The copper–ethanediamine–thiosulphate leaching of gold ore containing limonite with cetyltrimethyl ammonium bromide as the synergist

Hong Yu [a], Futing Zi [b], Xianzhi Hu [b],[*], Jin Zhong [a], Yanhe Nie [a], Pengzhi Xiang [a]

[a] Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650093, China
[b] Faculty of Science, Kunming University of Science and Technology, Kunming 650500, China

ARTICLE INFO

ABSTRACT

The leaching of thiosulphate gold for a gold ore containing limonite was investigated. The results indicate that the copper ion–ethanediamine(en)–thiosulphate system was more suitable than the copper ion–ammonia–thiosulphate system for gold extraction of the gold ore. The use of cetyltrimethyl ammonium bromide (CTAB) as an effective synergistic additive in the gold extraction process was demonstrated to increase the gold extraction rate and to reduce the thiosulphate consumption for the gold ore. One possible reason for this improvement may be that CTAB hydrolyses to $[CTA^+]$ and subsequently attracts the negative charged slime, thereby causing a change in the slurry rheology, which results in the gold surface's being exposed and thus easily leached in the thiosulphate leaching system. Another reason may be the formation of ion pairs, $[CTA^+]_3[Au(S_2O_3)_2^{3-}] \cdot nH_2O$ and $[CTA^+][AuBr_2^-] \cdot nH_2O$, which leads to the stabilisation of $[Au(S_2O_3)_2^{3-}]$ in the leaching system. The two effects of CTAB increase the gold extraction rate remarkably and sharply reduce the thiosulphate consumption. The gold dissolution rate of the gold ore could reach 94.3% and the thiosulphate consumption could be reduced to 1.12 kg/t ore in the thiosulphate gold leaching system containing 0.1 mol/L of sodium thiosulphate, 0.06 M ethanediamine, 0.005 M copper ion and 1.5 kg/t of CTAB and operated at a rate of agitation of 150 rpm.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

For many years, thiosulphate gold leaching has received considerable attention as an alternative technology to the cyanidation of gold ores due to environmental reasons and the reduction of the amount of easily extracted gold ore. (Abbruzzesse et al., 1995; Aylmore and Muir, 2001; Senanayake, 2007) (Li and Miller, 2006). Thiosulphate leaching is also effective for the treatment of refractory ores, especially for carbonaceous-type gold ores, through the prevention of preg-robbing (Alymore, 2001; Aylmore and Muir, 2001; Feng and van Deventer, 2010a; Muir and Aylmore, 2004; Senanayake, 2007, 2011; Xia, 2001).

Adding copper ions and ammonia into the thiosulphate solution of the mixture is the most widely used thiosulphate gold leaching liquor. One of the major problems in the thiosulphate gold leaching process is the high consumption of thiosulphate; this consumption is mainly due to thiosulphate decomposition, which is catalysed by the copper ammonia complex ions. To reduce the thiosulphate consumption, sulphite was added to the leaching solution to stabilise the thiosulphate (Kerley, 1981, 1983). Several researchers introduced additives, such as ethylene diamine tetraacetic acid to stabilise copper in solution at low reagent concentrations of ammonia (Feng and van Deventer, 2010b). Feng and van Deventer (2010b, 2011a,b) used orthophosphate, polyphosphate and

carboxymethyl cellulose as an additive in the leaching liquor, which can reduce the leaching passivation and improve the leach slurry rheology.

Ethylenediamine (en) and copper can form more stable complexes than that of the cupric ammine complex in solution. The cupric-en complexes could lower the cupric/cuprous redox equilibrium potentials and thus reduce the catalytic oxidation ability of Cu (II), which can reduce the amount of thiosulphate consumption. Ethylenediamine was also used as an additive by Xia (2008) for the leaching of gold from composite ores containing various sulphide minerals. The consumption of thiosulphate was largely reduced.

In this paper, the copper ion–ethanediamine(en)–thiosulphate liquor was used in the leaching of a gold ore containing limonite. To improve the leaching rate, cetyl trimethyl ammonium bromide (CTAB) was introduced as a synergistic additive in the leaching system. This study investigated the effects of the thiosulphate concentration, ethylenediamine addition, the presence of cupric ions, and several other variables affecting gold leaching.

2. Experiments

2.1. Materials

Ethylenediamine was mixed with distilled water to prepare 0.1 M of stock solution. $S_2O_3^{2-}$ in the form of sodium thiosulphate, Cu^{2+} in the form of copper sulphate, and NH_3/NH_4^+ in the form of ammonia water

* Corresponding author.
E-mail address: xianzhihu2@sina.com (X. Hu).

Table 1
The multi-element analysis of the raw ore.

Element	Au(g/t)	Ag(g/t)	As	Sb	Fe	Mn	S	C
Content,%	2.10	59.36	0.14	0.033	38. 10	3.60	0.024	0.66

Element	SiO$_2$	Al$_2$O$_3$	CaO	MgO	K$_2$O	Cu	Pb	Zn
Content,%	13.07	5.44	1.79	2.20	0.82	0.57	2.00	0.48

were added in the leaching solution and other reagents are analytical grade.

The gold ore sample was obtained from the Yunnan Gold Mine Group in China. Currently, the cyanidation of gold leaching has been halted due to environmental problems in the actual production. The multi-element analysis of the raw ore is presented in Table 1. Using an optical microscope, a scanning electron microscope (SEM), and X-ray diffraction methods, the phase constitutions of gold and iron in raw ore were obtained, as presented in Tables 2 and 3, respectively. The raw ore contains many fine grained particles that form the slime in the gold leaching process, which makes the extraction of gold difficult.

