



Leaching kinetics of enargite in alkaline sodium sulphide solutions



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ABSTRACT

Leaching of enargite samples containing approximately 12% As, 0.5% Sb and 39% Cu was studied in alkaline sulphide solutions containing sodium hydroxide and sodium sulphide. Kinetic parameters studied included temperature, particle size, reagent concentration, agitation rate and stoichiometry in high pulp density experiments. The extraction of arsenic was chemical reaction controlled with an activation energy of 74 kJ mol⁻¹, indicating the importance of temperature on the process. The relative contributions of total initial sulphide and hydroxide concentrations on leaching kinetics were determined and a new rate equation was developed

$$r_{As} = -\frac{d[As]}{dt} = k'[As]^{2.37} [S^{2-}]^{1.83} [OH^-]^{-3.31}, \quad \text{kg t}^{-1} \text{ h}^{-1}$$

where k' depends on system activation energy and can be predicted from this parameter (it had a value of 1.63×10^{-3} in this work). This rate equation was validated against data presented in other similar studies of enargite leaching. It is demonstrated that the hydroxide ion plays a direct role in the leaching reaction, rather than simply ensuring adequate sulphide speciation. Copper, iron, zinc, and silver were not extracted during the leaching procedure. Through chemical analysis, X-ray diffraction and scanning electron microscopy leach residues were characterised. Residues contained copper–sulphur compounds such as digenite, bornite and sodium copper sulphide (NaCu₅S₃).

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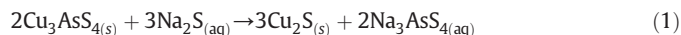
1. Introduction

The main source of copper from sulphide minerals is chalcopyrite (CuFeS₂), but it can often be associated with arsenic in sulphosalts. The most common of these sulphosalts is enargite (Cu₃AsS₄), and there are several copper deposits rich in enargite that have been or are being processed right now. El Indio in Chile, Lepanto in the Philippines, and Chelopech in Bulgaria are examples of such deposits (Filippou et al., 2007). Processing of copper ores (or any ores) that contain arsenic is challenging; arsenic is considered a carcinogen with high mobility in aqueous streams, which in time may lead to increased arsenic concentrations in rivers (Oyazun et al., 2004, 2006) and drinking water. Due to environmental and plant hygiene concerns, pyrometallurgical operations will penalize concentrates that contain arsenic over 0.5% by weight (sometimes less). The presence of arsenic can also increase shipping costs of concentrates, which are commonly imported/exported overseas (Castro, 2008; Filippou et al., 2007).

The alkaline sodium sulphide leach process has been developed for the removal of arsenic, antimony, mercury and tin. Initially this process

was used to upgrade silver concentrates by removing antimony mainly from tetrahedrite (Ackerman et al., 1993; Anderson et al., 1994; Edwards, 1985; Filippou et al., 2007; Holmes, 1943; Raudsepp, 1981). Two well-known operations that used this process are the Sunshine antimony refinery (Ackerman et al., 1993) in Idaho, USA, and the Equity silver mine (Edwards, 1985) in British Columbia, Canada. Both operations are now closed. The alkaline sodium sulphide leach process was later adopted for the removal of arsenic from copper sulphide ores (Carly and Ollivier, 1981; Coltrinari, 1977; Holmes and Coltrinari, 1973; Nadkarni et al., 1975). Arsenopyrite, which is not a copper source, has been reported to be refractory to the alkaline sulphide leach (Edwards, 1985).

The alkaline sodium sulphide leach process works at atmospheric conditions at temperatures between 80 to 110 °C (Filippou et al., 2007) just below the boiling point of a sodium hydroxide–sodium sulphide solution. In the presence of sulphide, arsenic is believed to be released from enargite forming sodium thioarsenate as shown in reaction (1):



It has been reported that in order to ensure the presence of sulphide ions, enough caustic must be added to avoid hydrolysis of sulphide to

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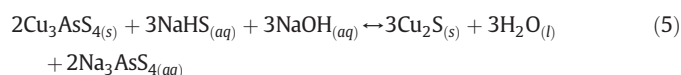
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hydrosulphide (Anderson and Twidwell, 2008; Carly and Ollivier, 1981; Coltrinari, 1977; Curreli et al., 2009; Holmes and Coltrinari, 1973; Nadkarni and Kusik, 1988; Nadkarni et al., 1975; Tongamp et al., 2010), which is thought to decrease leaching performance. Ideally the solution pH should be maintained above 12, which is approximately the pH above which sulphide ions are thought to exist (Anderson and Twidwell, 2008; Tongamp et al., 2010).

However, other researchers have reported that the free energy of formation for aqueous sulphide is actually approximately 111 kJ/mol, which means that the second dissociation constant of H₂S should be at approximately 10⁻¹⁷. This suggests that sulphide ions would predominate only at a pH of 17 or greater (Giggenbach, 1971; Licht, 1988; Protopopoff and Marcus, 2003). It is likely then that a predominance of hydrosulphide ions exists even at pH greater than 12 (as shown in Fig. 1).



Thus it is possible that hydrosulphide is the main sulphide species reacting during enargite dissolution, as shown in reactions (4) and (5). Reaction (5) has previously been proposed by Tongamp et al. (2009, 2010) and it is noteworthy that this reaction also includes hydroxide as a reacting species; inclusion of which will be discussed later in this article.



