

# Leaching Ecological Behavior of Indium from Lead-Containing Copper Matte Using Oxidation Roasting - Leaching Process

Dafang Liu <sup>1,2</sup>, Xingxiang Fan <sup>2,3\*</sup>, Yifeng Shi <sup>4</sup>, Kunbin Yang <sup>4</sup>

<sup>1</sup> Faculty of Metallurgy and Energy Engineering, Kunming University of Science and Technology, Kunming, Yunnan, 650093, CHINA

<sup>2</sup> Kunming Key Laboratory of Comprehensive Utilization Resources of Rare and Precious Metals, Kunming, Yunnan, 650033, CHINA

<sup>3</sup> Faculty of Metallurgical Material, Kunming Metallurgy College, Kunming, Yunnan, 650033, CHINA

<sup>4</sup> YCC Southwest Copper Branch, Kunming, Yunnan, 650102, CHINA

\* Corresponding author: fanxingxiang@tom.com

## Abstract

Lead-containing copper matte (LCCM) is an ecologically intermediate product from blast furnace smelting. In this paper, the thermodynamics of lead matte direct oxidation roasting and adding ferrous sulfate oxidation roasting have been ecologically discussed and the effect of roasting temperature,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  ratio, roasting time, thickness of material layer on the leaching of indium by using oxidation roasting are investigated. The material is characterized by XRD, SEM and XRF before and after leaching. In the course of roasting, the optimum ecological conditions of roasting temperature,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /LCCM mass ratio, roasting time and thickness of material layer are 600°C, 100%, 2.0 h and 10 mm, respectively. Above 93.10% of indium can be dissolved into the sulphuric acid solution under the optimum environment. The results show that addition of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in the roasting process is helpful for leaching and recovery of indium from the LCCM.

**Keywords:** ecological behaviour, lead-containing copper matte, oxidation roasting, indium, acid leaching, extraction

Liu D, Fan X, Shi Y, Yang K (2018) Leaching Ecological Behavior of Indium from Lead-Containing Copper Matte Using Oxidation Roasting - Leaching Process. Ekoloji 27(106): 667-676.

## INTRODUCTION

Indium is a kind of environmentally scattered element with extremely industrial exploitation value. There is always no independent indium deposit in the crust of the earth and the indium sources are very scattered in ecosystem, which is usually not reported in geochemical data sets (Ladenberger et al. 2015, Nusen et al. 2016). Indium is normally associated with iron mineral and non-ferrous metal minerals such as Pb and Zn. About 90% of indium product is recovered from Pb/Zn smelters in the world, for instance lead smelting hazardous dust (Zhang et al. 2017), zinc residue (Li et al. 2015a, Zhang et al. 2010), indium-bearing zinc ferrites (Zhang et al. 2013, Zhang et al. 2016b), lead-smelting dust (Sawai et al. 2015), indium-bearing zinc residue (Zhang et al. 2016a, Li et al. 2015b), copper-smelting ash (Bakhtiari et al. 2011), lead bullion (He et al. 2008), water quenching slag (He et al. 2011), lead smelting hazardous dust (Zhang et al. 2017), and blast furnace (BF) sludge produced in blast furnace iron-

making process (Shen et al. 2013). In addition, microwave radiation heating (Zhang et al. 2013), mechanical activation (Yao et al. 2013) and ultrasonic radiation (Shen et al. 2013) are used in the leaching of various indium containing materials in order to improve the leaching rate of indium.

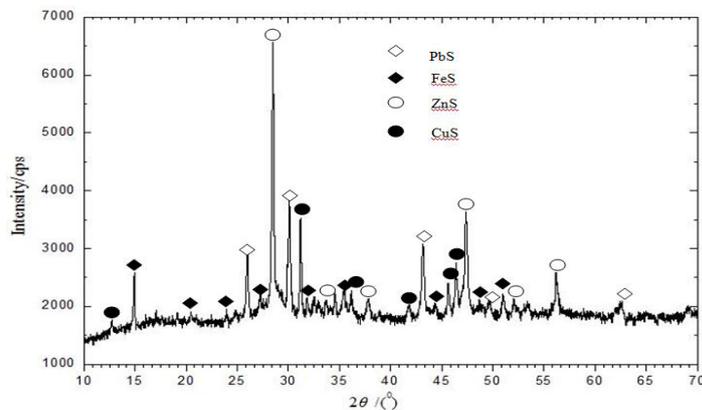
Indium is an important strategic metal due to its unique physical and chemical properties including high ductility, strong conductivity, low melting point, relative chemical stability (Grimes et al. 2017, Pereira et al. 2018), which is widely used in the electronics industry such as making liquid crystal displays, semiconductors, low-temperature solders, infrared photo detectors, solar cells and high-speed transistors (Hiroyuki et al. 2014, Rocchetta et al. 2015, Swain et al. 2015, Zimmermann et al. 2014).

