Recovery of Valuable Metals from High-Content Arsenic Containing Copper Smelting Dust

Xuepeng Li and Dachun Liu

Abstract Smelting-acid leaching process is a way to treat high-content arsenic containing copper. However, smelting process makes a low recovery of valuable metals and acid-leaching process makes large amounts of arsenic-iron slag. Arsenic sulphuration volatilization at a low temperature was studied in this paper and valuable metals were recovered with different methods. Arsenic recycled as As_2O_3 was separated from other valuable metals selectively and calcines were treated by acid pressure leaching. Indium and copper in leaching liquor were made into sponge indium/copper after the processes of extraction-re-extraction-displacing process (ERD process) and displacing process. $ZnSO_4 \cdot 7H_2O$ was collected after concentrating while recovering zinc. Metals, such as tin, bismuth and lead, were recycled as raw materials for tin metallurgy.

Keywords Copper smelting dust · Arsenic · Indium · Acid pressure leaching

Introduction

Copper smelting dust comes from copper smelting process. The main treatments are "reducing smelting-leaching" process and "hydrometallurgy" process. For the first process, metals, such as bismuth, lead and tin, are mainly reduced to alloy and arsenic, zinc, indium, and copper are mainly volatilized to dust. The main problem of this process is the low recovery of valuable metals [1–6]. The second process treats copper smelting dust by leaching, arsenic, zinc, indium, copper are leached to liquid and lead, bismuth, tin are left in slag for the pyrometallurgical processes. Moreover, arsenic is neutralized in the form of arsenic-iron slag by alkali and copper, indium, are replaced as sponge copper and indium by zinc powder. The

---

X. Li (✉) · D. Liu
Kunming University of Science and Technology, Kunming, Yunan, China
e-mail: 791392138@qq.com

D. Liu
e-mail: 1280919970@qq.com

© The Minerals, Metals & Materials Society 2017

H. Kim et al. (eds.), *Rare Metal Technology 2017*,
The Minerals, Metals & Materials Series,
DOI 10.1007/978-3-319-51085-9_19

main problems of this process are large amounts of arsenic and arsenic-iron waste which is hard to treat and the big risk of toxic AsH_3 gas in the process of replacing Cu and In [7–15]. Thus, it is very important to eliminate the influence of arsenic in the treatment copper dust. Arsenic sulphuration volatilization at low temperature was studied in this paper and valuable metals were recovered with follow-up process, such as acid pressure leaching.

Experimental

Materials and Procedure

Elements content and semi-quantitative analysis of copper smelting dust are shown in Tables 1 and 2. Vulcanizater is sulfur (saled), and catalysator is manganese dioxide (AR).

As shown in Tables 1 and 2, valuable metals are widely present in varying amounts in the copper smelting dust. The content of arsenic is high to 15.32 wt%, which is mainly in forms of As_2O_3. The phases of Pb, Cu and Zn are mainly oxide, sulfate and sulfide, respectively.

A muffle furnace was employed for the arsenic sulphuration volatilization at a low temperature, and the procedures are as follows: First, mixing copper smelting dust and sulfur evenly and reserving the mixture for 3 h at 350 °C; second, raising to the desired temperature.

A 5 L pressure reactor was used for the leaching process. Two steps were taken for the process: First, mixing calcines and H_2SO_4; then, putting the mixture in the pressure reactor with a certain pressure of oxygen.

Table 1 Competent of high-content arsenic copper smelting dust

Element	As	Zn	Pb	Bi	In	Cu	Sn
Pct (%)	15.32	12.52	17.46	3.16	0.125	3.12	3.82

Table 2 Semi-quantitative analysis of high-content arsenic copper smelting dust

Phase	$PbSO_4$	$ZnSO_4 \cdot H_2O$	ZnS	As_2O_3	$Cu_2As_2O_7 \cdot 3H_2O$
Pct (%)	30	25	6	18	3
Phase	$Cu_2O(SO_4)$	$Bi_2O_3(SO_4)$	SnO_2	Others	
Pct (%)	3	8	5	2	

