



Selective leaching of arsenic from enargite in NaHS–NaOH media

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ABSTRACT

The dissolution kinetics of arsenic from enargite (Cu_3AsS_4) was investigated in sodium hydrosulfide (NaHS) solution of concentration range 0.68 M–1.35 M S^{2-} and 1.25 M OH^- (NaOH) in the temperature range from 298 K to 363 K. The kinetic equation from evaluation of experimental data using several heterogeneous and pseudo-homogeneous reaction models was found to be $1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha) = kt$ and from the Arrhenius plot, using k values determined experimentally, an activation energy of 70.26 ± 4.74 kJ/mol was obtained. This result indicates that the rate-determining process for the reaction between Cu_3AsS_4 and NaHS is controlled by product layer diffusion process. Characterization of solid samples by XRD and chemical analysis by ICP showed that Cu_3AsS_4 was transformed to Cu_2S and complete removal of arsenic into solution can be achieved within 60 to 120 min.

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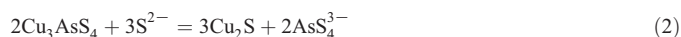
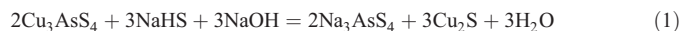
1. Introduction

Enargite (Cu_3AsS_4) and tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$) are the main minerals with high arsenic content that associate with copper and iron sulfides [covellite (CuS), chalcocite (Cu_2S), chalcopyrite (CuFeS_2), Bornite (Cu_5FeS_4), pyrite (FeS_2)] and are normally recovered by flotation and offered as copper resource to smelters for copper recovery. However the high content of arsenic effectively reduces value of the copper resource due to environmental implications of toxic arsenic that require additional processing steps for containment of arsenic. As demand for copper continues to grow, the need to source copper from all resources including those that contain high arsenic is necessary and as such more economical and environmentally friendly processing options will be sought. Reviews on copper resources containing enargite are covered widely in literature by many researchers (Lattanzi et al., 2008; Filippou et al., 2007; Mihajlovic et al., 2007; Baláž and Achimovičová, 2006a; Guo and Yen, 2005; Viñals et al., 2003; Welham, 2001; Padila et al., 1998).

For copper ores and concentrates with high arsenic contained as enargite for feed to smelters, first, separation by flotation to obtain a clean concentrate with arsenic content <0.5 wt.% and a dirty reject mainly containing enargite by employing slurry potential and pH control with depressants and activators can be achieved and is discussed in literature (Filippou et al., 2007; Senior et al., 2006; Guo and Yen, 2005; Kantar, 2002; Fornasiero et al., 2001; Pauporté and Schuhmann, 1996; Menacho et al., 1993). In the second case involving leaching, the transformation of enargite to CuO or Cu_2S by selectively dissolving

arsenic into solution with sodium hypochlorite (NaClO) or sodium sulfide (Na_2S) in alkaline solutions with NaOH gives very promising results (Lattanzi et al., 2008; Mihajlovic et al., 2007; Filippou et al., 2007; Baláž and Achimovičová, 2006a,b; Curreli et al., 2005; Delfini et al., 2003; Viñals et al., 2003; Delfini et al., 2003; Baláž et al., 2000; Jackson, 1986). Other hydrometallurgical treatment options through chloride and sulfates leaching, or in ammonical solutions and at elevated temperatures and pressures is reported elsewhere in literature (Filippou et al., 2007; Viñals et al., 2003; Canales et al., 2002; Herreros et al., 2002; Dutrizac and MacDonald, 1971).

In a recent study, Tongamp et al. (2009) have introduced sodium hydrosulfide (NaHS) as a leaching media for the conversion of enargite (Cu_3AsS_4) to Cu_2S in NaHS–NaOH solution. They have shown that near complete removal of arsenic (>99%) in enargite can be achieved within 4 to 6 h even for very high pulp density at 1000 g/L and have proposed Reaction (1) as overall reaction to represent conversion of Cu_3AsS_4 to Cu_2S in NaHS–NaOH media. NaHS dissociates to provide S^{2-} to substitute arsenic in enargite and NaOH addition maintains high alkaline environment, preventing hydrolysis of S^{2-} to HS^- and allow Reaction (1) to proceed. This reaction mechanism could be simplified to show direct role of S^{2-} ions offered by NaHS in the conversion of enargite or leaching of arsenic according to Reaction (2).