There is a large amount of copper produced in China every year. Thus, lots of dust is produced in the course of copper production by using pyrometallurgical

**Table 1.** Main Chemical composition of LCCD (mass fraction, %)

<b>Element</b>	<b>As</b>	<b>Fe</b>	<b>Cu</b>	<b>Zn</b>	<b>Pb</b>	<b>Sb</b>
<b>Content</b>	4.12	14.89	7.80	9.16	44.61	1.22
<b>Element</b>	<b>Bi</b>	<b>Sn</b>	<b>S</b>	<b>In</b>	<b>Ag</b>	<b>Au</b>
<b>Content</b>	0.68	2.95	14.04	1372.27	273.52	<b>0.81</b>

Note: Unit of In, Au and Ag is g/t

**Fig. 1.** XRD patterns of LCCM

method. Those dusts contain high valuable metals such as Cu, Pb, Zn, As, Bi, Sn, In and Cd. Reduction smelting process is mostly used for producing LCCM from copper smelter dust. LCCM is a kind of Pb/Cu sulfide contained in lead bullion and slags. As eutectic melts of PbS, Cu<sub>2</sub>S, FeS and ZnS, this sulfide product contains a certain amount of scattered metals and precious metals such as Au, Ag and In. Among them, indium with high valuable has caused considerable ecological interest. At present, there are several kinds of treatment processes for LCCM production including ammonia leaching (Park et al. 2007), atmospheric oxidation acid leaching (Fu et al. 2010, Raghavan and Mohanan 2000, Yin et al. 2014), pressure oxidation acid leaching (Jiang et al. 2011, Jin et al. 2009a, 2009b, Ni et al. 2014), fire smelting method (Huang et al. 2016). There are some ecological problems for low leaching rate and long time when LCCM was leached by atmospheric pressure oxidation leaching; iron of LCCM is completely leached under the pressure acid leaching conditions, and exists in trivalent form, which results to be difficult to separate indium and iron when extracting indium by D2EHPA; there are serious problem of indium highly disperse, low yield by means of the smelting of lead matte. In the current indium extraction process, it is quite difficult to achieve more economic efficiency during low indium prices period.

In this paper, we focus on the leaching ecological behavior of indium including oxidation roasting and sulfuric acid leaching. The oxidizing roasting LCCM adding ferrous sulfate was used to convert indium into indium sulphate, which could be fully leached under the condition of low acidity. The phase changes before

and after roasting were analyzed; and the effect of roasting temperature, ferrous sulfate ratio, roasting time, thickness of material layer during oxidation roasting were discussed. The purpose of this study was to determine the main factors of affecting the indium leaching in the course of oxidation roasting and provide recommendation to leaching and recovery of indium through LCCM oxidation roasting.

## METHODOLOGY

### Materials

LCCM materials are from the dust after copper reduction smelting in the blast furnace. The main elements in the raw material were firstly measured by spot energy dispersive X-ray fluorescencer (XRF) (Japan Natural Science ZSX-100e), which include Pb, Cu, Fe, Zn, As, Sn, Sb, Bi and small amount of In, Ag, and Au, as listed in **Table 1**. The contents of In, Ag, Au and Pb are as high as 1372.27 g/t, 273.52g/t, 0.81 g/t and 44.61%, respectively.

The mineralogical phases of LCCM material were characterized by X-ray Diffraction (XRD) (Rigaku Corporation, Tokyo, Japan), as shown in **Fig. 1**. Indium was determined by a WFX-310 flame atomic absorption spectrophotometer (FAAS). The main phases in LCCM material mainly consist PbS, ZnS, FeS and CuS. The scanning electron microscope (SEM) image of the LCCM material is shown in **Fig. 2**. It is obvious that the elements of Pb, Cu, Fe and Zn as well as In exist in LCCM according to the EDS peaks. The SEM results (JEOL Co., Tokyo, Japan) agree well with the results obtained from XRF and XRD.