Experimental Theory

A. Theory of arsenic sulphuration volatilization

The reaction between As_2O_3 and sulfur shows in Eq. (1):

$$As_2O_3 + 4.5S = As_2S_3 + 1.5SO_2(g) \tag{1}$$

The analysis above shows that As_2O_3 can be vulcanized to As_2S_3 under a low temperature which is not stable at this temperature rang (boiling point of 707 °C). On the other hand, As_2S_3 will be oxidized to As_2O_3 in the process of dust collection (as shown in Eq. (2)). The other valuable metals, such as indium, lead, tin, zinc and copper, are nearly non-volatile under that condition. Thus, it is available in theory for, selective separation of arsenic from the copper smelting dust (Fig. 1).

$$As_2S_{3(g)} + 4.5O_{2(g)} = As_2O_{3(g)} + 3SO_{2(g)} \quad \Delta G_T^0 = -1240.3 + 0.12T(\text{kJ/mol}) \tag{2}$$

B. Theory of pressure leaching

The phases of valuable metals remained in calcines are mainly oxide, sulfate and sulfide after the removal of arsenic by low-temperature vulcanized vitalization. Pressure leaching can increase the leaching rate of indium, copper and zinc while lead, tin and bismuth nearly can not be leached. The main reactions that take place during the leaching by H_2SO_4 can be expressed as follows:

$$In_2O_3 + 3H_2SO_4 = In(SO_4)_3 + 3H_2O \tag{3}$$

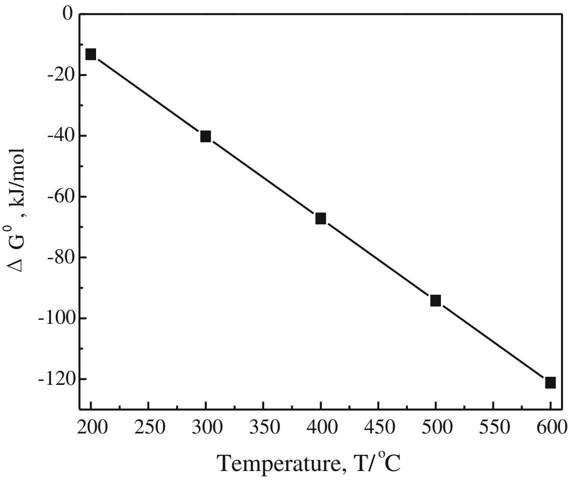


Fig. 1 Relationship between ΔG^0 and temperature of Eq. (1)

$$In_2S_3 + 4.5O_2 + H_2SO_4 = In_2(SO_4)_3 + H_2O + S \tag{4}$$

$$2CuS + O_2 + 2H_2SO_4 = 2CuSO_4 + 2H_2O + 2S \tag{5}$$

$$2CuS + 2H_2SO_4 + O_2 = 2CuSO_4 + 2H_2O + 2S \tag{6}$$

$$4Cu^{+} + O_2 + 4H^{+} = 4Cu^{2+} + 2H_2O \tag{7}$$

$$2ZnS + O_2 + 2H_2SO_4 = 2ZnSO_4 + 2H_2O + 2S \tag{8}$$

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O \tag{9}$$

Compared with the atmospheric pressure leaching, pressure leaching can increase the partial pressure of oxygen to oxidize the sulfate enough and can increase the activity of valuable metals in liquid, that is to say, pressure leaching can increase the leaching rate of valuable metals. Take Eq. (4) as an example, its equilibrium constant is as shown in Eq. (10).

$$K_c = \frac{a_{In_2(SO_4)_3} a_{H_2O} a_8}{a_{In_2S_3} a_{H_2SO_4} \left(\frac{P_{o_2}}{P^0}\right)^{4.5}} = \frac{a_{In_2(SO_4)_3} (P^0)^{4.5}}{a_{H_2SO_4} (P_{O_2})^{4.5}} \tag{10}$$

Because K_c is a constant value at a certain temperature, the activity of $In_2(SO_4)_3$ in liquid will increase when the partial pressure of oxygen increased. It means the content of $In_2(SO_4)_3$ will be increased by pressure leaching. It is the same to other sulfates.