The behavior of enargite conversion in NaHS media is very similar to that of sodium sulfide (Na_2S) (Filippou et al., 2007; Baláž and Achimovičová, 2006a,b; Delfini et al., 2003; Baláž et al., 2000), however, selection of NaHS was based on its application in copper flotation

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and also its higher sulfur content (~43%) per unit mole NaHS as compared to Na_2S (~13%) since leaching of arsenic from enargite is a function of sulfur $[\text{S}^{2-}]$ concentration.

In the current study, the effects of particle size, slurry stirring rate, NaHS concentration and temperature were investigated to study the reaction kinetics of enargite in NaHS–NaOH media and identify the rate-determining process for Cu_3AsS_4 in NaHS–NaOH media.

2. Experimental

2.1. Materials

The enargite ore sample (Mt Jinga, Taiwan) was first prepared by crushing/milling and sizing to obtain four size ranges: $-125 + 100 \mu\text{m}$, $-100 + 75 \mu\text{m}$, $-75 + 32 \mu\text{m}$, and $-32 \mu\text{m}$. Chemical composition of main elements was: 3.5 to 4.0 wt.% As, 12.0 to 12.6 wt.% Cu, and 20 to 24 wt.% Fe (Table 1) and X-ray diffraction pattern showed Cu_3AsS_4 , SiO_2 , and FeS_2 as main mineral constituents, shown in Fig. 1. The d -spacing values for enargite and corresponding 2θ degrees are 3.22\AA (28.58°), 3.21\AA (28.68°), 3.07\AA (30.12°), 2.84\AA (32.85°), 1.85\AA (56.38°) and they correspond well with the peaks identified in Fig. 1 and the d -spacing values calculated from the XRD pattern are 3.28\AA (28°), 3.18\AA (29°), 2.91\AA (32°) and 1.86\AA (56°). Assuming all arsenic is hosted as enargite, the ore sample contains up to 20.5 wt.% enargite and will contain about 9.4 wt.% copper, a slightly higher value over 12 wt.% Cu could be due to presence of other copper bearing minerals.

Sodium hydrosulfide (NaHS, 70% purity) and sodium hydroxide (NaOH, 90% purity) chemical grade reagents supplied by Wako Chemicals, Japan were used to prepare NaHS–NaOH alkaline solution for leaching of arsenic or conversion of Cu_3AsS_4 to Cu_2S .

2.2. Leaching

A 200 ml Teflon beaker fully enclosed with a thermometer fixed for monitoring temperature, exhaust line to prevent solution evaporation, and opening for sampling was used for all leaching experiments. Into the beaker, 150 ml leaching solution (50 to 100 g/L (0.68 to 1.35 M) NaHS + 50 g/L (1.25 M) NaOH) was introduced, adjusted temperature to required test temperature from 298 to 363 K and added 1.0 g of enargite sample. All tests for kinetic study were performed for 120 min and at varying stirring rate from 360 to 550 rpm. A 5 ml sample was continuously drawn from the leach slurry at specified time intervals (5, 10, 20, 30, 60, 90, and 120 min) for analysis of dissolved arsenic. Solid samples after experimental run were separated from solution for both chemical and phase analyses.

2.3. Characterization and chemical analyses

X-ray diffraction (XRD) measurements were performed by using Rigaku, RINT-2200/PC system with a $\text{Cu K}\alpha$ irradiation source ($\lambda = 1.5405 \text{\AA}$) at 40 kV and 50 mA. Samples were analyzed in a continuous scan mode between 10° and $80^\circ 2\theta$. Slurry solution pH and potential were measured for every test using laboratory Eh/pH meters. All solution analysis was conducted using an Inductively Coupled Plasma (ICP-AES/OES) atomic/optical emission spectrometer, SPS-3000 (Seiko Instruments Inc.).

