

## LEACHING OF HIGH ARSENIC CONTENT DUST AND A NEW PROCESS FOR THE PREPARATION OF COPPER ARSENATE

In this research, the high arsenic content dust of copper smelting, as a raw material, the extraction of copper and arsenic from the high arsenic content dust in the leaching system containing acidic and alkaline compounds was investigated. Meanwhile, the effects of acid/alkaline initial concentration, liquid to solid ratio, leaching temperature, leaching time on the leaching rate of copper and arsenic were studied. The optimum conditions for the leaching of high arsenic content dust and preparation of copper arsenate were determined. The results showed that acidic/alkaline leaching of high arsenic content dust was particularly effective. 93.2% of the copper, and 91.6% of the arsenic were leached in an acidic leaching process and 95% of the arsenic, while less than 3% of the copper, less than 5% of the antimony, less than 2% of the bismuth was also leached in an alkaline leaching process. A new method (the parallel flow drop precipitate method) was developed in the synthesis of copper arsenate process. The parallel flow drop method was employed to adjust the molar ratio (copper to arsenic) of the mixed solution of the acid-leaching solution and the alkali-leaching solution by taking the drop acceleration of an acidic leaching solution and an alkaline leaching solution at 10 mL/min and 12 mL/min, at a temperature of 60°C and a reaction time of 1 h. Copper arsenate was prepared by mixing an acidic leaching solution and an alkaline leaching solution. The main phases of copper arsenate were  $\text{CuHAsO}_4 \cdot 1.5\text{H}_2\text{O}$  and  $\text{Cu}_5\text{As}_4\text{O}_{15} \cdot 9\text{H}_2\text{O}$ . Copper arsenate contained 30.13% copper and 31.10% arsenic.

*Keywords:* high-arsenic dust; acidic leaching; alkaline leaching; copper arsenate; comprehensive utilisation of resources

### 1. Introduction

In recent years, with the decline in copper mining, grade recovery, and the lack of copper resources, low- and lean-grade sources have become the main raw materials for copper smelting businesses. Usually, the volume of dust generated during the copper smelting process represents (in the forms of high-arsenic dust, acid mud, and black copper) around 5-10% of the total input [1-3]. If the high-arsenic content dust was directly returned to the smelter to recycle its valuable metal components, the content of the impurities in the feed materials is increased; it will reduce the efficiency of equipment and enhance the required energy consumption for any such smelting process [4,5]. Also, the process of copper electro-refining and the quality of electrical-grade copper will be affected by the circulating accumulation of impurities. Arsenic-bearing compounds find a very limited market owing to their severe toxicity [6]. With the improving of environmental standards, arsenic-containing substances have to be treated as hazardous materials, therefore, it is necessary to separate high-arsenic content dust from the copper smelting system and recover valuable metals therefrom [7,8].

The conventional treatment of arsenic-containing minerals can be classified into two methods: pyrometallurgical and

hydrometallurgical processes [9-11]. The pyrometallurgical process generally involves anoxic roasting or reductive roasting at high temperatures, in which arsenic is volatilised as  $\text{As}_2\text{O}_3$  and then collected [12,13]. Nevertheless, the volatilised arsenic may lead to a source of secondary pollution. Therefore, most studies focus on hydrometallurgical treatments of such dusts, by using acidic or alkaline reagents. In most hydrometallurgical processes, the arsenic was extracted into solution by hot water leaching, acidic leaching, alkaline leaching, or pressure leaching, *i.e.*, the application of pressure leaching technology in the treatment of high-copper and high-arsenic dust as described elsewhere [14]. Research shows that copper and zinc can be separated from arsenic and iron in the leach by adding a small quantity of ferrous iron to the leaching system; however, the digestion of metal oxides (*e.g.*, Cu, Zn, Pb, Bi, or Sb) in the dust increases the consumption of acid, and thus causes an increase in the treatment cost. Therefore, a selective leaching process was developed for recovering copper and arsenic from copper-containing dust. Several techniques were proposed, and applied, in the treatment of high-arsenic content dust [15]. First, the preliminary separation of arsenic from other metals can be realised by the selective dissolution of arsenic. Then, the solidification process of arsenic through the formation of

