Research on the effect of alkali roasting of copper dross on 
leaching rate of indium

Dafang Liu\textsuperscript{a,}, Xingxiang Fan\textsuperscript{b,\ast}, Yifeng Shi\textsuperscript{c}, Kunbin Yang\textsuperscript{c}
\textsuperscript{a} Faculty of Metallurgy and Energy Engineering, Kunming University of Science and Technology, Kunming, Yunnan, 650093, China
\textsuperscript{b} Faculty of Metallurgical Material, Kunming Metallurgy College, Kunming, Yunnan, 650033, China
\textsuperscript{c} Yunnan Copper Co., Ltd, Kunming, Yunnan, 650102, China

Corresponding author: +86 13888355042; fax:086 0871 66050935.

E-mail address: fanxingxiang@tom.com (Xingxiang Fan).

Abstract: The byproduct copper dross produced during refining crude lead was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and fluorescence spectrometer (XRF), which showed that copper dross mainly contained lead, copper, zinc, arsenic, antimony, bismuth, sulfur and a small amount of indium and silver etc. The mineralogical phase change of oxidation roasting of copper dross by adding sodium hydroxide was analyzed with the help of XRD and SEM. The effects of water leaching, ratio of sodium hydroxide, roasting time, and roasting temperature on leaching rate of indium were investigated mainly. The experimental results showed that phase of lead metal and sulfides of lead, copper and zinc disappeared after oxidation roasting of copper dross by adding sodium hydroxide, new phase of oxides of lead, copper, zinc and sodium salt of arsenic and antimony appeared. Water leaching could remove arsenic, and acid leaching residue obtained was then leached with acid. The leaching rate of indium was higher 6.98% compared with alkali roasting of copper dross-acid leaching. It showed that removing arsenic by water leaching and acid leaching could increase the leaching rate of indium and be beneficial to reducing subsequent acid consumption of extracting indium by acid leaching. The roasting temperature had a significant effect on the leaching rate of indium, and leaching rate of indium increased with the rise of roasting temperature. When roasting temperature ranged from 450°C to 600°C, leaching rate of indium increased significantly with the rise of roasting temperature. When roasting temperature rose from 450°C to 600°C, leaching rate of indium increased by 60.29%. The amount of sodium hydroxide had an significant effect on the leaching rate of indium, and the leaching of indium increased with the increase of the amount of sodium hydroxide, and the leaching rate of indium was obviously higher than that of copper dross blank roasting and acid leaching.

1. Introduction
Indium is one kind of rare and dispersed element which deserves exploring valuably industrially. Indium has no separate orebody on the earth’s crust, mostly accompanied with lead and zinc etc. nonferrous metals and iron minerals with low content and large distribution. In the world around 90\% of indium is produced from the byproducts of lead and zinc smelters. Indium is recycled from smelting slag, anode slime and off gas fume as byproduct when smelting lead and zinc. Indium is mainly
applied in electronics, LCD screen, low melting point alloys, additives in refined chemical industry and atomic energies etc\textsuperscript{[1-2]}. Copper dross is the byproduct produced when fire refining crude lead. Besides lead and copper, copper dross also contains zinc, tin, antimony and arsenic, etc. and a small amount of indium, silver, gold, etc. rare and dispersed and precious metals\textsuperscript{[3]}. In 2014, the lead amount produced in China was 4.2213 million tons. The amount of copper dross produced when refining crude lead was about 2\% of crude lead. Therefore the comprehensive recycling has an important significance.

At present the treatment of copper dross mainly has two methods, namely pyrometallurgical\textsuperscript{[4]} treatment and hydrometallurgical treatment. Pyrometallurgical treatment includes soda-iron dust method\textsuperscript{[5]}, vacuum method\textsuperscript{[6]}, and chlorination method\textsuperscript{[6]}, etc. Hydrometallurgical treatment includes ammonia leaching method\textsuperscript{[7]}, acid leaching method\textsuperscript{[8]} and alkali leaching method\textsuperscript{[9]}, oxidation roasting-acid leaching method\textsuperscript{[10]}. All of these methods mainly focus on the extraction of copper and lead, little and even not mentioning the extraction of indium. Based on the comprehensive description of treatment of copper dross, this paper puts forward alkali roasting-water leaching-dilute sulfuric acid leaching process, analyzing the phase change before and after roasting, emphasizing the correlation of arsenic removal by water leaching and leaching rate of indium, and the effect of roasting temperature, ratio of alkali and roasting time on leaching rate of indium to provide the basis of extracting indium by alkali roasting of copper dross.