Results and Discussions

Low-Temperature Vulcanized Vitalization Experiments

High-content arsenic containing copper dust was vulcanized for 3 h at 350 °C and then volatilized in certain temperature in a muffle furnace. Evaporation temperature and amount of vulcanizater are decided in this part.

A. **Effect of evaporation temperature on evaporation rate**

As shown in Fig. 2, the evaporation rate of arsenic increases while temperature increasing. The suitable vitalization temperature is 630 °C through the experiments. Under that conditions the evaporation of arsenic is 91.39% and the content of arsenic in calcines is reduced to 1.1%, meanwhile, the evaporation rates of Pb, Zn, In, Cu, Bi, Sn are 5, 6, 5.65, 2.31, 2.21, 5.51%, respectively.

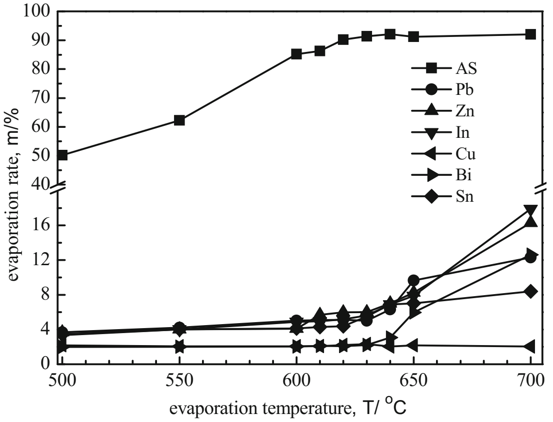


Fig. 2 The effect of vitalization temperature on the evaporation rate of arsenic and other valuable metals, vulcanizater of 13 wt%, vulcanized for 3 h at 350 °C

B. Effect of amount of vulcanizater on evaporation rate

As shown in Fig. 3, the evaporation rate of arsenic increases while the addition amount of vulcanizater increasing, meanwhile, the evaporation rates of other metals are very low. The better amount of vulcanizater addition is 13 wt% through the experiments (Fig. 4).

It was indicated that the selectively removal of arsenic by low-temperature vulcanized vitalization is feasible through the experiments. The determined conditions are below: the amount of vulcanizater addition is 13 wt%; vulcanized for 3 h in 350 °C then volatilized for 3 h at 630 °C. Under those conditions, the evaporation rate of arsenic can reach to 91.39%, the content of arsenic remained in calcines was reduced to 1.1%. Meanwhile, the evaporation rates of Pb, Zn, In, Cu, Bi, Sn are 5, 6, 5.65, 2.31, 2.21, 5.51%, respectively.

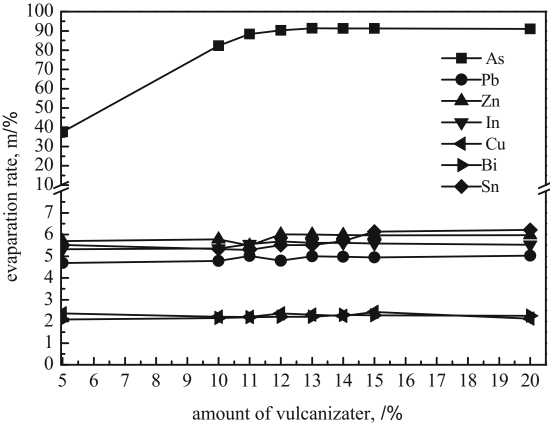
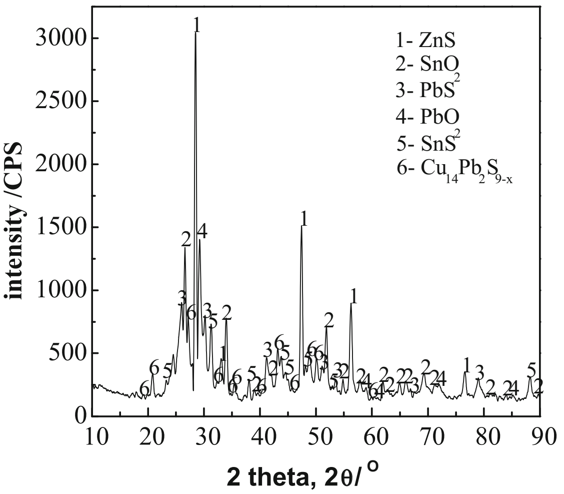