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a stable, and insoluble, arsenate compound becomes much more economical and thus more attractive. Therefore, the objective of this study was to evaluate the technical possibilities of recycling copper and arsenic from high-arsenic content dust using a sulphuric acidic leaching process and a sodium hydroxide leaching process. The factors affecting the leaching rate of copper and arsenic were studied, such as: the acidic leaching rate include the concentration of the acid/alkali, leaching time, temperature, liquid-to-solid ratio, and agitation speed. Meanwhile, the kinetics of the leaching process was analysed. A new method – the parallel flow drop precipitate method – was developed for the synthesis of copper arsenate by mixing an acidic leaching solution and an alkaline leaching solution. In this way, arsenic was formed as a copper arsenate product. These results can assist in the development of hydrometallurgical processes for treating arsenic-rich dust.

## 2. Materials and method

### 2.1. Experimental material

The high-arsenic content dust used in this study was supplied by a copper plant in Baiyin city, China. The chemical analysis results are listed in Table 1. The XRD spectrum of the high-arsenic content dust is shown in Fig. 1. As shown in Table 1 and Fig. 1, the results indicate that copper was present not only in the form of a soluble phase ( $\text{CuSO}_4$ ) but also in the form of insoluble copper sulphide ( $\text{Cu}_2\text{S}$ ,  $\text{CuO}\cdot\text{CuO}_2$ ,  $\text{Cu}_3\text{As}$ , and  $\text{Cu}_3\text{AsS}_4$ ). Arsenic was present in the form of  $\text{As}_2\text{O}_3$ ,  $\text{Cu}_3\text{As}$ ,  $\text{Cu}_3\text{AsS}_4$ , and  $\text{PbAs}_2\text{O}_6$ .

TABLE 1

Chemical composition of the arsenic-rich dust

Component	Cu	Zn	Sb	Bi	Pb	As	Fe	S
Wt%	7.85	8.8	0.26	0.41	17.4	13.52	4.87	3.16

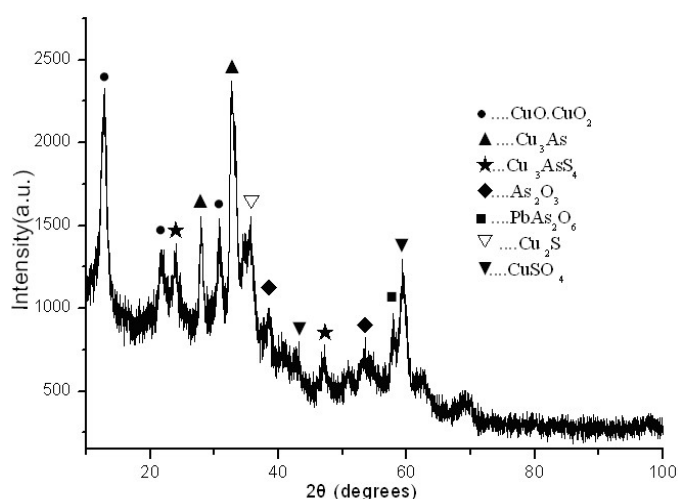


Fig. 1. XRD pattern of the arsenic-rich dust

### 2.2. Experimental methods

The process conditions used for preparing copper arsenate were studied. These adopted arsenic-rich dust as the raw material and used  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  as the leaching agent. Leaching experiments were conducted in a magnetic stirrer under specific initial  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  concentration, leaching temperature, leaching time, liquid to solid ratio and stirring speed. Pulp was poured into a filtration bottle, and the solids were separated from the liquids by a vacuum pump after the leaching experiment. Residue left on the filter paper was weighed, and then oven-dried at  $110^\circ\text{C}$ . The copper arsenate was synthesised by using the parallel flow drop precipitate method by taking both an acidic leaching solution, and an alkaline leaching solution. A certain concentration of a certain amount of deionised water was placed in a reactor as the base fluid. Then, the acidic leaching solution and alkaline leaching solution were simultaneously dripped into the bottom liquid which had been heated to a certain temperature and the sample stirred vigorously. The drop acceleration of the acidic leaching solution and alkaline leaching solution was adjusted in this process. The advantage of this method was that it could ensure that the reactants have a high degree of supersaturation by controlling the rate of addition of components to the solution. In addition, the reaction temperature, reaction time, and pH were easy to control; due to the higher degree of supersaturation of the solution, the nucleation rate was faster than the growth rate, and a small grain size copper arsenate was obtained. The instruments used for the analysis and characterisation of the samples included an X'Pert PRO-type X-ray power diffractometer, VIS723 visible light spectrophotometer, and an AA320N atomic absorption spectroscope. After the leaching experiment, the copper and arsenic concentrations were determined by EDTA titrimetric method. The leaching rate of copper ( $\eta_{\text{Cu}}$ , %) was calculated according to Eq. (1).

