



Rapid atmospheric leaching of enargite in acidic ferric sulfate media



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ABSTRACT

A new method is presented for the rapid dissolution of enargite enhanced by the addition of pyrite as catalyst in acidic ferric sulfate media. At atmospheric conditions the effects of the ratio of pyrite (FeS₂) to enargite (Cu₃AsS₄), temperature, solution potential, iron concentration, sulfuric acid concentration, particle size, and pulp density were evaluated. The best conditions were found to be at 80 °C with a pyrite to enargite ratio (Py:En) of 4, which gave complete copper extraction within 24 hours. The dissolution rate appears to be insensitive to changes in iron and acid concentrations. Elemental sulfur formed a porous layer on the surface of enargite particles, while pyrite surfaces remained clean. Arsenic presented the same dissolution rate as copper and all of the arsenic reported to solution, predominantly in the form of As(III).

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1. Introduction

Copper minerals containing arsenic such as enargite (Cu₃AsS₄) commonly occur in minor quantities in many ore deposits. But this presence has acquired importance over the last few years due to the depletion of relatively high grade copper deposits and the search for new resources to supply the growing global demand for copper.

Various treatments have been proposed to enable the processing of enargite-containing ores and concentrates. Some past studies proposed the separation of enargite from other valuable minerals such as chalcopyrite by flotation using electrochemical control and other means (Fornasiero et al., 2001; Guo and Yen, 2005; Mihajlovic et al., 2007). The purpose of these earlier studies was to obtain a clean chalcopyrite concentrate containing only traces of enargite in order to avoid smelter penalties and to facilitate separate treatment of the various minerals. In the past, copper concentrates containing considerable amounts of arsenic have been roasted before being treated in a smelter. At the El Indio smelter in Chile, this process was used to reduce the arsenic content from 10% in the concentrate to only 0.1% in the roasted product, and the arsenic was captured as arsenic trioxide (As₂O₃) in bag filters (Smith, 1986). Another hydrometallurgical route to obtain concentrates suitable for smelting has been the application of alkaline leaching. Sodium sulfide (Na₂S) can be used to leach arsenic selectively from enargite as follows:

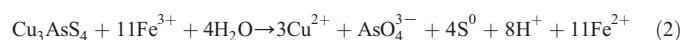


Balaz and Achimovicova (2006) found that the extent of arsenic extraction from enargite using sodium sulfide was only 5% after 10 min of

leaching at 55 °C. However, when the enargite was mechanically activated with a planetary mill, the arsenic extraction increased to 85% at 55 °C and was nearly complete when the temperature was increased to 80 °C.

In many studies, enargite dissolution in acid media has been shown to be slower than chalcopyrite (Filippou et al., 2007). One of the first studies in acid sulfate media was conducted by Brown in (1931). He found that leaching an almost pure specimen of enargite in a solution containing sulfuric acid and ferric sulfate extracted only 2% of copper after 60 days at 35 °C, and only 0.5% after 30 days with sulfuric acid alone. A simple study by Sullivan (1933) working with an enargite sample containing 45.02% Cu and 13.22% As, extracted less than 3% of the copper after 146 days at 35 °C with a solution containing 5% of iron by mass as ferric sulfate.

A more detailed study of natural and synthetic enargite dissolution by Dutrizac and MacDonald (1972) confirmed the slow kinetics of dissolution in acid sulfate media at temperatures from 60 to 70 °C. They observed that copper and arsenic dissolve at the same rate, and that the residue consists solely of elemental sulfur. The presence of Fe(III) in solution had a beneficial effect on the dissolution rate up to 0.2 M, above which higher concentrations did not have any effect. They also observed that the oxidation of sulfur to sulfate was in the range of 5 to 50%, and thus suggested the reaction for the dissolution of enargite as follows:



By this reaction, only 50% of the copper was extracted from finely ground enargite (–149 μm) after seven days at 85 °C with 0.1 M H₂SO₄ and 0.1 M Fe(III) in solution.

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Table 1
XRD mineralogical analysis of the: A) Butte enargite, and B) Huanzala pyrite massive samples.

Mineral	Ideal formula	Mass %
A		
Quartz	SiO ₂	7.9
Enargite	Cu ₃ AsS ₄	62.0
Pyrite	FeS ₂	16.1
Tennantite	(Cu,Ag,Fe,Zn) ₁₂ As ₄ S ₁₃	6.5
Sphalerite	(Zn,Fe)S	1.3
Bornite	Cu ₅ FeS ₄	2.7
Covellite	CuS	2.3
Siderite	Fe ₂ + CO ₃	0.8
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	0.5
B		
Quartz	SiO ₂	0.8
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	0.9
Fluorite	CaF ₂	4.6
Sphalerite	(Zn,Fe)S	1.0
Marcasite	FeS ₂	0.4
Pyrite	FeS ₂	92.3

Chloride media has been studied for enargite leaching by several authors. *Herreros et al. (2002)* leached enargite using chlorine which was produced in-situ by the reaction between sodium hypochlorite and hydrochloric acid in the leaching reactor. They noticed that the dissolution of enargite occurred in two distinct stages. The first stage is very fast, and is controlled by diffusion through a liquid boundary layer. The second stage is slow, and is controlled by diffusion through a solid product layer. This solid product was estimated to be non-porous elemental sulfur. Leaching at 25 °C for 40 min for fine particles (<15 μm) gave 38% Cu extraction, and only 4.8% Cu extraction for coarse particles (50 to 75 μm). The formation of sulfur coatings on the particles was assumed to be the cause of the slow dissolution.

