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Technical note

Selective leaching of arsenic from enargite concentrate using alkaline leaching in the presence of pyrite

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This research is applicable to solving problems related to arsenic pollution.

1. Introduction

It is difficult to separate enargite $(Cu₃AsS₄)$ from copper sulfide minerals such as chalcopyrite (CuFeS₂) and chalcocite (Cu₂S) in conventional flotation due to their similar flotation properties, which usually decreases the purity of copper product and causes environmental problems in the subsequent pyrometallurgical process. Recently, several researchers have selectively separated enargite from copper sulfide minerals using electrochemical control, pre-oxidation and selective flotation reagents to obtain a clean copper concentrate ([Tongamp et al., 2010](#page--1-0); [Senior et al., 2006\)](#page--1-1). Despite extensive research, the removal of arsenic-bearing minerals from copper ores is still a challenge ([Long et al., 2014\)](#page--1-2).

To recover copper from copper ores or concentrates containing quantities of enargite, selective separation of enargite from non‑arsenic copper sulfides by flotation is necessary to produce a low-arsenic copper concentrate and a high-arsenic copper concentrate. The lowarsenic concentrate can be sent to the smelting process without financial penalties for excessive arsenic content ([Bruckard et al., 2010](#page--1-3)). Hydrometallurgy is a promising technique to eliminate arsenic from copper concentrate containing large amounts of enargite. Due to the slow dissolution rate of enargite in acidic solutions, more researchers have focused on the alkaline leaching of enargite. Many types of alkaline media, such as NaOH-Na2S, NaOH-NaHS and NaOH-NaClO, have been used to selectively leach arsenic from enargite [\(Viñals et al., 2003](#page--1-4);

[Balá et al., 2000;](#page--1-5) [Curreli et al., 2005](#page--1-6); [Parada et al., 2014;](#page--1-7) [Tongamp](#page--1-0) [et al., 2010](#page--1-0)). After leaching in different solutions, arsenic is converted to AsS_4^3 ⁻ or AsO₄³⁻in the leach solution; the solid residue, which is rich in CuO or Cu2S, is then suitable to smelt directly. The reactions are given as follows:

 $2Cu_3AsS_4 + 3NaOH + 3NaHS = 3Cu_2S + 3H_2O + 2Na_3AsS_4$ (2)

 $2Cu₃AsS₄ + 22NaOH + 35NaClO = 6CuO + 11H₂O + 2Na₃AsO₄$ $+ 8Na_2SO_4 + 35NaCl$ (3)

The leaching behavior of enargite in NaHS media and $Na₂S$ media is extremely similar [\(Filippou et al., 2007](#page--1-8); [Tongamp et al., 2010\)](#page--1-0). Both sodium sulfide and sodium hydrosulfide can provide S^{2-} anions, which substitute arsenic in enargite during the leaching process. Some researchers have also investigated the leaching kinetics of enargite in alkaline solutions [\(Parada et al., 2014](#page--1-7); [Ruiz et al., 2014\)](#page--1-9) and found that the removal of arsenic from enargite was chemical reaction-controlled.

Since enargite, which commonly associates with copper sulfides, causes both environmental contamination from toxic arsenic and negative impact on the human body in copper smelting, a more economical and environmentally friendly pre-processing method for arsenic removal and copper recovery is evidently needed. In this work, the leaching of enargite flotation concentrate containing large amounts of pyrite in alkaline solution with sodium hydroxide only was studied.

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Fig. 1. X-ray diffraction analysis of the enargite concentrate.

There is no need for the addition of other sulfide species such as sodium sulfide or sodium hydrosulfide due to the fact that pyrite may be a source of S^{2-} anions.

2. Experimental

2.1. Materials

The enargite concentrate used in this work was prepared from arsenic bearing copper ores by crushing, grinding and flotation. The particle size of samples was 95% passing $75 \mu m$. The elements of interest in solid samples and leach solutions were analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP, IRIS Intrepid II XSP). The crystalline phases were detected using X-ray

Table 1 Results of $L16(4^5)$ orthogonal experiments.

No.	Experimental factor	Arsenic dissolution (%)	No.	Experimental factor	Arsenic dissolution (%)
	A(K)	B (min)	C(g/L)	D (mL/g)	
$\mathbf{1}$	1(433)	1(90)	1(100)	1(3)	29.5
$\,2$	$\mathbf{1}$	2(120)	2(150)	2(4)	59.1
3	$\mathbf{1}$	3(150)	3(200)	3(5)	93.9
4	$\mathbf{1}$	4 (180)	4(250)	4(6)	93.1
5	2(443)	1	2	3	82.9
6	$\overline{2}$	$\overline{2}$	$\mathbf{1}$	4	55.8
7	$\overline{2}$	3	4	$\mathbf{1}$	94.0
8	$\overline{2}$	4	3	$\overline{2}$	98.2
9	3(453)	$\mathbf{1}$	3	$\overline{4}$	97.5
10	3	$\overline{2}$	4	3	97.0
11	3	3	$\mathbf{1}$	$\overline{2}$	89.1
12	3	$\overline{4}$	$\overline{2}$	$\mathbf{1}$	94.9
13	4(463)	$\mathbf{1}$	4	$\overline{2}$	96.3
14	4	$\overline{2}$	3	$\mathbf{1}$	98.4
15	$\overline{4}$	3	$\overline{2}$	$\overline{4}$	98.1
16	4	4	$\mathbf{1}$	3	93.0
K_1	275.6	306.2	267.1	316.8	
K ₂	330.9	310.3	335.0	342.4	
K_3	378.2	374.8	388.1	366.8	
K_4	385.8	379.2	380.4	344.5	
$K_1/4$	68.9	76.6	66.8	79.2	
$K_2/4$	82.7	77.6	83.7	85.6	
$K_3/4$	94.6	93.7	97.0	91.7	
$K_4/4$	96.4	94.8	95.1	86.1	
Range	27.5	18.3	30.2	12.5	

powder diffraction (XRD, Rigaku, TTR-III) in 2 θ scale using CuKα radiation ($k = 1.5406 \text{ Å}$, 50 kV and 100 mA) at the scanning rate of 10 degrees/min, varied from 10 to 70 degrees. Leach residues were characterized by scanning electron microscopy (JSM-6360LV, JEOL) and

Fig. 2. Effect of leaching temperature (a), NaOH concentration (b), leaching time (c), and liquid-to-solid ratio (d) on enargite dissolution. Temperature was fixed at 443 K, NaOH concentration at 150 g/L, leaching time at 120 min and liquid-to-solid ratio at 4 mL/g except for special statement. Blue lines represent the percentage of arsenic dissolution from enargite. Red lines represent arsenic grade in leach residue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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