

Pressure leaching technique of smelter dust with high-copper and high-arsenic

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Abstract: The application of pressure leaching technology in the treatment of high-copper and high-arsenic dust was studied. The pressure leaching technique was determined as follows: the liquid to solid ratio (mL/g) of 5:1, the leaching temperature of 453 K, the retention time of 2 h, the initial sulfuric acid concentration of 0.74 mol/L, the oxygen partial pressure of 0.7 MPa, and the agitation speed of 500 r/min. Under these conditions, 95% of copper and 99% of zinc and only 6% of iron in the dust were leached, while about 20% of arsenic was also leached. The leaching technique was optimized further to restrain the leaching of arsenic by adding a small quantity of ferrous iron into the leaching system ($c(\text{Fe}^{2+})=0.036$ mol/L). Copper and zinc can be effectively separated from arsenic and iron in the leach. The optimal pressure leaching technique of high-copper and high-arsenic smelter dust is proved to be effective.

Key words: copper; arsenic; smelter dust; pressure leaching

1 Introduction

Copper smelter dust (copper dust) contains several valuable metals, such as copper, lead, zinc, and bismuth. If copper dust is directly returned to flash smelting furnace, the content of the impurities (arsenic, bismuth, and zinc) in the feed materials will be raised greatly and the processing capability of furnace will be reduced. The process of copper electro-refining and the quality of electric copper will be affected greatly by the circulating accumulation of the impurities, such as bismuth, antimony, arsenic, and iron. Furthermore, the injurant of arsenic concentrates in the fume during the flash smelting, which will shorten the service life of vanadium catalyst for the production of sulfuric acid. Therefore, it is necessary to separate copper dust from the copper smelting system and reclaim valuable metals comprehensively from the dust[1–2]. Hydrometallurgical methods were applied in the treatment of copper dust since 1970's[3]. The industrial operation proves that hydrometallurgical methods are efficient in the recovery of valuable metals from the metallurgical wastes[4–5].

Abundant researches were carried out on the hydrometallurgical process of copper dust[6–9]. At present, most of the large-scale enterprises in China apply a unite technique of hydro- and pyro-metallurgy in

the treatment of copper dust, i.e., copper dust is firstly leached by water or dilute sulfuric acid and then the leaching residues are sent to the pyrometallurgical deoxidizing process to produce crude lead[10]. This technique is proved to be effective in the treatment of low-copper smelter dust and the valuable metals can be preliminarily reclaimed. However, this technique is not suitable for the treatment of high-copper and high-arsenic flue dust because the valuable metals of copper and zinc cannot be easily leached with high efficiency and arsenic shows strong dispersity in the hydrometallurgical process and cannot be treated with centralization. The treatment of high-copper and high-arsenic flue dust is an interesting subject for copper metallurgy.

The disposal of arsenic is a key problem for metallurgical industry and a lot of relevant work has been conducted[11–12]. Several techniques were proposed and applied in the treatment of high-arsenic dust[13–15]. Although the preliminary separation of arsenic from other metals can be achieved by the selective dissolution of arsenic, the further process of arsenic from the leaching solutions cannot be evaded. Comparatively, the solidification process of arsenic through the formation of a stable and insoluble ferric arsenate compound in the leaching is much more economical and attractive[16–19].

Pressure hydrometallurgy and the process chemistry have been developed greatly in recent 50 years[20–22]. In this work, the application of pressure leaching technique in the treatment of high-copper and high-arsenic dust was proposed. During the pressure leaching of high-copper and high-arsenic flue dust, the valuable metals of copper and zinc are leached into the solutions while all other valuable heavy metals such as bismuth and lead as well as the injurants of arsenic and iron are kept in the residues. The valuable metals such as copper, zinc, lead, and bismuth can be respectively recovered by subsequent processes.

2 Experimental

2.1 Raw materials

The chemical analysis results of main elements in high-copper and high-arsenic dust are listed in Table 1. The phase analysis results of copper are shown in Table 2. Backscattered electron image of the copper dust and energy spectra are shown in Figs.1 and 2, respectively. The results indicate that a large quantity of copper exists not only in the form of soluble phase but also in the form of indissoluble copper sulfide. The particle of point A is similar to the bornite phase while that of point B is similar to the chalcocite phase. The dust grains of point C are similar to some complex oxysalts containing several metals. The phase analysis of arsenic is further analyzed and the results are shown in Table 3. As presented by Table 3, over 50% of arsenic exists in the form of dissolvable phase.