Biological leaching of enargite has also been investigated (*Acevedo et al., 1998; Canales et al., 2002; Escobar et al., 1997; Munoz et al., 2006*). All investigators noted that mesophiles were unable to break down enargite. When thermophiles were used, surface modification occurred with formation and later oxidation of sulfur to sulfate. The dissolution was slightly faster compared with sulfate media, but complete dissolution of enargite was difficult to achieve. An inhibitory effect of arsenic in solution on bacterial viability was also observed, but this effect was less apparent when ferric was also present. Another inconvenience using thermophiles was the limitation on the amount of suspended

solids (*Batty and Rorke, 2006*). A limit of approximately ~12.5% solids by mass was proposed to avoid shearing the microbial cells and accelerating their death rate.

High pressure leaching of enargite concentrates containing pyrite has been also investigated. *Ruiz et al. (2011)* leached an enargite concentrate containing about 40% pyrite in sulfuric acid at temperatures in the range of 160 to 200 °C and an oxygen partial pressure of 345 to 1034 kPa. The results showed that the dissolution of enargite in the presence of pyrite was considerably faster than the dissolution of pure enargite. By leaching an enargite-pyrite concentrate sample of particle size $-75 + 53 \mu\text{m}$ at 200 °C and 689 kPa O₂, all copper was extracted in 15 min. They concluded that ferric ions generated during the leaching process were responsible for the enhanced dissolution of enargite in the presence of pyrite. *Nadkarni and Kusik (1988)* also observed a positive effect when pyrite was added to the high pressure leaching of enargite but their study did not present an explanation to the observed effect.

In summary, previous studies have shown that oxidative leaching of enargite in sulfuric or hydrochloric acid media, with and without bacteria, at atmospheric pressure is inefficient. Those studies in general agree that the dissolution of enargite forms majority elemental sulfur, but there is no consensus as to whether this sulfur layer is porous or non-porous, or whether this layer contributes to enargite passivation. In addition, no studies reported in literature investigated enargite leaching at controlled solution potentials. A range of suitable potentials to be applied could be obtained by electrochemical studies of the sample to be leached. Even though there are a number of electrochemical studies of enargite (*Asbjornsson et al., 2003; Munoz et al., 2006*), none of them integrates enargite electrochemistry with a way to improve its leaching kinetics.

However, in our laboratory, with a combination of simple electrochemical measurements on particles, an appropriate control of the solution potential, and the addition of a sulfide that is usually found in copper concentrates, we observed a catalytic effect of pyrite on the dissolution of enargite. This same effect has also been observed for the dissolution of chalcopyrite, resulting in the conception of a new process (*Tshilombo, 2004; Dixon et al., 2008*). The present study reveals how the addition of pyrite in solution creates a process that is capable of leaching enargite to completion, and is thus the only process capable of leaching copper-arsenic concentrates at atmospheric pressure in sulfate media without fine grinding or the use of bacteria, or chloride. Therefore, the objective of this work was to study, under different solution conditions, the enhanced dissolution of enargite by the presence of pyrite in an acidic ferric sulfate media at atmospheric conditions.

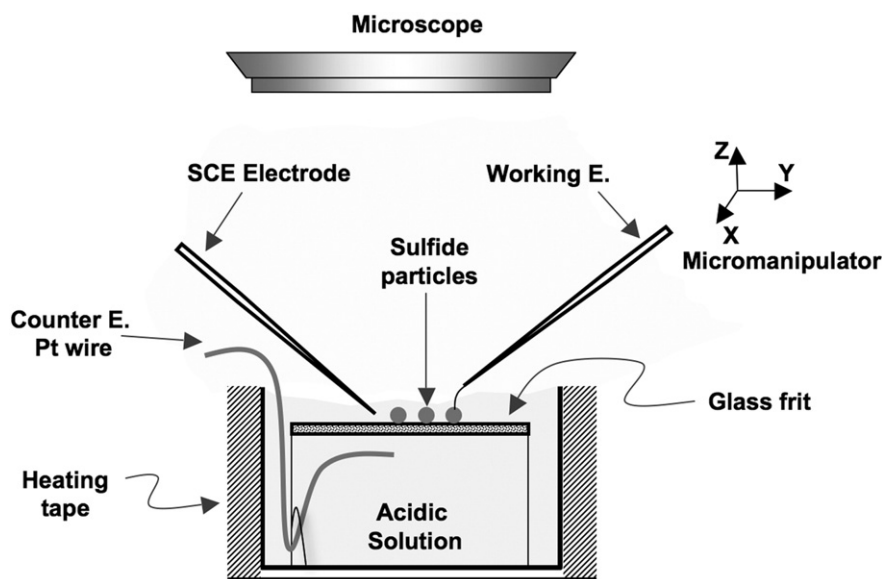


Fig. 1. Schematic representation of the experimental electrochemical cell.

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