Table 1

Chemical contents for the enargite ore separated into different size fractions.

Size fraction (μm)	Chemical analysis (wt.%)		
	As	Cu	Fe
$-75 + 32$	3.65	12.32	23.37
$-100 + 75$	3.68	12.19	21.20
$-125 + 100$	3.91	12.53	20.10

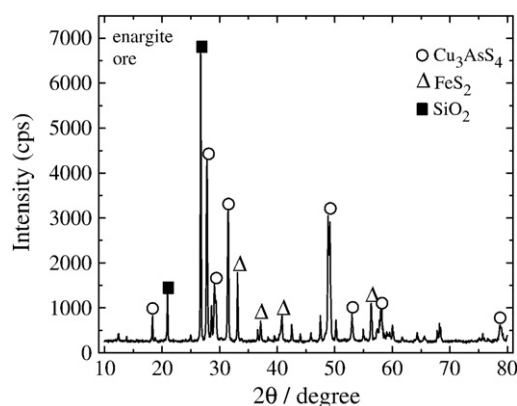


Fig. 1. Characteristic X-ray diffraction pattern of enargite ore with arsenic content of 3.65 wt.%.

3. Results and discussion

3.1. Effect of particle size

At fixed reagent concentration (100 g/L (1.35 M) NaHS + 50 g/L (1.25 M) NaOH) and slurry temperature (353 K), arsenic leaching behavior of 1.0 g enargite sample in 150 ml solution for the four size fractions was investigated. According to Fig. 2, arsenic leaching from all the four size fractions rapidly reached up to 40% in the first 10 min. As leaching is progressed, arsenic removal from $-32 \mu\text{m}$ proceeds faster reaching 80% in 30 min and complete arsenic removal observed within 60 min. The $-75 + 32 \mu\text{m}$ fraction also proceeds faster reaching 80% in 60 min and over 99% in 120 min. However, arsenic removal for $-100 + 75 \mu\text{m}$ and $-125 + 100 \mu\text{m}$ proceeds slowly and remains consistently below 60% throughout the 120 min leaching period. The result generally indicates higher arsenic removal for the smaller size fraction which is attributed to by increased surface area of the sample.

3.2. Effect of NaHS concentration

The leaching profile of the $-75 + 32 \mu\text{m}$ enargite fraction in NaHS solution of different concentrations; 50 (0.68 M), 75 (1.01 M), 100 g/L (1.35 M) + 50 g/L (1.25 M) NaOH for 120 min is shown in Fig. 3.

Slurry temperature and stirring rate were fixed at 353 K and 550 rpm respectively. At 100 g/L (1.35 M) NaHS addition, over 99% arsenic is removed within 120 min, however, the leaching rate decreases when NaHS concentration is reduced to 75 (1.01 M) and 50 g/L (0.68 M), reaching up to 85% and 55% for the two NaHS concentrations respectively in 120 min. Low arsenic removal at 50 and 75 g/L NaHS

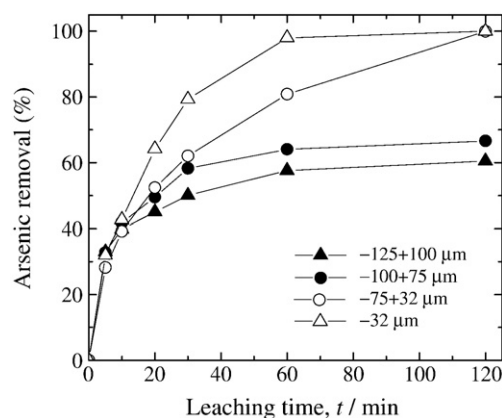


Fig. 2. Leaching arsenic from enargite ore of different size fractions at 353 K and slurry stirred at 550 rpm for 120 min. NaHS concentration at 100 g/L (1.35 M) and NaOH at 50 g/L (1.25 M).

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