2. Experiment

2.1. Raw materials

Experimental raw material was copper dross produced during refining crude lead. Analyzing copper dross by using XRF, it was shown that copper dross mainly contained lead, copper, zinc, antimony and sulfur, the rest were arsenic, tin and bismuth and a small amount of indium, silver, etc. According to qualitative analysis, the results were shown in Table 1.

| Element | As   | Fe  | Cu  | Zn  | Pb  | Sb  | Bi  | Sn  | S   | In  | Ag  | Au  |
|---------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Content | 6.31 | 0.24| 10.78| 5.11| 38.08| 3.66| 2.68| 1.35| 6.90| 5086.22| 321.08| 0.89|

Unit of In, Ag and Au is g/t

Copper dross was characterized by using XRD, the results were shown in Figure 1. It could be seen from Figure 1 that mineralogical phases in copper dross mainly were Pb, PbS, CuS, ZnS, As\textsubscript{2}O\textsubscript{3}, Bi\textsubscript{2}O\textsubscript{3} and Sb\textsubscript{2}O\textsubscript{3}, etc.

Copper dross was analyzed by using SEM, the results were shown in Figure 2. It could be seen from Figure 2 that copper dross mainly contained lead, sulfur, copper, bismuth and zinc, which were consistent with the results of XRD and XRF.
2.2. Instruments and agents

Instruments: Electric resistance furnace (model: 5X2-10-13, Shanghai Shiyan Electric Furnace Factory), Intelligent Digital Display Thermostat Water Bath (model: XMTD-204, Jintan City Jingda Instrument Manufacture Co., Ltd.), Precision Power Electric Mixer (model: JJ-1, Jintan City Chengdong Xinrui Instrument Manufacturer), Water Circulating Vacuum Pump (model: SHB-III, Beijing Zhongxing Weiye Instrument Co., Ltd.), Electronic Scale (model: TY5002, Shanghai Precision Scientific Instrument Co., Ltd.), Jaw Crusher (model: 100x60, Nanchang General Chemical Examination Figuring Machine Factory).

2.3. Experiment method

After weighing certain amounts of copper dross, sodium hydroxide was added and blended fully according to the requirements of experiment, and then placed in stainless steel vessel and smoothed out. Thickness of feed layer was controlled. When the temperature in the electric resistance furnace reached to the temperature required by the experiment, the feed was put into the furnace to carry out oxidation roasting by blowing air. When roasting was completed, the roasted feed was taken out to be cooled to room temperature. Then water was added and heated to leach and remove arsenic. After filtering, the leached residue removing arsenic was heated and leached with dilute sulfuric acid. After leaching was completed, the leached residue was filtered and washed and the volume of leachate was measured to determine the content of indium. The leaching rate was calculated according to formula (1).

\[ \eta = \frac{c \times v}{m \times a} \times 100\% \]  \hspace{1cm} (1)

\(\eta\) - Leaching rate of indium, %; \(c\) - Content of indium in leachate, g/L; \(v\) - Volume of leachate, L; \(m\) - Mass of copper dross, g; \(a\) - Content of indium in copper dross, g/t.

3. Experiment results and discussions

3.1. Change of mineralogical phase during oxidation roasting

After weighing certain amounts of copper dross, the amount of sodium hydroxide added was 100% of mass of copper dross, and blended fully, and then placed in stainless steel vessel and smoothed out. Thickness of 10mm of feed was controlled. When the temperature in the electric resistance furnace
reached to 600℃, the feed was placed into the furnace to carry out oxidation roasting for 4h by blowing air. When roasting was completed, the roasted feed was taken out to be cooled to room temperature. The roasted product was analyzed by using XRD, the results were shown in figure 3. It could be seen that roasted products mainly were PbO, Na2PbO3, Na3AsO4, Na3SbO4, CuO, ZnO, Bi2O3, etc. Compared with figure 1, sulfides in copper dross such as PbS, CuS and ZnS were transformed to PbO, CuO, ZnO, etc and then As2O3 and Sb2O3 were transformed to sodium salt. Lead metal disappeared and new phases such as PbO, Na2PbO3, Na3AsO4, Na3SbO4, etc. appeared. The reason was that PbO, As2O3, Sb2O3 reacted with sodium hydroxide to form Na2PbO3, Na3AsO4, Na3SbO4, respectively.

