

## Reaction of enargite ( $\text{Cu}_3\text{AsS}_4$ ) in hot concentrated sulfuric acid under an inert atmosphere. Part II: High-quality enargite



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### ABSTRACT

Based upon the information obtained from the sulfuric acid baking of an enargite concentrate, a second series of experiments were performed using a high-quality enargite powder. The results obtained from the sulfuric acid baking of high-quality enargite provided significant insights towards a more rigorous plan of attack in identifying the meaningful range of parameters and perhaps the time and temperature range in which the rate of the baking reaction should be studied. Hence, the effects of baking time, baking temperature, sulfuric acid dosage, nitrogen flow rate, and particle size on the water extraction of copper and arsenic were studied, as well as the mineralogical transformations associated with sulfuric acid baking. It was found that baking of enargite for extended times at a temperature of 200 °C had no effect on the extraction of Cu and As, which leveled off at ~73.7% and ~59.4%, respectively. Arsenic loss to the gas phase corresponding to 7 h of baking was found to be ~10.4%. Increasing the baking temperature in the range of 200–260 °C at a constant time of 6 h had no beneficial effect, but it adversely increased the arsenic loss to ~54.7% at 260 °C. Increasing the nitrogen flow rate in the range of 163–813 mL/min at a constant baking temperature of 200 °C for extended times slightly increased the arsenic loss. Under identical baking conditions, sulfuric acid dosage had the greatest effect on the extraction of Cu and As, with effective extraction levels being achieved at a sulfuric acid to enargite weight ratio of about 3.7. No systematic effect of particle size was observed on the extraction of Cu and As from enargite. Upon sulfuric acid baking, enargite transformed into  $\text{CuSO}_4$ ,  $\text{CuO} \cdot \text{CuSO}_4$ ,  $\text{As}_2\text{O}_3$ , and  $\text{S}_8$ , all of which, except  $\text{S}_8$ , are soluble in water. Based on the experimental results, the following reaction is suggested for the sulfuric acid baking of enargite:



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### 1. Introduction

In Part I of this series of articles, it was established that enargite present in the El Brocal concentrate reacted with hot concentrated sulfuric acid to produce water-soluble compounds, namely a hydrated iron sulfate ( $\text{HFe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ), a mixed copper/iron sulfate ( $\text{Cu}_{0.47}\text{Fe}_{0.53}\text{SO}_4 \cdot \text{H}_2\text{O}$ ), and arsenolite ( $\text{As}_2\text{O}_3$ ), all of which readily dissolved in water. In view of the fact that minerals other than enargite (such as pyrite and galena) also react with hot concentrated sulfuric acid to generate their corresponding sulfates, it is difficult to isolate the behavior of enargite, because of its competition with other reacting sulfides which consume sulfuric acid at different levels. Characterization of the baked product

was also complicated, due to the complex mineralogical composition of the El Brocal concentrate.

In view of the forgoing, it is appropriate to study the effect of operating parameters on the sulfuric acid baking of a high-quality enargite mineral. It is worth noting that obtaining high-quality specimens of enargite was found to be extremely difficult, and the authors of this article could only secure a couple of specimens over the course of this project. Taking into account the information obtained from sulfuric acid baking of the enargite concentrate, the effects of baking time, baking temperature, sulfuric acid dosage, nitrogen flow rate, and particle size on the water extraction of copper and arsenic were studied. The results of this research appeared to be critical for a better understanding of sulfuric acid baking of enargite, which resulted in a meaningful selection of experimental parameters, the results of which are reported in Part III of this series of articles. In Part III, the effects of various operating parameters on the kinetics of sulfuric acid baking of enargite in the time range of 1–4 h will be investigated and the reaction stoichiometry will be determined based upon the results for complete extraction of copper and arsenic.

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## 2. Materials and methods

### 2.1. Materials

The enargite powder used was obtained by crushing and grinding a high-quality enargite specimen from Julcani Mine, Peru. The specimen was carefully ground using a mortar and pestle, and then the ground mineral was divided into several particle size classes ( $+106\ \mu\text{m}$ ,  $+75-106\ \mu\text{m}$ ,  $-75 + 63\ \mu\text{m}$ ,  $-63 + 53\ \mu\text{m}$ ,  $-53 + 45\ \mu\text{m}$ , and  $-45\ \mu\text{m}$ ) by a wet screening procedure using standard sieves. The XRD analysis of the ground enargite (Fig. 1) showed all relevant enargite peaks, with no other major impurities detected.

According to mixed acid digestion and ICP analysis, the enargite powder contained  $\sim 41.3\ \text{wt.}\%$  Cu and  $\sim 13.6\ \text{wt.}\%$  As. Carbon disulfide (Alfa Aesar, HPLC grade  $+99.8\%$ ) and lead acetate test papers (Fisher Scientific) were used in the analysis of products from the baking experiments. Sodium hydroxide solution (0.1 N) was prepared from sodium hydroxide pellets (Sigma Aldrich, reagent grade  $+98\%$ ). Phenolphthalein indicator was purchased from BDH.