$$\eta_{\text{Cu}} = \frac{C_{\text{Cu}} \times V}{m \times C_{\text{Cu}}^*} \times 100\% \quad (1)$$

Where,  $C_{\text{Cu}}$ ,  $V$ ,  $m$ , and  $C_{\text{Cu}}^*$  represent the Cu concentration in the leaching solution (g/L), the leaching volume (L), the mass of the blast furnace dust (g), and the Cu content of the arsenic-rich dust (%). The leaching rate of arsenic was similar to the calculated copper leaching rate.

## 3. Results and discussion

### 3.1. Acidic leaching of high-arsenic content dust

Copper and arsenic from copper arsenides can be extracted through acidic leaching using different oxidants such as:  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{3+}$ , etc. Meanwhile, other metals were enriched in the slag. To improve the leaching rate of copper and arsenic, industrial-grade oxygen was used as an oxidant. Small bubbles of the industrial-grade oxygen were blown into the reaction system through a gas distribution tube. Sulphuric acid was used as a leaching agent in this acidic leaching process.

### 3.1.1. Effect of temperature on the copper and arsenic leaching rates

The effect of temperature was investigated at 2 h by keeping other conditions constant (*i.e.*, a liquid-to-solid ratio of 5 mL/g and an  $\text{H}_2\text{SO}_4$  concentration of 0.4 mol/L). The results obtained are illustrated in Fig. 2. It could be deduced that the leaching rates of copper and arsenic were functions of reaction temperature; increasing the reaction temperature increases the leaching of copper preferentially, however, when reaction temperature increases beyond 80°C, it has little effect on the leaching process. For arsenate, the solubility of  $\text{HAsO}_2$  increases with increasing temperature, which indicates that the higher temperature is beneficial to the leaching of high-arsenic content dust [16]. To ensure the high leaching rate of copper and arsenic, the optimal leaching temperature was determined to have been 80°C.

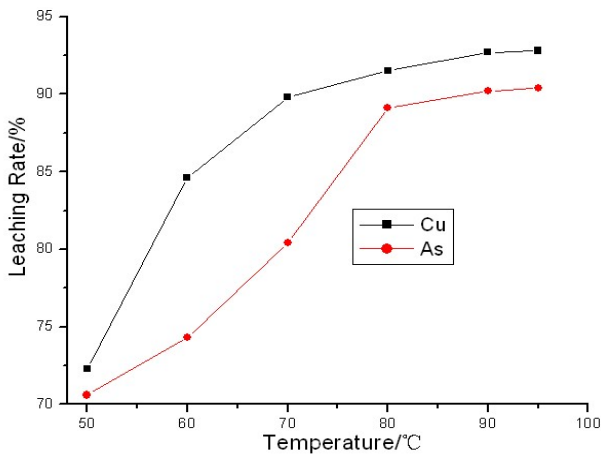


Fig. 2. Effect of temperature on the copper and arsenic leaching rates

### 3.1.2. Effect of initial $\text{H}_2\text{SO}_4$ concentrations on the copper and arsenic leaching rates

The effect of the initial  $\text{H}_2\text{SO}_4$  content was investigated at 2 h by keeping other conditions constant (*i.e.*, a liquid-to-solid ratio of 5 mL/g and a temperature of 80°C). The results obtained are shown in Fig. 3 from whence it may be seen that, as the initial  $\text{H}_2\text{SO}_4$  concentrations increased, the copper and arsenic leaching rate also increased. Nevertheless, when the concentration of  $\text{H}_2\text{SO}_4$  was 0.4 to 1.0 mol/L, the leaching rate of copper and arsenic increased by only 4.4% and 6%. These showed that the initial  $\text{H}_2\text{SO}_4$  concentration exerted little effect on the leaching rate. To reduce the consumption of sulphuric acid, the initial  $\text{H}_2\text{SO}_4$  concentration was set to 0.4 mol/L.