Fig. 3 The effect of the addition amount of vulcanizater on the evaporation rate of arsenic and other valuable metals, vulcanized for 3 h in 350 °C then volatilized for 3 h at 630 °C

Fig. 4 The XRD analysis of the calcines. It shows the elements Zn, Cu, Pb, Sn are in the forms of oxide and sulfide



Pressure Leaching Experiments

Calcines are treated by H_2SO_4 pressure leaching. The influence of leaching temperature, sulfuric acid concentration and liquid-solid ratio (L/S) are discussed in this part.

A. **Effect of leaching temperature on leaching rate**

As shown in Fig. 5, the leaching rates for elements, such as Cu, Zn and In, are 80, 75, 35% respectively at 90 °C under atmospheric pressure. Meanwhile, Pb, Bi and Sn can barely be leached. The leaching rates of Cu, Zn and In has been raised dramatically by pressure leaching. However, the leaching rates for Cu, Zn and In reached to 98.99, 90.2 and 96.5% at 150 °C. While the changes for Pb, Bi and Sn were not obviously at the same temperature. Thus, the leaching temperature can be taken as 150 °C.

B. **Effect of H_2SO_4 content on leaching rate**

As shown in Fig. 6, the leaching rates reached to 98.99, 90.2 and 96.5% for Cu, Zn and In when H_2SO_4 concentration is 150 g/L. The leaching rates are barely changed with the increase of sulfuric acid concentration for Pb, Bi and Sn. Thus, 150 g/L of the sulfuric acid was taken as one of the leaching parameters.

C. **Effect of L/S on leaching rate**

As shown in Fig. 7, the leaching rate of Cu, Zn and In raises when L/S increased. When L/S is 4:1, the leaching rates of Cu, Zn and In are 96.27, 94.6 and 88.6%, respectively. Meanwhile, Pb, Bi and Cu can barely be leached. Although the leaching rates are a bit lower than L/S of 5:1 and 6:1, the ratio of 4:1 is suitable for

Fig. 5 The influence of temperature on the leaching rate of valuable metals. The parameters for such experiments are below: H_2SO_4 concentration is 150 g/L, L/S is 6:1, leaching time is 2 h, the pressure in pressure reactor is 0.7–0.8 MPa, the partial pressure of oxygen is about 0.3–0.4 MPa

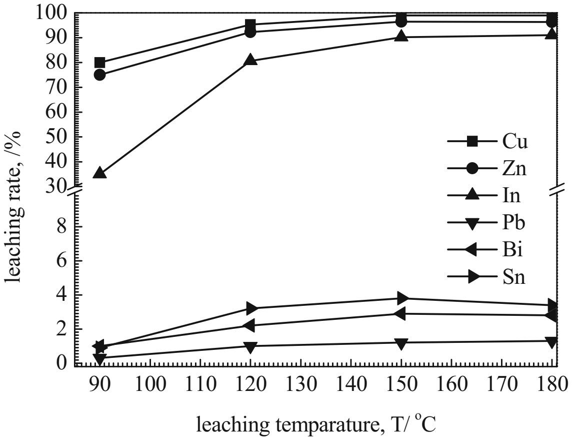
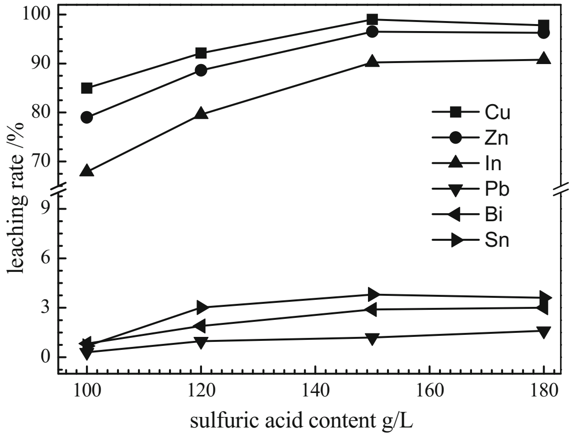


Fig. 6 The concentration influence of H_2SO_4 on the leaching rates of valuable metals. The parameters for such experiments are below: leaching temperature is 150 °C, L/S is 6:1, leaching time is 2 h, the pressure in pressure reactor is about 0.7–0.8 MPa, the partial pressure of oxygen is about 0.3–0.4 MPa



saving the leaching volume. Thus, L/S value of 4:1 can be taken as one of the leaching parameters.