### 2.2. Experimental apparatus and procedures

The experiments were performed in a standard tube furnace (Thermolyne 21100 model) connected to a nitrogen gas cylinder which was equipped with a regulator connected to a flow meter. A Pyrex glass tube (length  $\times$  diameter:  $76 \times 5\ \text{cm}$ ) was used to allow for observation during the reaction. It was quite suitable for the baking experiments because Pyrex tubes can handle experiments at temperatures up to  $400\ ^\circ\text{C}$ . The temperature was controlled within  $\pm 1\ ^\circ\text{C}$ . A porcelain boat (length  $\times$  height  $\times$  width:  $100 \times 15 \times 10\ \text{mm}$ ) was employed for the baking experiments. The same boat and experimental set-up as reported in Part I (Safarzadeh and Miller, 2014) were used in the experiments.

A certain amount high-quality enargite powder ( $\sim 2.0\ \text{g}$ ) was weighed and thoroughly mixed with the required amount of sulfuric acid in the boat. Then the boat was weighed and transferred to the tube furnace, which was preheated to the desired temperature. The experiment was performed under a flow of nitrogen to provide an oxygen free atmosphere. Lead acetate test papers were used inside the tube to detect for the formation of  $\text{H}_2\text{S}$  gas.

At the end of each baking experiment, the sample was cooled down to room temperature under the flow of nitrogen to prevent any oxidation reactions at high temperatures outside the furnace. The outlet gases were captured in a 2 L Erlenmeyer flask containing a 2.5% hydrogen peroxide solution. Sulfuric acid in the solution was measured by the

standard sodium hydroxide titration method. The amount of  $\text{SO}_2$  gas was then calculated based on the fact that 1 mol of  $\text{SO}_2$  gas generates 1 mol of sulfuric acid.

If baked to dryness, the baked material was removed from the boat and ground using a mortar and pestle. A sample was taken for XRD. A high-resolution X-ray microtomography (HRXMT) system (Xradia, MicroXCT-400) was used to analyze selected baked samples. At the end of each experiment, the elemental sulfur formed inside the tube was rinsed with carbon disulfide. However, sulfuric acid droplets which formed inside the tube were also included with the elemental sulfur which was dissolved. Therefore, the total weight of elemental sulfur and sulfuric acid was reported. Arsenic loss to the gas phase was calculated based upon the mass balance between the enargite powder and the baked enargite if the mixture had been baked to dryness.

Approximately 2.0–3.0 g of the baked material were used for the leaching experiments. The water leaching experiments were performed in a 500 mL Erlenmeyer flask. The baked concentrate was leached for 45 min at  $70\ ^\circ\text{C}$ . The volume of DI water was about 200 mL. At the end of each leaching experiment, the suspension was filtered and solid residues were rinsed with DI water and dried in a furnace at  $70\ ^\circ\text{C}$  overnight. The residues were then weighed and sampled for XRD analysis.

The filtrate was subjected to pH and  $E_h$  measurements. A sample of filtrate was analyzed for copper and arsenic by ICP-OES. Each solution was analyzed 3 times and the average value was considered as the concentration in subsequent calculations. The experimental parameters considered and their levels are listed in Table 1. The experimental parameters and their levels were selected based upon the results of the baking experiments reported in Part I (Safarzadeh and Miller, 2014). Each experiment was performed twice, and the average of the two runs was used for final calculations.

## 3. Results and discussion

### 3.1. Baking time

The effect of baking time was investigated over the range of 4–7 h at a constant temperature of  $200\ ^\circ\text{C}$ . Fig. 2 shows the extraction of Cu and As upon water leaching. As can be inferred from Fig. 2, the extraction of Cu and As remained almost unchanged at average values of  $\sim 73.7\%$  and  $\sim 59.4\%$ , respectively. Arsenic loss to the gas phase corresponding to 7 h of baking was found to be  $\sim 10.4\%$ . This As loss is almost 10 times more than the arsenic loss observed by baking the enargite concentrate in the muffle furnace under similar conditions. The pH and  $E_h$  of the PLS remained almost constant at pH 2.1 and  $\sim 625\ \text{mV}$  (vs. SHE) as the

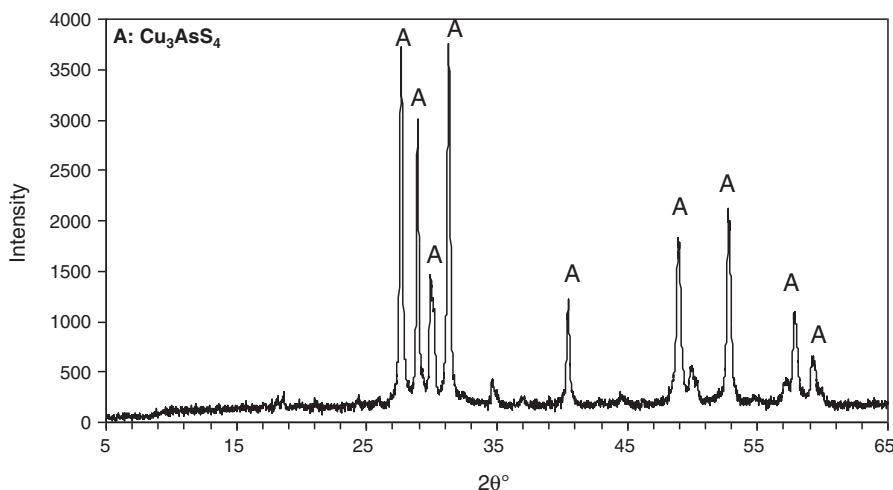


Fig. 1. The XRD pattern of the high-quality enargite powder used in the second series of acid bake-leach experiments.

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