### 3.1.3. Effect of liquid-to-solid ratio on the copper and arsenic leaching rate

The effect of liquid-to-solid ratio was analysed at 2 h by keeping other conditions constant (*i.e.*, a reaction temperature of 80°C and an  $\text{H}_2\text{SO}_4$  concentration of 0.4 mol/L). The results

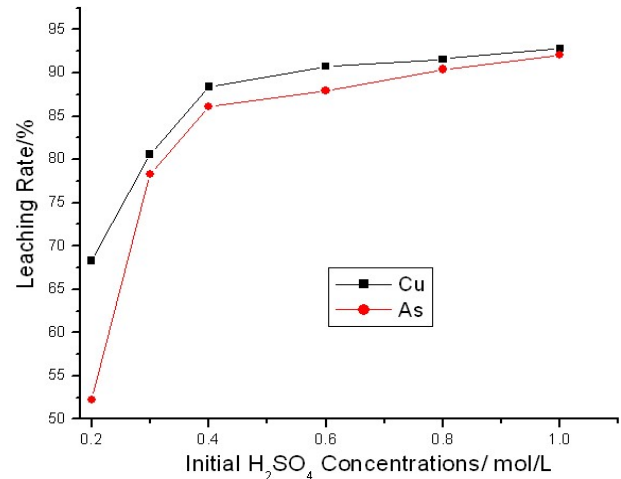


Fig. 3. Effect of initial  $\text{H}_2\text{SO}_4$  concentrations on the copper and arsenic leaching rates

obtained are shown in Fig. 4, from whence it may be seen that, as the liquid-to-solid ratio increased the copper and arsenic leaching rate also increased. When the liquid-to-solid ratio was less than 5 mL/g, the leaching rate of copper and arsenic increased rapidly with increasing liquid-solid ratio. Further increases in the liquid-to-solid ratio to 5 mL/g yield a relatively stable rate of leaching of copper and arsenic; because the liquid-to-solid ratio was increased, the amount of dissolved solid per unit liquid decreased and hence the rate of dissolution was elevated [17]. Therefore, the most appropriate liquid-to-solid ratio was deemed to have been 5 mL/g.

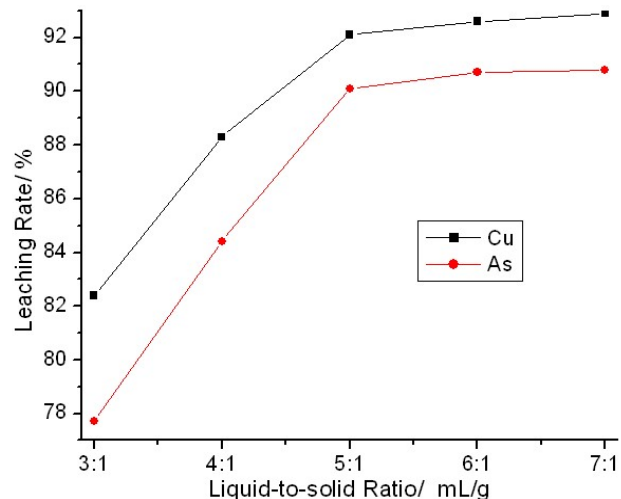


Fig. 4. Effect of liquid-to-solid ratio on the copper and arsenic leaching rates

In conclusion, the acidic leaching technique of high-arsenic content dust was determined as follows: a leaching temperature of 80°C, an initial sulphuric acid concentration of 0.4 mol/L, a liquid to solid ratio of 5 mL/g, a reaction time of 2 h, an industrial-grade oxygen at a partial pressure of 0.2 MPa, and an agitation speed of 400 rpm. Some 93.2% of the copper, and 91.6% of the arsenic were leached under these conditions.

### 3.2. Alkaline leaching of high-arsenic content dust

Arsenic from copper arsenides can be extracted through alkaline leaching. Meanwhile, copper was enriched in the alkaline leaching residue and recovered in the smelting process. To improve the leaching rate of arsenic, industrial-grade oxygen was used as the oxidant in this alkaline leaching process. Small bubbles of the industrial-grade oxygen were blown into the reaction system through a gas distribution tube.