Table 1 Chemical composition of copper dust (mass fraction, %)

Cu	Pb	Bi	Zn	As	Cd	Fe	Sn
11.91	12.98	1.71	9.80	4.94	1.95	1.71	3.59

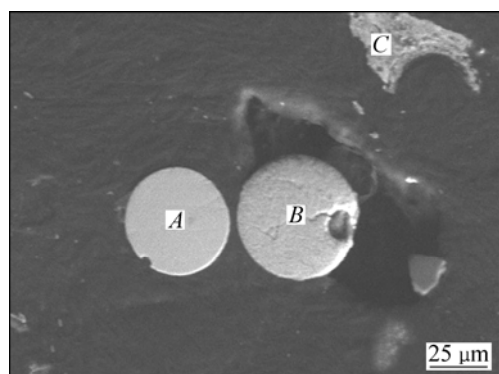


Fig.1 Backscattered electron image of copper dusts

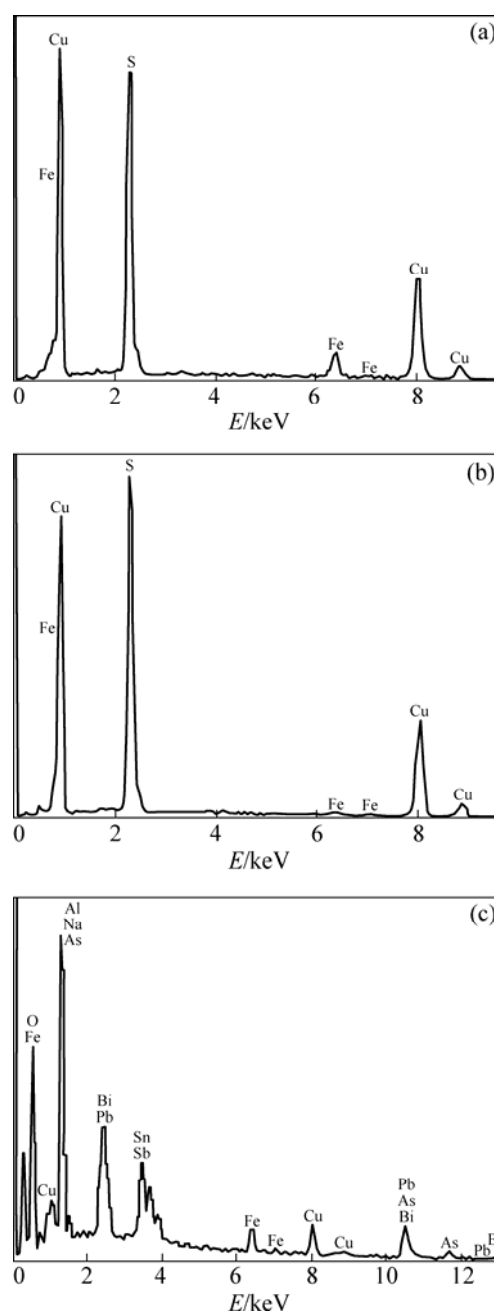


Fig.2 Energy spectra of points A (a), B (b), and C (c)

2.2 Experimental methods

All pressure leaching tests were conducted in a 1.0 L titanium-lined autoclave. The standard procedure for each test was summarized as follows.

Copper dust and sulfuric acid were slurried at a certain ratio of liquid to solid and conditioned prior to being introduced to the reactor. Then, the autoclave was

Table 2 Phase analysis of copper in flue dust

Water soluble phase		Oxide phase		Sulfide phase		Others		Total	
Content/%	Occupied in total/%	Content/%	Occupied in total/%	Content/%	Occupied in total/%	Content/%	Occupied in total/%	Content/%	Occupied in total/%
5.43	47.93	1.54	13.59	4.21	37.16	0.15	1.32	11.33	100.00

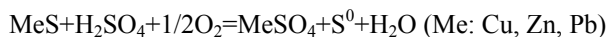
Table 3 Phase analysis of arsenic in flue dust

Water soluble phase		Oxide phase		Sulfide phase		Others		Total	
Content/%	Occupied in total/%	Content/%	Occupied in total/%	Content/%	Occupied in total/%	Content/%	Occupied in total/%	Content/%	Occupied in total/%
5.74	65.68	1.14	13.04	1.38	15.79	0.48	5.49	8.74	100.00

closed and the heating unit was engaged. Upon reaching the desired operating temperature, oxygen flow commenced until the pressure reached the desired level and automatic stirring began and the time of reaction initiation was recorded. During the leaching, the agitation speed was fixed at 500 r/min. At the termination of the pressure leaching reaction, the autoclave was cooled immediately and depressurized. The slurry was then vacuum filtered, and the residue was washed by a small quantity of boiling water. The volumes of the pregnant and wash solutions were recorded. The residue was dried and its mass was recorded. The solutions and the residues were sent to chemical analysis respectively and the extraction of metals was calculated on the basis of the chemical composition of the residues.