![XRD patterns of roasting products](image)

**Fig. 3 XRD patterns of roasting products**

### 3.2. Effect of water leaching of roasted products on leaching rate of indium

Roasting conditions: the addition amount of sodium hydroxide added was 50% of the quality ratio of copper dross, roasting temperature was 600℃, and roasting time was 4h. Water leaching conditions: liquid/solid ratio was 4:1, leaching temperature was 95℃, and the stirring speed was 200rpm. Acid leaching conditions: the concentration of sulfuric acid was 3mol/L, liquid/solid ratio was 4:1, leaching temperature was 95℃, and the stirring speed was 200rpm.

Under the above-mentioned conditions, the effect of direct acid leaching and that of water leaching and then acid leaching of roasted products on leaching rate of indium were investigated, and the results were shown in figure 4. When the time of water leaching was 3h, the compositions of leached residue were shown in Table 2, the ratio of residue was 56.05% and the ratio of arsenic removed was 96.18%. The diffraction result of leached residue was shown in figure 5. From figure 4, it could be seen that in case of both conditions, namely after water leaching and then acid leaching, the leaching rate of indium increased with the prolonged time of leaching; compared with figure 5 and figure 3, main mineralogical phase in figure 5 was the peak of lead sulfate, the diffraction peaks of sodium arsenate, sodium plumbate and sodium antimonate disappeared, the peaks of lead oxide, tin oxide, copper oxide etc. strengthened. This showed that after copper dross was roasted with alkali and water leached the removal of arsenic was complete. Then leached residue was leached with acid. The ratio of indium leaching could be increased by 6.98% compared with that of alkali roasting of copper dross and then direct acid leaching. The main reason was that after direct acid leaching the leachate contained arsenic, especially the existence of As5+ could neutralize the solution. When the pH value was between 2.0 and 3.4, indium began to precipitate as 5In2O3·3As2O3·nH2O[11] which was hard to be leached with sulfuric acid and as a result remained in leached residue. Thus the leaching rate of indium was decreased and it was necessary to remove arsenic by water leaching.
Effect of the amount of sodium hydroxide on leaching rate of indium

Leaching conditions were fixed as item 2.2. The addition amount of sodium hydroxide added was changed as 0%, 40%, 60%, 80%, 100% and 120% of the quality ratio of copper dross. Effects of ratio of sodium hydroxide on leaching rate of indium were shown in figure 6.

From figure 6, it could be seen that when sodium hydroxide was not added to carry out roasting, the leaching rate of indium was only 63.06%. The leaching rate of indium rose basically in a straight line with the increase of the amount of sodium hydroxide. When ratio of the sodium hydroxide was 100%, the leaching rate of indium was 97.94%, increasing by 34.88% compared with the condition which sodium hydroxide was not added. This showed that roasting with sodium hydroxide was beneficial to the increase of leaching rate of indium. When ratio of sodium hydroxide continued was increased, the increase of leaching rate of indium was slowed down. Comprehensively considering

Table 2 Compositions of water leaching residue (%)

| Element | As  | Fe  | Cu  | Zn  | Pb  | Sb  | Bi  | Sn  | S   | In  | Ag  | Au  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Content | 0.42| 0.18| 18.96| 9.08| 42.44| 3.47| 4.78| 1.32| 8.95| 9004.47| 561.08| 1.43|

Unit of In, Ag and Au is g/t

3.3. Effect of the amount of sodium hydroxide on leaching rate of indium
producing cost and subsequent treating sequences, the amount of sodium added was defined as 100% of copper dross.

3.4. Effect of roasting temperature on leaching rate of indium
Leaching conditions were fixed as item 2.2. Roasting temperature was controlled by 450°C, 500°C, 550°C, 600°C and 650°C, respectively, while keeping the amount of sodium hydroxide, the thickness of feed and the time of roasting constant. Effects of the different roasting temperature on leaching rate of indium were shown in figure 7.

It could be seen from figure 7 that under the same leaching conditions, when roasting temperature ranged from 450°C to 600°C, the leaching rate of indium increased by 60.29%. But when roasting temperature excelled 600°C, the increase of leaching rate of indium was slowed down with the rise of temperature. When roasting temperature was 650°C, the leaching rate of indium was 98.29%, only
increased by 0.35% compared with that under the temperature of 600℃. Therefore roasting temperature was defined as 600℃.