Irrespective of sulphide speciation, all researchers agree that removal of arsenic is faster at higher pH, and their results strongly support this conclusion. Similarly, increasing the concentration of sodium sulphide is known to increase arsenic recovery (Anderson and Twidwell, 2008; Curreli et al., 2009; Nadkarni and Kusik, 1988; Tongamp et al., 2009, 2010). Thus, in general researchers agree that increasing sodium hydroxide and sodium sulphide concentrations increases arsenic leaching rates (Anderson and Twidwell, 2008; Curreli et al., 2009; Nadkarni and Kusik, 1988; Tongamp et al., 2009, 2010). However, corrosion issues brought by caustic conditions and the high price of sodium sulphide

make it desirable to optimise their respective dosages. A rate equation explaining the influence of each of these parameters would thus be highly useful.

Even though previous research has shown that alkaline sodium sulphide leaching of enargite efficiently removes arsenic, there are several scientific questions that remain and that bear significant consequences for process design. For example, the rate controlling step remains controversial. Baláz et al. (2000) have concluded that alkaline sodium sulphide leaching is controlled by a chemical reaction whereas more recent work by Tongamp et al. (2010) has found that a diffusion process was rate determining. As discussed above, the relative importance of total sulphide and hydroxide concentrations in the leaching process has also not been elucidated. This is an important issue as a recent patent has shown that leaching can occur at sub-stoichiometric (see reaction (5)) total sulphide concentrations (Nakon and Way, 2012). This work revisits the alkaline sulphide leaching process adding these issues to the discussion. The kinetics of leaching of a natural enargite sample is measured and the rate controlling step is identified. A new rate equation for the dissolution of arsenic from enargite as a function of total sulphide and hydroxide concentrations is developed and is shown to adequately predict experimental data from this work and from previous studies. Additionally, high pulp density tests are performed to demonstrate the practical importance of this parameter on arsenic extraction. Finally, a detailed study of the new phases that form during leaching is performed to lend credence to the kinetic testing results.

2. Material and methods

2.1. Sample preparation

The enargite sample used was from Butte, Montana. Leaching samples were prepared by crushing with a laboratory cone crusher and grinding using a ring mill. The crushed sample was mixed by coning and quartering followed by splitting through a 10 channel splitter, obtaining 100 gram samples which were ground to achieve different particle sizes ranging from approximately a P₈₀ of 100 μm to 30 μm. Each ground sample of 100 grams was then homogenized by coning and quartering and then smaller samples were obtained. A sample with P₈₀ of approximately 40 μm was used for kinetic experiments at different temperatures. The particle size distribution for this sample is shown in Fig. 2.

For Quantitative X-Ray Diffraction using Rietveld refinement (QXRD) the samples were ground under ethanol in a vibratory McCrone Micronising Mill for 7 min. Continuous-scan X-ray powder-diffraction data were collected over a range 3–80°2θ with CoKα radiation on a Bruker D8 Focus diffractometer equipped with an Fe monochromator

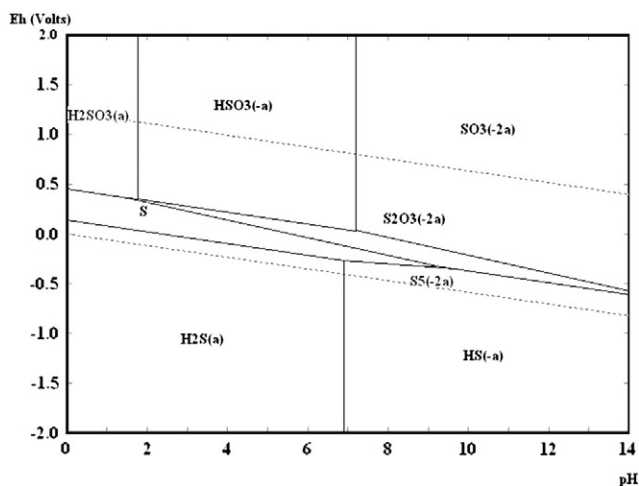


Fig. 1. Metastable S–H₂O Eh–pH diagram at 25 °C considering pK_2 from reaction (3) (plotted with HSC Chemistry software version 7.1).

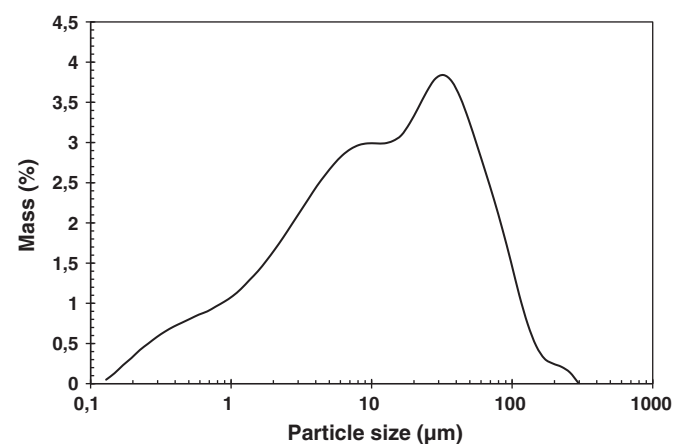


Fig. 2. Particle size distribution for the enargite sample used for determination of the rate controlling process, P₈₀ = 40 μm.

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