



In-situ oxidative arsenic precipitation as scorodite during carbon catalyzed enargite leaching process

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ABSTRACT

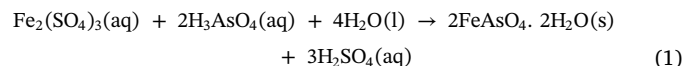
This study explores the in-situ precipitation of scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) during the atmospheric enargite leaching in acid chloride media. The temperature, oxygen sparging rate and the different fractions of the catalyst and ferric ions were the effective parameters on the scorodite precipitation process. Crystalline scorodite was precipitated out of the leach solution in the absence of seed at temperatures above 80°C where the ratio of both AF5 to concentrate and activated carbon (AC) to concentrate were 1:1. The minimal dosage of ferric ions to form the scorodite residue was 5 g/L . Seed addition facilitated the scorodite precipitation process where the primary scorodite particles precipitated after 6 h of enargite leaching. Via this process it was shown that the residual concentration of arsenic in the pregnant leach solution can be reduced as low as 50 mg/L . A series of the toxicity characteristic leaching procedure (TCLP) tests on the generated scorodite exhibited a low arsenic release ranging from 0.2 to 0.7 mg/L , showing an acceptable stability of the scorodite in the residue.

1. Introduction

Atmospheric leaching of enargite (Cu_3AsS_4) leads to arsenic dissolution and a subsequent process is often required to immobilize arsenic into an environmentally stable residue, which is shown to be a challenging subject for metals and mining industry [1]. Arsenic fixation is frequently implemented through the hydrometallurgical processes which are grouped into: lime neutralization, sulfide precipitation, co-precipitation of arsenic using ferric ions, scorodite precipitation and encapsulation technology [2].

The lime neutralization is a simple technique in which arsenic is immobilized in the form of calcium arsenate and/or calcium arsenite at pH 11–12. However, arsenic-calcium residues exhibit poor long-term stability and none of them pass the toxicity characteristic leaching procedure (TCLP) test [2–4]. The co-precipitation of arsenic with ferric ions is the best demonstrated available technology by the U.S. Environmental Protection Agency (EPA) [5]. In this technique, arsenic co-precipitates with the ferric to form As(III)-ferrihydrite (FH) residue at an Fe:As ratio $> 3:1$. The main drawbacks associated with this method are the availability of iron (in some cases iron is not readily available in the plant site), the large volume of the arsenical FH sludge with low filterability. In addition, the FH phase is subjected to physical and chemical changes over time and will transform to alpha goethite ($\alpha\text{-FeOOH}$), which consequently leads to arsenic release to the

environment [6–9]. Scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) is a crystalline ferric arsenate, which has high arsenic content (25–30 wt%), low iron requirements (Fe:As molar ratio of 1–1.5:1) and promising settling and filtration properties [6,7]. Dutrizac and Jambor (1988) had generated scorodite precipitates by means of high temperature pressure oxidation (HTPOX) technique in which the temperature and oxygen pressure were $150\text{--}230^\circ\text{C}$ and 2000 kPa , respectively [10]. The reaction occurring in HTPOX is shown in Eq. (1). The HTPOX process is efficient process however has a high capital and operating costs [2,7].



An alternative method to generate scorodite precipitates at ambient pressure and 97°C in chloride solutions was proposed by Dutrizac and Jambor [11]. Demopoulos et al. [12] further improved the atmospheric scorodite crystallization through a slow stepwise neutralization (up to pH 1.1) in a chloride solutions (1–6 M) and a temperature ranging from 80 to 95°C [12]. It was shown that the crystalline scorodite only precipitated at 95°C from a 2 g/L As (V)-bearing solution in the absence of seed. However, the addition of 2 g/L seed decreased the precipitation temperature to 80°C [12]. Debehausen et al. (2001) have investigated scorodite precipitates in a sulfate media where arsenic was oxidized to As(V) by hydrogen peroxide [13]. The co-precipitation of the gypsum can be prevented by multistage precipitation process [9,14,15]. In the

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hydrometallurgical processing of arsenic, hydrogen peroxide in 30% stoichiometric excess can function as an effective oxidizing agent [13,15]. The oxidation efficiency of H₂O₂ is pH sensitive making pH control very important [13]. Fujita et al. [16] have studied the effect of Cu salt addition on the scorodite precipitation process [16] showing that increasing the copper concentration up to 20 g/L does not exhibit an obvious effect on the scorodite yield and precipitation. It was also shown that the generated scorodite precipitates were fine and poorly crystalline when the arsenic concentration was < 10 g/L [16]. The process pH is important as a pH value of > 1.2 led to a finer scorodite particles formation and an increase in the dissolved arsenic concentration, likely due to adverse effect of jarosite formation [17]. The favorable pH range for the formation of the stable scorodite precipitates was 0.3–1 [17] which is about the same of the enargite leaching process [18].

