time was maintained at 140 ± 4 h, which was determined by the operating conditions including the sulfide oxidation and the corresponding gold recovery, as described previously (Miller and Hansford, 1992; Arrascue and van Niekerk, 2006; van Aswegen et al., 2007).

The pulp samples in the six flacks were analyzed to monitor the pH, redox potential and oxidation level. The weight lost due to evaporation during the bioprocess was compensated for with distilled water. After the bioprocess, the samples were centrifuged in tubes for 10 min at 9000 rpm (6000 × *g*) to separate the liquid and solid (Schippers et al., 1996). The supernatant solutions were treated with $CaCO_3$ to remove Fe^{3+} and As^{5+} (there was < 10 g/L of Fe^{3+} after alkali treatment) and then recycled to the mixed section before the biooxidation. For the subsequent TU leaching experiment, all the oxidation products were collected.

2.4. Single TU leaching

After biooxidation, the bio-residue was equally divided into 9 parts and then assigned to 3 groups according to their pretreatment methods (Table 2). X indicated washing and filtering; Z meant leaching without any treatment; and W represented washing, filtering and leaching with a bacteriostatic reagent. For the washing and filtering section, the residue was washed with 500 mL of diluted sulfuric acid solution (pH 1.5) twice and filtered by vacuum filter. The pore size of the filter