D. Effects of leaching time on leaching rate

As shown in Fig. 8, the leaching rate of Cu, Zn and In raises when leaching time increased. The leaching rate of Cu, Zn and In almost stay stable after 2 h. Therefore, the optimization time for the leaching experiments is 2 h.

E. Treatment on leaching liquid

After acid leaching, Cu, Zn and In were almost leached to leaching liquid. Table 3 shows the components of one-step leaching liquor and residue.

As shown in Table 3, Sn, Pb, Bi mainly remained in the residue. On the other hand, Zn, Cu and In were leached. Sn, Bi, Pb mostly remained in residue can be used as raw materials for tin metallurgy. The component of five-time-step leaching liquid is shown in Table 4.

Fig. 7 The influence of L/S on the leaching rates of valuable metals while leaching temperature is 150 °C, H_2SO_4 concentration is 150 g/L, leaching time is 2 h with 0.7–0.8 MPa in pressure reactor, the partial pressure of oxygen is about 0.3–0.4 MPa

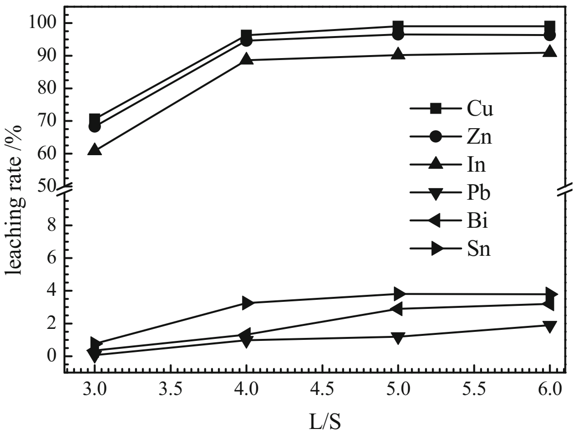


Fig. 8 The influence of leaching time on the leaching rates of valuable metals, leaching temperature is 150 °C, H_2SO_4 concentration is 150 g/L, L/S is 4:1 with 0.7–0.8 MPa in pressure reactor, the partial pressure of oxygen is about 0.3–0.4 MPa

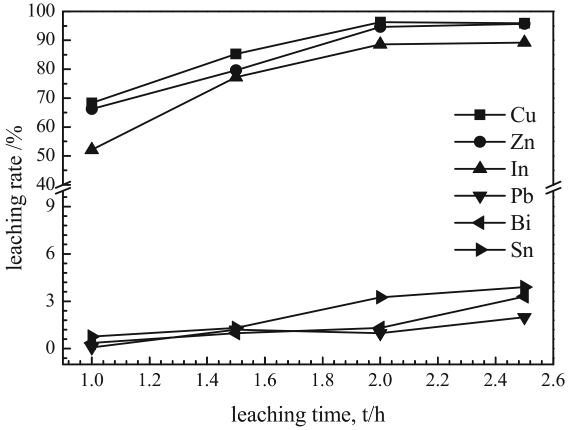


Table 3 Component of one-step leaching liquor and leaching slag

	Zn	Cu	In	Pb	Bi	Sn	As
Leaching liquor (g/L)	11.3	2.35	0.21	0.08	0.12	0.37	0.15
Residue (%)	1.0	0.07	100 g/t	25.45	6	6.89	1.89

Table 4 Component of five-time-step leaching liquor and leaching residue

	Zn	Cu	In	Pb	Bi	Sn	As
Leaching liquor (g/L)	53.9	11.95	1.2	0.38	0.72	1.02	0.56

As shown in Table 4, Zn, Cu and In were concentrated after five-time-step leaching. Indium was extracted by di(2-ethylhexyl) phosphoric acid (P204) then re-extracted and replaced by zinc power to sponge indium. Copper was replaced by zinc power to sponge copper. Because of the low content of As, there was no AsH_3 gas while displacing Cu through instrument test. Zn was made to $ZnSO_4$ $7H_2O$ by concentrating.