3.5. Effect of roasting time on leaching rate of indium
Leaching conditions were fixed as item 2.2. Roasting time was controlled by 0.5h, 1.0h, 1.5h, 2.0h, 2.5h and 3.0h, respectively. The results of effect of different roasting time on leaching rate of indium were shown in figure 8. It could be seen that when roasting time was between 0.5 and 2.0h, with the prolonged time of roasting the leaching rate of indium increased significantly. When roasting time exceeded 4h, the leaching rate of indium tended to be in equilibrium. When roasting time was 5h, the leaching rate of indium increased by 0.4% compared with that of 4.0h. This showed that when roasting time exceeded 4.0h, roasting time had little effect on leaching rate of indium. Therefore roasting time was defined as 4.0h.

![Fig.8 Effect of roasting time on leaching rate of indium](image)

3.6. Comprehensive experiment
Based on the above-mentioned experiment results, it could be seen that the leaching rate of indium was significantly by roasting temperature, ratio of sodium hydroxide and water leaching. The optimal process conditions acquired were as follows: roasting conditions: the amount of sodium hydroxide added was 50% of the quality ratio of copper dross, roasting temperature was 600℃, and roasting time was 4h; water leaching conditions: liquid/solid ratio 4:1, the leaching temperature 95℃, and the stirring speed 200rpm; acid leaching conditions: the concentration of sulfuric acid 3mol/L, liquid/solid ratio 4:1, the leaching temperature 95℃ and the stirring speed 200rpm. Under these conditions, the leaching rate of indium reached 98.76%. This experiment result was consistent with the result of conditional experiment result. The leached residue mainly contained lead, sulfur, tin, antimony, bismuth, etc. Characterized by XRD and SEM, the results were shown in figure 9 and figure 10. From figure 9, it could be seen that the newly-formed mineralogical phases in leaching residue were PbSO₄ which peak was very strong, and the little rest were Sb₂O₃, SnO₂, etc. mineralogical phases. Compared with water leaching residue in figure 5, lead oxide and lead metal etc. phases disappeared. From figure 10, it could be seen that the main peaks were sulfur, lead and oxygen, the rest was copper, showing leaching residue mainly contained sulfur, lead and oxygen and a small amount of copper. When leaching water leaching residue by adding sulfuric acid, lead oxide and sulfuric acid reacted to form lead sulfate which entered leaching residue during leaching.
Fig. 9 XRD patterns of leaching residue (a: leaching residue; b: roasting products)

Fig. 10 SEM images and EDS patterns of leaching residue

Table 3 Compositions of leaching residue (%) 

| Element | A  | F  | C  | Z  | P  | S  | B  | S  | In | Ag | Au |
|---------|----|----|----|----|----|----|----|----|----|----|----|
| Cont    | .21| .08| .13| .22| 8.58| .53| .65| .01| .77| 6.43| 3.87| .45|
|         | .21| .08| .13| .22| 8.58| .53| .65| .01| .77| 6.43| 3.87| .45|

Unit of In, Ag and Au is g/t

4. Conclusions

Characterizing copper dross produced when refining crude lead by XRD, SEM, and XRF, it shown that copper dross mainly contained lead, copper, zinc, antimony, tin and sulfur, the rest were arsenic, tin, antimony, bismuth and a small amount of indium and silver etc, which were in the form of Pb, PbS, CuS, ZnS, As₂O₃, Bi₂O₃ and Sb₂O₃, etc.

Copper dross was roasted by adding alkali, and arsenic was removed completely after leaching roasted products with water. Leaching residue was leached with acid, the leaching rate of indium could be increased by 6.98%. It was shown that it is necessary to increase the leaching rate of indium after alkali roasting. Roasting temperature had significant influence on leaching rate of indium. Leaching rate of indium increased with the increase of roasting temperature. When roasting temperature ranged from 450°C to 600°C, leaching rate of indium increased significantly with the increase of roasting temperature. When roasting temperature increased from 450°C to 600°C, ratio of sodium hydroxide
had a significant influence on leaching rate of indium, leaching rate of indium increased basically in a straight line with the increase of ratio of sodium hydroxide. Roasting with sodium hydroxide could significantly increase leaching rate of indium compared with that of blank roasting.

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