#### 3.2.1. Effect of the initial NaOH concentration on metal recovery

To investigate the influence of the initial NaOH concentration on the leaching of the high-arsenic content dust, experiments were conducted involving leaching under different conditions (*i.e.*, different initial sodium hydroxide concentrations and reaction times). As shown in Fig. 5, the leaching of arsenic increased with increasing initial NaOH concentration. From the increased leaching rate of arsenic, when the initial NaOH concentration and time were less than 1.0 mol/L and 3 h, respectively, the leaching rate of arsenic increased rapidly. Nevertheless, when the initial NaOH concentration and time were more than 1.0 mol/L and 3 h, respectively, the leaching rate of arsenic was practically unchanged. This is because, when the NaOH content was increased to a certain extent, the solubility of  $As_2O_3$  no longer increased [18]. Therefore, for the purpose of high-rate extraction of arsenic and the effective separation of arsenic from copper, the optimum reaction conditions were set to 3 h at 1.0 mol/L.

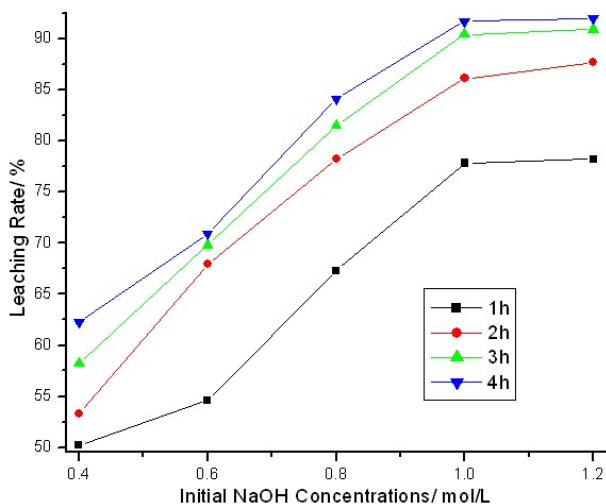


Fig. 5. Effect of initial NaOH concentration on the arsenic leaching rates

#### 3.2.2. Effect of temperature on the arsenic leaching rate

To investigate the effect of the reaction temperature on the leaching of this high-arsenic content dust, experiments were carried out involving leaching under different reaction temperatures and times. As shown in Fig. 6, the leaching rate of arsenic

increased with increasing reaction temperature at a constant reaction time, due to reinforcing the Brownian motion of the mineral particles and enhancing the diffusion rate of  $OH^-$  [19]. From the increasing leaching rate of arsenic, when the reaction temperature and time were less than  $85^\circ C$  and 3 h, the leaching rate of arsenic increased rapidly. Nevertheless, when the reaction temperature and time were more than  $85^\circ C$  and 3 h, the leaching rate of arsenic remained practically unchanged. Therefore, the optimum reaction conditions were set to 3 h at  $85^\circ C$ .

