



Enargite concentrate processing by the combination of mechanochemical, hydrometallurgical and precipitation methods



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ABSTRACT

This paper investigates the possibility of enargite concentrate treatment using an environmentally friendly route. Enargite Cu_3AsS_4 contains dangerous arsenic, and this element can be removed by leaching with Na_2S in very alkaline environment ($\text{pH} > 12.5$). Arsenic passes into the leach, while the copper sulfide produced represents a raw material suitable for pyrometallurgy. We have shown that more than 80% of the arsenic can be extracted by atmospheric alkaline leaching at 95 °C, when mechanical pretreatment of enargite concentrate in an attritor is applied. The solubilized arsenic can be transformed into solid Na_3AsS_4 . The solid product Cu_2S can be further treated with elemental iron by mechanochemical reduction in a planetary mill. The final product forms a Cu/FeS composite from which iron can be separated by leaching with HCl. The proposed two-step process of milling (enhancement of arsenic removal (I)) and obtaining of elemental copper (II) illustrates the principal possibility of transforming minerals into metals.

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1. Introduction

Enargite, with its chemical formula Cu_3AsS_4 , prevails among the copper bearing minerals with high copper content, but this is combined, unfortunately, with high arsenic content. The presence of this undesirable element significantly affects both the quality and physical properties of the copper product. Moreover, some of arsenic compounds are carcinogenic substances, which are reflected in the increased prevalence of lung and skin cancer observed in human populations with multiple exposures through industrial inhalation (Kitchin, 2011; Wang et al., 2007). The atmospheric release of arsenic involves multiple environmental risks in most copper smelters. Thus, alternative hydrometallurgical processing routes for the treatment of such materials need to be developed.

There are several options for enargite treatment: ammonia leaching (Gajam and Raghavan, 1983), bioleaching (Takatsugi et al., 2011) and acid leaching (Dutrizac and Morrison, 1984). However, the most effective solution for removing arsenic from the enargite seems to be alkaline leaching (Baláž et al., 2000; Curreli et al., 2009; Mihajlovic et al., 2007; Tongamp et al., 2009; Awe and Sandström, 2010). Alkaline leaching of concentrates in sodium sulfide (Na_2S) solutions in the presence of highly alkaline reducing conditions is selective with respect to arsenic. The process of Cu_3AsS_4 conversion or transformation to Cu_2S is represented by the Eq. (1):



Sodium sulfide and sodium hydroxide are the components of the leaching medium. Na_2S creates a high reducing environment with potentials < -500 mV, while NaOH keeps the pH value of the solution above 12.5 and prevents the hydrolysis of sulfide ions, responsible for the substitution of arsenic in enargite (Tongamp et al., 2009). Another important factor for effective arsenic removal from enargite is the positive influence of temperature. A higher temperature means higher efficiency (Curreli et al., 2009; Tongamp et al., 2010a).

Mechanical activation is the appropriate option to improve the leachability and effectivity. In the case of high-energy milling the increase in specific surface area, decrease in mineral crystalline phase content, and reduction of particle size are the main factors, which have a favorable influence on the leaching processes in extractive metallurgy (Baláž, 2000; Welham, 2001). Mechanical activation is thus an efficient, simple and straightforward method for the physical and chemical pretreatment of concentrates (Baláž, 2000, 2008; Welham, 2001; Delogu and Mulas, 2010; Kumar et al., 2011).

Besides the alkaline leaching of the mechanically activated enargite concentrate and the subsequent crystallization of the liquor with accumulated arsenic content, it is also desirable to study the possibility of mechanochemical reduction of the produced Cu_2S with elemental iron. The possibility of mechanochemical reduction of sulfides was theoretically investigated (Matteazzi and LeCaër, 1992). The kinetics of mechanochemical reduction for several model sulfides was also studied (Baláž et al., 2005, 2007). From these studies it follows that it is possible to obtain elemental copper in appropriate conditions.

For the purposes defined above (to extract As and to produce elemental Cu), two types of mills were used in this work. In the first case, the stirred ball mill (attritor) working in a wet mode was applied. This mill type is being frequently applied in hydrometallurgical practice

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(e.g. ACTIVOX™ and ISA-MILL™ processes) for the enhancement of leaching (Baláz, 2008). In the second case, the planetary ball mill working in a dry mode was tested to perform the solid state transformation of copper sulfide to copper metal.

This paper proposes a process of enargite concentrate treatment with precipitation of the arsenic containing filtrate, obtained after selective alkaline leaching. The mechanochemical reduction of copper sulfides, obtained directly after the dearsenification of the enargite concentrate was also studied. The proposed process represents an environmentally friendly route, where no dangerous wastes remain after the treatment of the enargite concentrate. All experiments were run under laboratory conditions.

2. Experimental

2.1. Material and chemicals

The investigations were carried out on enargite concentrate (Chile) with the chemical composition summarized in Table 1.

The mineralogical composition was as follows: enargite Cu_3As_4 (JCPDS 85–1603), tennantite $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ (JCPDS 76–0101), sphalerite ZnS (JCPDS 05–0566), chalcocite Cu_2S (JCPDS 02–1286), digenite Cu_2S (JCPDS 02–1284) and pyrite FeS_2 (JCPDS 42–1340) documented by XRD analysis (Fig. 2, part 1).