3 Results and discussion

Sulfides in copper dust will dissolve in sulfuric acid media, and the extent of the leaching process is influenced by the conditions greatly. The probable reaction in the leaching of sulfides is as follows:



While the valuable metals of copper and zinc are leached into the solutions, a certain quantity of arsenic will be inevitably leached. The probable reaction of the leaching of arsenic sulfide is as follows:



Promoting the leaching of copper and zinc and inhibiting the leaching of arsenic simultaneously are key problems in the process of high-copper and high-arsenic dust.

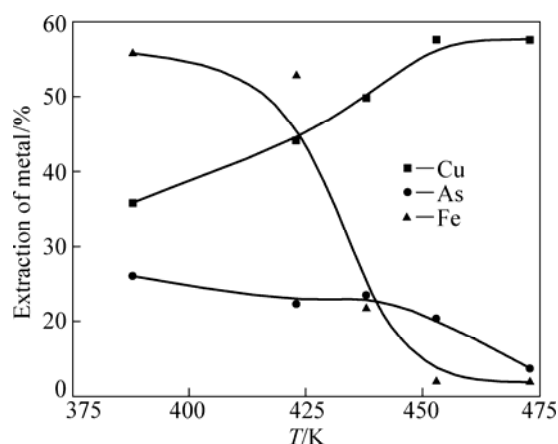
Firstly, the atmospheric leaching of copper dust as a contrast test is carried out under the following conditions: the liquid to solid ratio (mL/g) of 5:1, the initial sulfuric acid concentration of 0.74 mol/L, and the leaching temperature of 368 K. The air is continuously pumped into the slurries during the leaching. After 2 h of retention, the extractions of copper, arsenic and iron are 50.90%, 53.87% and 75.37%, respectively. With an increase in retention time from 2 to 4 h, the extraction of copper increases to 55.98%, while that of arsenic reduces to 31.47%. The extraction of iron is still as high as 75.13%. The results show that much higher extraction of valuable metals and separation from arsenic and iron

cannot be easily achieved under the atmospheric leaching conditions. The pressure leaching tests are further conducted.

3.1 Leaching temperature

The effect of leaching temperature on the extraction of metals is studied under the conditions as follows: the liquid to solid ratio (mL/g) of 5:1, the initial sulfuric acid concentration of 0.74 mol/L, the oxygen partial pressure of 0.7 MPa, the retention time of 2 h, and the agitation speed of 500 r/min. For each test, the extraction of zinc is always higher than 97%.

Fig.3 illustrates the effect of leaching temperature on the extractions of copper, iron and arsenic. The results indicate that the extraction of copper is raised from 51.79% to 95.27% with the increase of leaching temperature from 388 to 453 K. Further increasing temperature to 473 K yields a relatively stable leaching of copper. As shown in Fig.3, the extraction of arsenic decreases slowly with the increase of leaching temperature, while that of iron decreases much more rapidly. At higher temperature, iron is easily hydrolyzed and further precipitated in the form of ferric alum[22]. Arsenic is usually co-precipitated into the residues with the precipitation of iron, which results in a significant decrease of the leaching of arsenic. Thus, the appropriate leaching temperature is selected as 453 K.

**Fig.3** Effect of leaching temperature on extraction of metals

3.2 Retention time

The effect of retention time on the leaching of metals is studied at 453 K. Other experimental conditions are the same with those of leaching temperature tests.

For each test, the extraction of zinc is always higher than 98%.

Fig.4 illustrates the effect of retention time on the extractions of copper, iron and arsenic. The results indicate that the extraction of copper is raised from 81.97% to 95.27% with the increase of retention time from 1 to 2 h, while that of iron is greatly reduced from 32.50% to 3.86%. The results further indicate that the leaching of copper and iron does not change obviously with further increase of the retention time. The leaching of arsenic does not change obviously with the retention time.