This study proposes a novel in-situ method for oxidative precipitate of arsenic during the copper leaching process from enargite concentrates. In this process the copper leaching, arsenic oxidation and scorodite precipitation occur in one step, where an activated carbon (AC) or Lewatit® AF5, made by Lanxess, were used to catalyze the process. Another study by our group [18] has suggested that the in-situ formation of hydrogen peroxide in the presence of carbon catalyst assists the in-situ arsenic oxidation and so its precipitation.

In this study, the effect of various operational parameters such as temperature, oxygen addition rate and ferric dosage on arsenic oxidation and its in-situ precipitation as scorodite were explored. Stability of the produced scorodite was studied and its properties were characterized by XRD, TGA and SEM studies.

2. Experimental study

2.1. Materials

The head assay of the enargite sample used in this study is shown in Table 1. The Rietveld X-Ray Diffraction (XRD) analysis confirmed that the concentrate consists of 45.6% enargite and 43.0% pyrite with P₈₀ of 53 μm, as presented in (Table 2).

Table 1
Head assay of enargite sample.

| Element | Copper | Iron | Arsenic | Sulfur | Zinc | Silver |
|-------------|--------|------|---------|--------|------|--------|
| Composition | wt% | | | | | ppm |
| | 24.4 | 20.0 | 8.5 | 39.0 | 0.7 | 99 |

Table 2
XRD results for head concentrate.

| Mineral | Chemical Formula | Mass % |
|-----------------|--|--------------|
| Enargite | Cu ₃ AsS ₄ | 45.6 |
| Pyrite | FeS ₂ | 43.0 |
| Sphalerite Iron | (Zn,Fe)S | 2.6 |
| Quartz | SiO ₂ | 2.5 |
| Chalcopyrite | CuFeS ₂ | 2.4 |
| Tennantite | (Cu, Fe) ₁₂ As ₄ S ₁₃ | 1.4 |
| Bornite | Cu ₅ FeS ₄ | 0.8 |
| Arsenopyrite | FeAsS | 0.6 |
| Galena | PbS | 0.6 |
| Covellite | CuS | 0.5 |
| Total | | 100.0 |

In the leaching experiments, hydrated cupric chloride (Acros Organics-99%) was used as a source of cupric ions, hexahydrate ferric chloride (sigma Aldrich -98%) as a source of ferric ions and sodium chloride (Fisher chemicals-99%) as a source of chloride ions. The two catalysts used in the test were granular coconut-shell-based activated carbon and Lewatit® AF5, which was a novel microporous carbon-based catalyst.

2.2. Leaching experiments

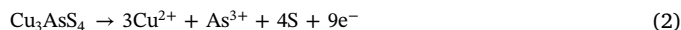
Atmospheric leaching experiments were systematically carried out in a 2 L glass reactor surrounded by a jacketed heater in order to control temperature. The central port of the reactor lid was fitted with an overhead mechanical stirrer with a dual blade glass impeller to ensure proper mixing of the solution. A reflux condenser was also fitted to the reactor lid preventing excessive evaporation of the solution at high temperature. A temperature controller probe and oxygen sparger were also inserted into the reactor through reactor lid ports. Oxygen sparging was controlled using an oxygen flow meter.

In order to carry out the enargite leaching tests, 1 L of solution containing 0.5 M HCl, hexahydrate ferric chloride, hydrated cupric chloride and sodium chloride were added into the test reactor. 50 g of enargite concentrate was then added to the solution. Each test was performed for 96 h. A 15 mL sample was withdrawn from the solution using a syringe. The solution loss was compensated by the addition of 15 ml of solution (0.5 M HCl and average concentration of ferric chloride and cupric chloride). The samples were then centrifuged and filtered to separate the insoluble particles from the liquid phases with a Filtropur S 0.45 μm syringe filter made by SARSTEDT. The arsenic concentration was analyzed by ICP-OES. Free acid titration was also performed on the samples in order to measure the free acid concentration during the leaching. The leach solution was pressure filtered after 96 h. The residue was washed twice using 1 L of 10% hydrochloric acid. The mineralogy of the solid residue was examined using XRD.

3. Result and discussion

3.1. Effect of temperature on the arsenic recovery

The arsenic dissolution rate is often in close relation with the copper leaching rate in the hydrometallurgical processing of enargite. Therefore, it is imperative to detail the mechanism of arsenic dissolution in the atmospheric leaching process. The reactions involved in the dissolution of copper and arsenic in a ferric sulfate media are illustrated in Eqs. (2) and (3) [18]. Unlike the sulfate media, cupric is the main oxidant in the chloride media and cuprous is subsequently formed as the final enargite oxidation product (Eq. (4)) [19–21]. In order to improve the enargite leaching kinetics both ferric and cupric were added to the chloride leach solution.



The effect of temperature on arsenic dissolution rate in the absence of a catalyst within 96 h is shown in Fig. 1. The dissolution rate of arsenic is identical to that of copper at a temperature range of 60–90 °C, which agrees well with literature [22]. As illustrated in Fig. 1, increasing the temperature up to 90 °C improved the arsenic recovery from 24% to 70%. This implies that temperature has a pronounced effect on the arsenic dissolution.

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