The following chemicals were used: sodium sulfide $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (98% purity, Sigma Aldrich, USA), sodium hydroxide NaOH (98% purity, Itea, Slovakia), sulfur S (99.5% purity, Sigma Aldrich, USA), arsenic trisulfide As_2S_3 (99.99% purity, Acros Organics, USA) and iron Fe (99% purity, Sigma Aldrich, USA).

2.2. Milling

The mechanical activation of enargite concentrate was performed in a stirred ball mill (attritor) Molinex PE 075 (Netzsch, Germany) under the following conditions: mass of the concentrate 100 g, 2000 g of steel balls (diameter 2 mm) as milling means, 200 ml of water as milling medium, milling time 60 min, and revolutions of the milling shaft 1000 rpm.

The mechanochemical reduction of the produced copper sulfide was performed in a high-energy planetary ball mill Pulverisette 6 (Fritsch, Germany) in an argon atmosphere under the following conditions: tungsten carbide balls with total mass of 360 g, mass of the sample 3 g, mass of iron 1.2 g, rotation speed of 550 rpm, and milling time of 10–60 min.

2.3. Leaching

Leaching with Na_2S was investigated in a 500 ml glass reactor into which 400 ml of leaching solution and 4 g of enargite concentration were added. The leaching solution consisted of Na_2S and NaOH . The concentration of Na_2S ranged from 50 to 200 g/L. The concentration of NaOH was one half of the Na_2S concentration. The leaching time varied from 1 to 20 min at temperatures from 40 to 95 °C, and a stirring rate of 500 rpm. Aliquots (5 mL) of the solution were withdrawn at appropriate time intervals for the determination of the dissolved arsenic content by atomic absorption spectroscopy.

Leaching with HCl was investigated in a 500 mL glass reactor into which 400 mL of 0.1 M HCl and 1.3 g of sample were added. The leaching time varied from 1 to 20 min at laboratory temperature and a stirring rate of 500 rpm. Aliquots (5 mL) of the solution were

withdrawn at appropriate time intervals for the determination of the dissolved iron content by atomic absorption spectroscopy. The leaching was performed in an inert argon atmosphere.

2.4. Precipitation

The precipitation of the arsenic as $\text{Na}_3\text{As}_4\text{S}_4$ was performed by a procedure, which is a modification of the scheme described in (Tongamp et al., 2010b). For the precipitation process, a solution with arsenic content, obtained after the alkaline leaching of the enargite concentrate was used. The concentration of the solution was increased up to 35 g/L using As_2S_3 . As_2S_3 was dissolved in 75 mL $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (150 g/L) and NaOH (50 g/L) solution and stirred with a magnetic stirrer at 500 rpm for 10 min at 90 °C. After conditioning the arsenic solution, elemental sulfur was added in the amount of one half of the weight of arsenic, and the solution was heated for another 10 min. The heating was then stopped and the solution was gently cooled at laboratory temperature.

2.5. Characterization

The specific surface area, S_A was measured using the low-temperature nitrogen adsorption method using Gemini 2360 apparatus (Micromeritics, USA).

X-ray diffraction measurements were carried out using the D8 Advance diffractometer (Bruker, Germany) equipped with a Θ/Θ goniometer, CuK_α radiation (40 kV, 40 mA), secondary graphite monochromator, and scintillation detector. For phase analysis the software Diffrac^{plus} Eva with ICDD – PDF2 database was used.

The analysis of filtrates and residues after dissolution was carried out by atomic adsorption spectroscopy on the equipment SPECTRAA 240 FS/240Z (Varian, Australia).

The slurry solution pH was measured using the laboratory pH meter.

2.6. Processing of the recovery data

The kinetics of leaching was described by the equation (Dutrizac, 1982):

$$\eta_{\text{As}} = k_1 + k_2 t_L + k_3 t_L^2 \quad (2)$$

where η_{As} is the recovery of arsenic into leach solution (0–1); k_1 is the dimensionless constant; k_2 , k_3 are leaching rate constants and t_L is leaching time (s). The initial rate constants $k_0 = k_2 + 2k_3 t_S$ were deduced by fitting the data to Eq. (2) and then deducing the slope at $t_S = 0$ min.

3. Results and discussion

3.1. Mechanical activation of the enargite concentrate

As the aim was to compare the arsenic removal from the as-received and mechanically activated enargite concentrate, mechanical activation of the sample was performed. It is supposed that the mechanically activated sample has a smaller particle size, higher specific surface area and improved reactivity (Welham, 2001; Juhász, 1974; Juhász and Kolláth, 1993). Mechanical activation was performed in a stirred ball mill (attritor) applying a wet mode. This mode enables the production of small particles and the achievement of a high specific surface area, without inducing chemical changes in the obtained concentrate (Baláz, 2000, 2008).

The particle size distribution before and after wet milling is depicted in Fig. 1. The as-received sample was sieved under 150 μm (Fig. 1, pattern 1). The mean particle size was 26 μm . In the case of the sample that was mechanically activated for 60 min (Fig. 1, pattern 2), there was a shift to the lower values and the mean particle size acquired the value 7 μm . No particles were larger than 70 μm . Moreover, there was

Table 1
Chemical composition of enargite concentrate (Chile).

| Element | Cu | As | S | Fe | Zn | Al | Na | K | Ca | SiO_2 |
|---------|------|------|-------|----|------|------|------|------|------|----------------|
| % | 41.9 | 3.85 | 31.05 | 11 | 1.17 | 0.26 | 0.02 | 0.06 | 0.06 | 2.35 |

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