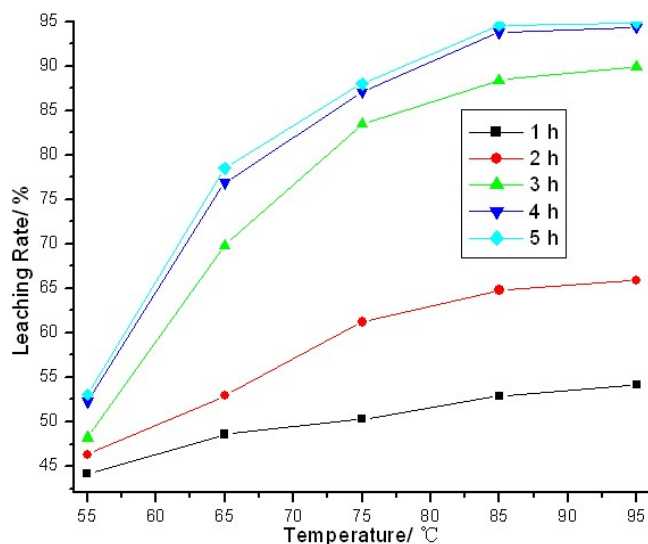


Fig. 6. Effect of temperature on the arsenic leaching rates

#### 3.2.3. Effect of liquid-to-solid ratio on the arsenic leaching rate

To reveal the influence of the liquid-to-solid ratio on the leaching of the high-arsenic content dust, experiments were carried out involving leaching at different liquid-to-solid ratios and different initial sodium hydroxide concentrations. As shown in Fig. 7, the leaching of arsenic increased with increasing liquid-to-solid ratio at the same initial NaOH concentration. From the increased leaching rate of arsenic, when the liquid-to-solid ratio and the initial NaOH concentration were smaller than 4 mL/g and 1.0 mol/L, the leaching rate of arsenic increased rapidly. Nevertheless, when the liquid-to-solid ratio and the initial NaOH concentration were more than 4 mL/g and 1.0 mol/L, the leaching rate of arsenic was practically unchanged. These results may be attributed to the high arsenic content in the dust at low liquid-to-solid ratios, which led to inadequate dispersion of mineral particles and heat transfer between the mineral particles and the sulphuric acid. As the liquid-to-solid ratio was increased, the mineral particles were better dispersed and made contact, and reacted with, the NaOH [20]. Therefore, the optimum reaction conditions were set to 4 mL/g at 1.0 mol/L.

On the basis of NaOH leaching tests, the optimal leaching conditions were as follows: a leaching temperature of  $85^\circ C$ , a liquid to solid ratio of 4 mL/g, an initial sodium hydroxide concentration of 1.0 mol/L, a reaction time of 3 h, an industrial-

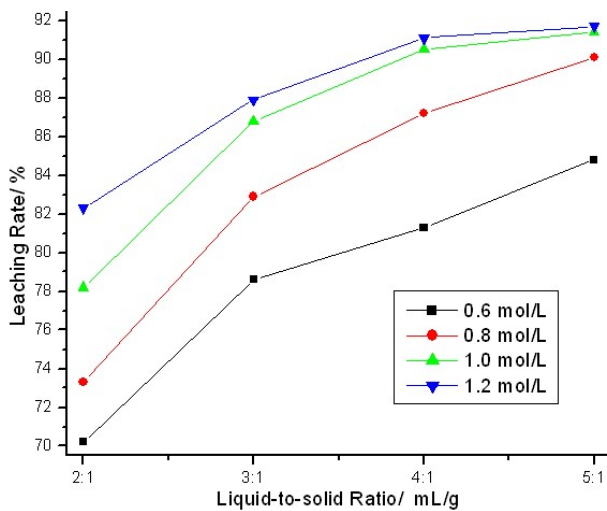


Fig. 7. Effect of liquid-to-solid ratio on the arsenic leaching rates

grade oxygen at a partial pressure of 0.3 MPa, and an agitation speed of 400 rpm. Under these conditions, 95% of the arsenic, less than 3% of the copper, less than 5% of the antimony, and less than 2% of the bismuth were also leached. The chemical analysis results for the main elements in the acidic leaching residue and NaOH leaching residue are listed in Table 2. According to the experimental results, the separation of copper and arsenic was achieved by acidic leaching and alkaline leaching, and copper was enriched in the alkaline leaching residue. All other valuable heavy metals, such as bismuth, lead, and antimony remained in the acidic, and alkaline, leaching residues can be recovered by subsequent processing.

### 3.3. Copper arsenate synthesis

The leach liquor was found to contain: Cu, 59.8 g/L, As, 10.7 g/L in the acidic leaching solution and As, 20.7 g/L in the NaOH leaching solution. Based on the parallel flow precipitation method, an acidic leaching solution and an alkaline leaching solution were adopted to synthesise crystalline copper arsenate at a molar ratio of the copper to arsenic of 2:1 (the drop acceleration of acidic leaching solution was 10 mL/min, the drop acceleration of the alkaline leaching solution was 12 mL/min) at 60°C, and the reaction time was 1 h. After the reaction, the sediment was filtered. The filter cake was refined and washed

three times in water before being oven-dried at 100°C for 12 h. Fig. 8 demonstrates the XRD patterns of the crystalline copper arsenate: as shown, the main phases of copper arsenate were  $\text{CuHAsO}_4 \cdot 1.5\text{H}_2\text{O}$  and  $\text{Cu}_3\text{As}_4\text{O}_{15} \cdot 9\text{H}_2\text{O}$ , with 30.13% copper, and 31.1% arsenic therein.