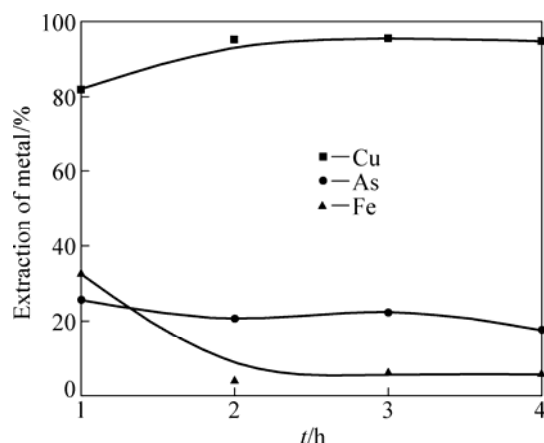


Fig.4 Effect of retention time on extraction of metals

After 2 h of retention, the concentration of iron in the leaching solutions is limited to 7.5×10^{-4} mol/L. Much lower iron is of great advantages to the subsequent process of the leaching solutions. So, the appropriate retention time is finally determined as 2 h.

3.3 Initial sulfuric acid concentration

The effect of the initial sulfuric acid concentration on the leaching of metals is studied. The experimental conditions are the same as those of retention time tests except the retention time of 2 h. The extraction of zinc is as high as 98.72% when the initial sulfuric acid concentration is 0.74 mol/L. Even when the initial acidity is as low as 0.25 mol/L H_2SO_4 , the extraction of zinc still exceeds 90%. The valuable metal of zinc is much easier to be extracted.

Fig.5 illustrates the effect of the initial sulfuric acid concentration on the extractions of copper, iron and arsenic. The results indicate that the leaching of arsenic is similar to that of iron. The extractions of arsenic and iron are reduced obviously with the increase of initial sulfuric acid concentration from 0 to 0.50 mol/L. With further increase of initial acidity, the extractions of arsenic and iron are raised greatly. As shown in Fig.5, the leaching of copper is promoted with the increase of the initial sulfuric acid concentration from 0 to 0.50 mol/L.

The extraction of copper is raised slightly with further increase of initial acidity. For the purpose of high extraction of copper and effective separation of copper from arsenic and iron, the appropriate initial sulfuric acid concentration is determined as 0.74 mol/L.

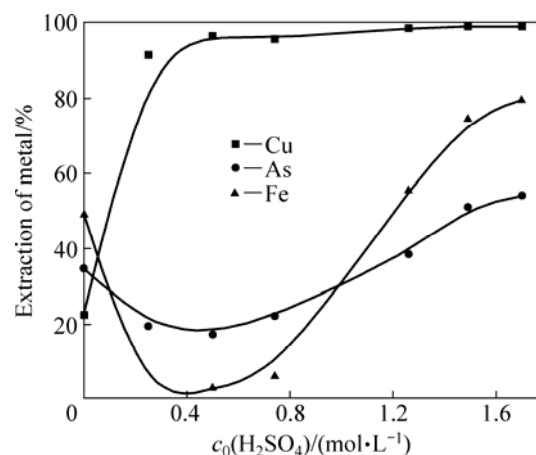


Fig.5 Effect of initial sulfuric acid on extraction of metals

3.4 Oxygen partial pressure

The effect of oxygen partial pressure on the leaching of metals is studied. The experimental conditions are the same as those of initial acidity tests except the initial acidity of 0.74 mol/L H_2SO_4 . For each test, the extraction of zinc is always higher than 98%.

Fig.6 illustrates the effect of oxygen partial pressure on the extractions of copper, iron and arsenic. The results indicate that the extraction of copper is raised with the increase of oxygen partial pressure from 0.3 to 0.7 MPa. With further increase of oxygen partial pressure, the oxygen partial pressure has no obvious influence on the leaching of copper. So, the appropriate oxygen partial pressure is selected as 0.7 MPa.

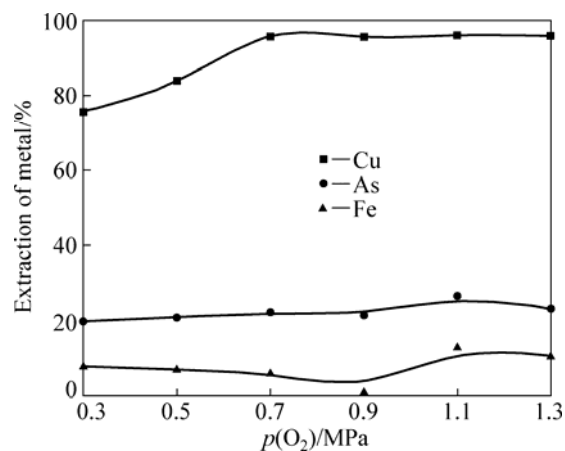


Fig.6 Effect of oxygen partial pressure on extraction of metals

3.5 Co-precipitation of arsenic and iron

On the basis of leaching tests, the pressure leaching technique can be determined as follows: the liquid to