After the experiments above, the valuable metals mentioned above in high-content arsenic containing copper dust were comprehensive recovered.

Conclusions

As was selectively separated by volatile sulfide at low temperature under the conditions, the addition amount of vulcanizater is 13 wt%, vulcanized for 3 h at 350 °C then volatilized for 3 h at 630 °C. Under those conditions, the evaporation rate of arsenic is 91.39%, the content of arsenic remained in calcines was reduced to 1.1%. The influence of As was eliminated for it was selectively removed and recycled. Thus, the risk of toxic AsH_3 gas in displacing process and big amount of arsenic-iron slag were avoided. The evaporation rates of Pb, Zn, In, Cu, Bi and Sn are 5, 6, 5.65, 2.31, 2.21, 5.51% respectively.

The calcines were leached by pressure leaching, the leaching rates of Cu, Zn, In were 96.27, 94.6, 88.6% respectively under the conditions concentrate of H_2SO_4 150 g/L, L/S 4:1, leaching time 2 h, pressure for 0.7–0.8 MPa. Sn, Bi and Pb stayed remained in leaching residue and can be used as raw materials for tin metallurgy. The elements component of Cu, Zn, In in leaching liquid is up to 11.95, 53.9, 1.2 g/L respectively after they were leached for 5 times. Sponge indium and copper were obtained which were replaced by zinc power. For element zinc, it was made into $ZnSO_4$ $7H_2O$ by concentrating.

References

1. W. Chen et al., Study on the new process for treating copper converter dusts. Non-ferrous Min. Metall. **3**(19), 45–47 (2003)
2. Y. Xu et al., A new process for comprehensive utilization of high-arsenic dust from Isa furnace. China Nonferrous Metall. **5**, 16–18 (2005)
3. H. Li, The process practice for recycle of lead, copper and bismuth from the fume of the copper converter. Yunnan Metall. **2**(40), 52–56 (2011)
4. Z. Liu, Analysis and suggestion on comprehensive recovery process of copper smelting dust. China Nonferrous Metall. **5**, 44–48 (2015)
5. S. Ruan, Y. Lu, On comprehensive recovery of valuable metals from ESP dust in copper smelting. Nonferrous Smelting **6**, 41–44 (2003)
6. Z. Yu, Comprehensive utilization of copper converter dust. Nonferrous Smelting (1), 37–40 (1997)
7. T. Li, Process and practice of hydrometallurgical treatment of as-enriched dust. China Nonferrous Metall. **5**, 11–14 (2015)
8. J.-J. Ke, R.-Y. Qiu, Recovery of metal values from copper smelter flue dust. Hydrometallurgy **12**(2), 217–224 (1984)

9. Z. Xu et al., Pressure leaching technique of smelter dust with high-copper and high-arsenic. Chin. J. Nonferrous Metals **18**(1), S59–S63 (2008)
10. M. Li, Comprehensive recovery of valuable elements in copper smelting process. China Nonferrous Metall. **2**, 71–73 (2014)
11. Z. Wang et al., The new technics processing of recovering valuable metals by using hydrometallurical process to treat the copper dust. Hunan Nonferrous Metals **6**(26), 20–23 (2010)
12. L. Guan et al., Leaching process for comprehensive recovery of valuable metals from copper smelter dust with low indium. Chin. J. Rare Metals **1**(32), 88–93 (2008)
13. A.J. Monhemius, P.M. Swash, Removing and stabilizing as from copper refining circuits by hydrothermal processing. JOM **9**, 30–33 (1999)
14. Y. Liao et al., Research on kinetics of leaching of arsenic from dust containing high arsenic. J. Sichuan Univ. (Eng. Sci. Ed.) **3**(45), 200–206 (2015)
15. A.A. Samuel, S. Ake, Selective leaching arsenic and antimony from a tetrahedrite rich complex sulphide concentrate using alkaline sulphide solution. Miner. Eng. **23**, 1227–1236 (2010)