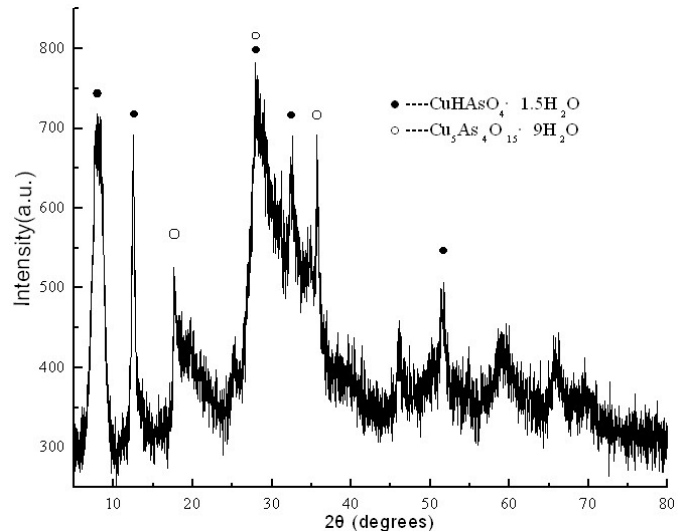


Fig. 8. XRD spectrum of the crystal copper arsenate

## 4. Conclusion

Leaching experiments to remove copper and arsenic were conducted to investigate the effect of the reaction time, reaction temperature, liquid to solid ratio, and the initial acid/alkali concentration on the acid/alkali leaching of high-arsenic content dust. On the basis of these acid/alkali leaching tests, the optimum leaching conditions were determined. Based on the parallel flow precipitation method, the process conditions best suited to preparing copper arsenate by using an acidic leaching solution and an alkaline leaching solution were studied.

- 1) The acidic leaching technique of high-arsenic content dust was optimised. A leaching temperature of 80°C, an initial sulphuric acid concentration of 0.4 mol/L, a liquid to solid ratio of 5 mL/g, a reaction time of 2 h, an industrial-grade oxygen at a partial pressure of 0.2 MPa, and an agitation speed of 400 rpm were deemed to have been optimal. Some 93.2% of the copper, and 91.6% of the arsenic, were leached under these conditions.

TABLE 2

Chemical composition and phase composition of the leaching residue

Leaching residue		Cu	As	Sb	Pb
Acid leaching residues	Chemical composition /% (chemical analysis)	1.14	2.81	2.96	32.8
	phase composition (XRD analysis)	$\text{Cu}_2\text{S}$	$\text{Cu}_3\text{AsS}_4$	$\text{Sb}_2\text{O}_3$	$\text{PbAs}_2\text{O}_6$
Alkali leaching residues	Chemical composition /% (chemical analysis)	23.49	1.24	2.42	35.08
	phase composition (XRD analysis)	$\text{CuO} \cdot \text{CuO}_2$	$\text{Cu}_3\text{As}$	$\text{NaSb(OH)}_6$	$\text{PbSO}_4$

- 2) The optimal leaching technique was determined as follows: a leaching temperature of 85°C, a liquid to solid ratio of 4 mL/g, an initial sodium hydroxide concentration of 1.0 mol/L, a reaction time of 3 h, industrial-grade oxygen at a partial pressure of 0.3 MPa, and an agitation speed of 400 rpm. Under these conditions, 95% of the arsenic, less than 3% of the copper, less than 5% of the antimony, and less than 2% of the bismuth were also leached.
- 3) The parallel flow drop precipitate method was employed to synthesise crystalline copper arsenate by using a molar ratio of copper to arsenic of 2:1 at 60°C, and a reaction time of 1 h. The main phases of the resulting copper arsenate were  $\text{CuHAsO}_4 \cdot 1.5\text{H}_2\text{O}$  and  $\text{Cu}_5\text{As}_4\text{O}_{15} \cdot 9\text{H}_2\text{O}$ , and there was 30.13% copper, and 31.1% arsenic in the copper arsenate.

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