The data in Table 2 indicates that the gold in the ore primarily exists in the form of native gold with a distribution rate of 95.72%; the secondary forms of gold exist in sulphide and iron mineral with distribution rates of only 1.90% and 0.76%, respectively. The gold particle size is less than 0.030 mm in general. The natural gold enclosed in the limonite mainly is fissure gold, followed by the intergranular gold, generally in the size range of 0.010–0.030 mm.

Table 3 indicates that 67.22% of the iron in the ore exists in the form of hematite and limonite and 23.65% exists in the form of magnetite. As is known, limonite easily undergoes argillisation; gold that is mainly enriched in limonite is difficult to extract.

2.2. Extraction of gold

All experiments were performed at room temperature (17 °C–22 °C), the gold leaching test was performed in a 500-mL conical flask using a mechanical stirrer. 150 mL of a leaching solution was added to 100 g of the gold ore. A natural pH of approximately 10 was used in the experiments. Gold leaching tests were performed at a rotation speed of 300 rpm. Samples were taken continuously at set intervals during a total leaching time of 24 h. The samples were subjected to iodine titration to determine the concentration of $S_2O_3^{2-}$ immediately, and the gold concentration was detected by ICP-AES analysis. The absorbance of $Cu(en)_2^{2+}$ was determined at 550 nm using a UV-722 apparatus. The gold extraction rate of the ore was calculated by the gold concentration dissolved in the leaching liquor and the gold content in the ore.

3. Results and discussion

The copper and ammonia were widely used in the systems; however, we also used ethylenediamine to replace ammonia and cetyltrimethyl ammonium bromide as the synergistic additive in the leaching liquor. Therefore, two gold thiosulphate leaching systems were used in this investigation simultaneously.
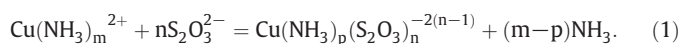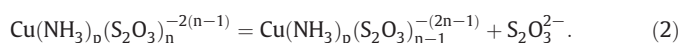
3.1. Effect of copper ion concentration

The effects of copper ion concentration on the gold extraction rate and the thiosulphate consumption in the copper ion–ammonia–thiosulphate system and the copper ion–ethanediamine(en)–thiosulphate system were investigated. The results for the gold extraction rate and the thiosulphate consumption are shown in Figs. 1 and 2, respectively. Copper ion concentration was varied from 0 to 0.05 M whilst the ethylenediamine concentration was kept at 0.06 M; the concentration of sodium thiosulphate was 0.1 M, and the concentration of NH_3/NH_4^+ was 0.5 M (Feng and van Deventer, 2010b, 2011b).
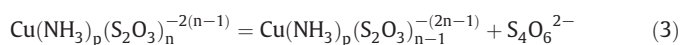
In the Cu^{2+}–ammonia–thiosulphate system, increasing copper(II) enhances the redox reaction via the mixed complexes on the basis of the equilibrium shown in Eq. (1) and the rate determining steps in Eqs. (2) and (3) (Senanayake and Zhang, 2012). Whilst $S_2O_3^{2-}$ formed in Eq. (2) is dimerised to $S_4O_6^{2-}$, the latter is hydrolysed to other products, as discussed later. In addition, excessive copper ions with S^{2-} may be from CuS, which covered the gold surface and hindered the dissolving of gold.

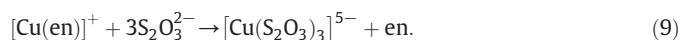$$Cu(NH_3)_m^{2+} + nS_2O_3^{2-} = Cu(NH_3)_p(S_2O_3)_n^{-2(n-1)} + (m-p)NH_3. \quad (1)$$

First order reaction:

$$Cu(NH_3)_p(S_2O_3)_n^{-2(n-1)} = Cu(NH_3)_p(S_2O_3)_{n-1}^{-(2n-1)} + S_2O_3^{2-}. \quad (2)$$

Second order reaction:

$$Cu(NH_3)_p(S_2O_3)_n^{-2(n-1)} = Cu(NH_3)_p(S_2O_3)_{n-1}^{-(2n-1)} + S_4O_6^{2-} \quad (3)$$

where m = 4, n = 1, 2, and p = 2, 3.

In the Cu^{2+}–ethanediamine–thiosulphate system, Xia (2008) prepared $Cu(en)_3^{2+}$ by mixing copper sulphate with ethylenediamine at a molar ratio of 1:3, and copper ions involved in the reactions described by Eqs. (4)–(9). However, according to Huheey, tri-ethylenediamine copper(II) is labile in water and dissociates to di-ethylenediamine copper(II) (Huheey et al., 1983). As a result, the primary species of copper in the leaching system were $Cu(S_2O_3)_3^{5-}$ and $Cu(en)_2^{2+}$.

$$2en + Cu^{2+} \rightarrow Cu(en)_2^{2+} \quad (4)$$

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \quad (5)$$

$$Cu^{2+} + 4OH^- \rightarrow Cu(OH)_4^{2-} \quad (6)$$

$$Cu(en)_2^{2+} + OH^- \rightarrow Cu(OH)_2 + 2en \quad (7)$$

$$en + Cu^+ \rightarrow [Cu(en)]^+ \quad (8)$$

$$[Cu(en)]^+ + 3S_2O_3^{2-} \rightarrow [Cu(S_2O_3)_3]^{5-} + en. \quad (9)$$

Table 2
The phase constitution of gold in the raw ore.

Phase constitution	Bare gold	Gold enclosed by sulphite	Gold enclosed by iron ore	Gold enclosed by carbonate	Gold enclosed by silicate	Total
Content, g/t	2.01	0.016	0.04	0.004	0.03	2.10
Distribution,%	95.72	0.76	1.90	0.19	1.43	100.00