solid ratio of 5:1, the leaching temperature of 453 K, the initial sulfuric acid concentration of 0.74 mol/L, the oxygen partial pressure of 0.7 MPa, the retention time of 2 h, and the agitation speed of 500 r/min. Under these conditions, 95% of copper and 99% of zinc and only 6% of iron are leached, while about 20% of arsenic is also leached. The optimizing tests are further conducted to restrain the leaching of arsenic by co-precipitation of arsenic and iron.

A small quantity of ferrous sulfate is introduced into the slurry before the pressure leaching test. The effect of ferrous iron on the extraction of metals is demonstrated in Table 4. It can be seen that the leaching of zinc is not influenced at all and that of copper is interfered slightly because of the entraining loss, while that of arsenic is completely inhibited after ferrous iron of 0.036 mol/L is introduced into the leaching system. All other valuable heavy metals such as bismuth, lead, tin and antimony are kept in the leaching residues and can be recovered respectively by subsequent processes.

Table 4 Effect of ferrous iron on extraction of metals

$c(\text{Fe}^{2+})/(\text{mol}\cdot\text{L}^{-1})$	Extraction/%			
	Cu	Zn	As	Fe
0	94.97	98.79	18.59	5.46
0.036	92.03	98.44	0	0

In conclusion, the pressure leaching technique of high-copper and high-arsenic dust can be further optimized by adding a small quantity of ferrous iron into the leaching system ($c(\text{Fe}^{2+})=0.036$ mol/L). As a result, the valuable metals of copper and zinc can be effectively separated from arsenic and iron.

3.6 Repeated tests of pressure leaching technique

Fig.7 illustrates the repeated test results of the optimal pressure leaching technique of copper dust. As shown in Fig.7, the effective and stable leaching of copper and zinc and ideal separation of copper and zinc

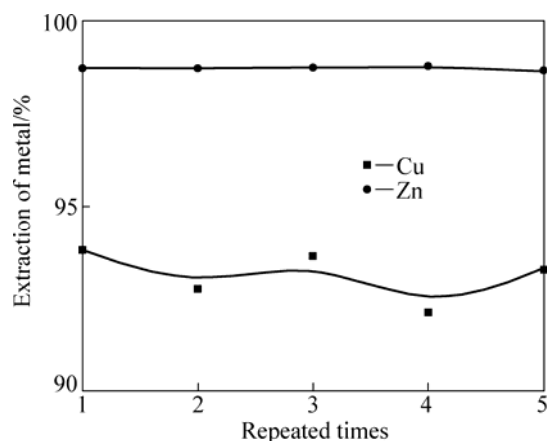


Fig.7 Repeated test results

from arsenic and iron can be achieved by the optimal pressure leaching technique. The concentrations of copper and zinc in pregnant solutions are 0.23 and 0.19 mol/L, respectively, while those of the impurities of iron and arsenic are only 7.5×10^{-4} and 0.011 mol/L, respectively.

4 Conclusions

1) Copper exists not only in the form of soluble phase but also in the form of indissolvable copper sulfide. Dust grains with quite complex composition also exist in the copper dusts. These dust grains are similar to some complex oxysalts, containing several metals.

2) The valuable metal of copper in the dust is difficult to be efficiently leached under the atmospheric leaching conditions. The valuable metal of zinc is easily to be extracted by pressure leaching.

3) The pressure leaching technique of high-copper and high-arsenic dust is determined as follows: the liquid to solid ratio (mL/g) of 5:1, the leaching temperature of 453 K, the retention time of 2 h, the initial sulfuric acid concentration of 0.74 mol/L, the oxygen partial pressure of 0.7 MPa, and the agitation speed of 500 r/min. Under these conditions, 95% of copper, 99% of zinc and only 6% of iron in the dust are leached, while about 20% of arsenic is also leached.

4) The pressure leaching technique can be optimized by adding a small quantity of ferrous iron into the leaching system ($c(\text{Fe}^{2+})=0.036$ mol/L). The whole arsenic in copper dust can be restrained in the leaching residues due to the co-precipitation with iron. The optimal pressure leaching technique is proved to be effective and stable.

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