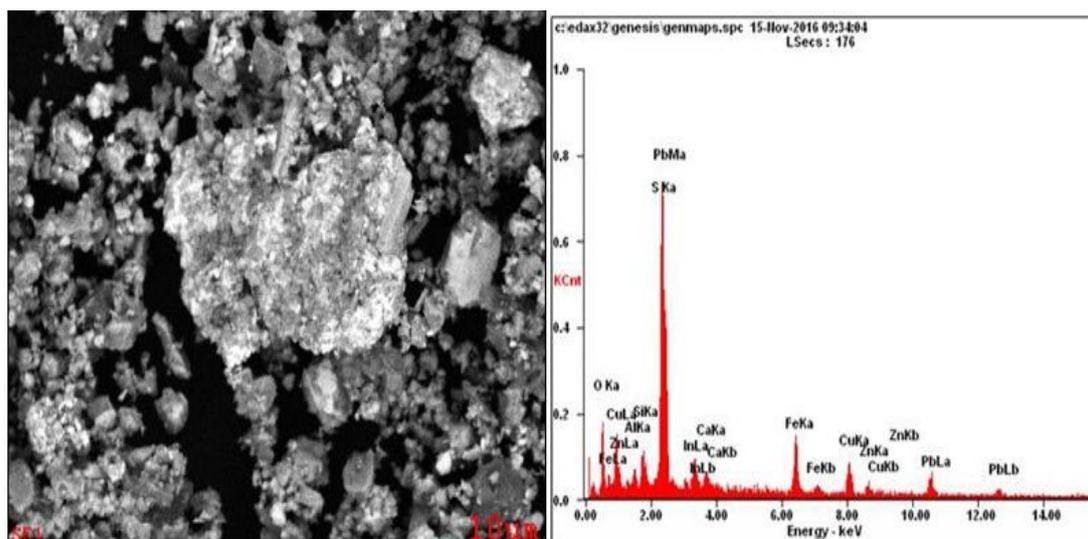


Fig. 2. SEM images & EDS patterns of LCCM

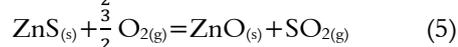
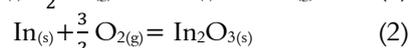
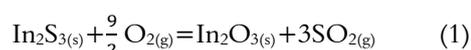
### Reagents & Instruments

The following experimental instruments were used: Resistance Furnace (Type: 5X2-10-13, Supplier: Shanghai Shiyuan Resistance Furnace Factory); Digital Display Thermostatic Water Bath (Type: XMTD-204, Supplier: Jintan Precision Instruments Manufacturing Co., Ltd.); Precision Electric Stirrer (Type: JJ-1, Supplier: Jintan Chengdong Xinrui Instruments Factory); Water Circulating Vacuum Pump (Type: SHB-III A, Supplier: Beijing Zhongxing Weiye Instruments Co., Ltd.); Electronic Balance (Type: TY5002, Supplier: Shanghai Precision Instruments Co., Ltd.); Jaw Crusher (Specification: 100×60, Supplier: Nanchang Universal Sample-making Machine Manufacturer).

Reagents employed in this work:  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (analytical reagent: Tianjin Fengchuan Chemical Reagent Science & Technology Co., Ltd.); Sulfuric Acid (analytical reagent: Xilong Chemical Co., Ltd.).

### Experiment Principle

Direct oxidation of LCCM roasting, the reaction occurred as follows:



According to the thermodynamic data in **Table 2**, the relationship between the  $\Delta G_T^\ominus$  and  $T$  can be obtained as follows:

$$\text{Eq(1): } \Delta G_T^\ominus = -1460718 + 233.859T, \text{ J}$$

$$\text{Eq(2): } \Delta G_T^\ominus = -925919 + 257.4T, \text{ J}$$

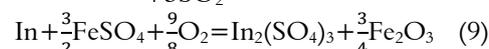
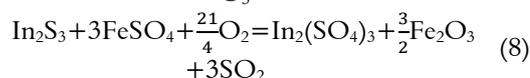
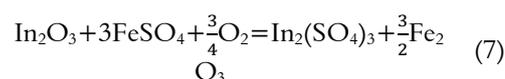
$$\text{Eq(3): } \Delta G_T^\ominus = -417772 + 85.354T, \text{ J}$$

$$\text{Eq(4): } \Delta G_T^\ominus = -404133 + 83.346T, \text{ J}$$

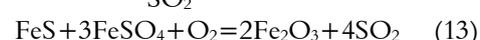
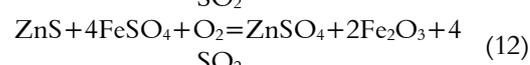
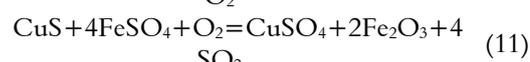
$$\text{Eq(5): } \Delta G_T^\ominus = -443256 + 73.638T, \text{ J}$$

$$\text{Eq(6): } \Delta G_T^\ominus = -609594 + 135.098T, \text{ J}$$

When adding ferrous sulfate, in the course of oxidation roasting, the materials of LCCM are mixed with ferrous sulfate ( $\text{FeSO}_4$ ), the main reactions between indium and  $\text{FeSO}_4$  could be presented as follows:



Meanwhile, other metals such as Pb, Cu and Zn would react with  $\text{FeSO}_4$ , the reaction can be considered as follows:



By means of the thermodynamic data **Table 2**, calculating the relationship between the  $\Delta G_T^\ominus$  and  $T$  of Equation (8) ~ (13) can be obtained as follows:

**Table 2.** Thermodynamic data

phase	In <sub>2</sub> O <sub>3</sub>	In <sub>2</sub> S <sub>3</sub>	In	In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	FeSO <sub>4</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>2</sub>	O <sub>2</sub>
$\Delta S_{298}^{\ominus}/J \cdot K^{-1}$	107.947	163.594	57.823	302.085	120.959	87.446	248.111	205.016
$\Delta H_{298}^{\ominus}/J$	-925919	-355640	0	-2725458	-928848	-825503	-296813	0
phase	PbSO <sub>4</sub>	CuS	CuSO <sub>4</sub>	ZnS	ZnSO <sub>4</sub>	FeS	PbS	
$\Delta S_{298}^{\ominus}/J \cdot K^{-1}$	148.532	66.526	109.244	57.739	110.541	60.291	91.211	
$\Delta H_{298}^{\ominus}/J$	-920062	-48534	-769982	-201669	-981357	-100416	-98324	

**Table 3.**  $\Delta G_T^{\ominus}$  of the equation (1) ~ (13) ( the calcination temperature was 723,923K, respectively)

$T = 773 K$	Eq(1)	Eq(2)	Eq(3)	Eq(4)	Eq(5)	Eq(6)	Eq(7)	Eq(8)
$\Delta G_T^{\ominus}/kJ$	-1291.638	-739.819	-356.061	-343.874	-390.016	-511.918	-112.916	-1207.771
$T = 773 K$	Eq(9)	Eq(10)	Eq(11)	Eq(12)	Eq(13)			
$\Delta G_T^{\ominus}/kJ$	-404.995	-480.215	-221.143	-286.671	-341.102			
$T = 923 K$	Eq(1)	Eq(2)	Eq(3)	Eq(4)	Eq(5)	Eq(6)	Eq(7)	Eq(8)
$\Delta G_T^{\ominus}/kJ$	-1244.866	-688.339	-338.990	-327.205	-375.288	-484.898	-74.650	-1068.296
$T = 923 K$	Eq(9)	Eq(10)	Eq(11)	Eq(12)	Eq(13)			
$\Delta G_T^{\ominus}/kJ$	-354.816	-628.378	-325.383	-392.927	-448.931			

$$\text{Eq(7): } \Delta G_T^{\ominus} = -251249.5 + 191.332T, J$$

$$\text{Eq(8): } \Delta G_T^{\ominus} = -1711976.5 + 697.379T, J$$

$$\text{Eq(9): } \Delta G_T^{\ominus} = -588584.25 + 253.27T, J$$

$$\text{Eq(10): } \Delta G_T^{\ominus} = 55396 - 740.817T, J$$

$$\text{Eq(11): } \Delta G_T^{\ominus} = 155686 - 521.202T, J$$

$$\text{Eq(12): } \Delta G_T^{\ominus} = 97446 - 531.282T, J$$

$$\text{Eq(13): } \Delta G_T^{\ominus} = 48702 - 539.148T, J$$

The experiment determines the range of calcining temperature in 723~923K. When the calcination temperature was 723and 923K, respectively,  $\Delta G_T^{\ominus}$  of the equation (1) ~ (13) was shown in **Table 3**.

It can be seen from **Table 3** that when the calcination temperature is 723 and 923K,  $\Delta G_T^{\ominus}$  of the equation (1) ~ (13) is all below zero, indicating that the reaction of the equation (1) ~ (13) occurred thermodynamically when the roasting temperature ranges from 773 to 923T.

### Experimental Procedures

In the oxidizing roasting process, according to experimental demand, certain amount of LCCM material is mixed with FeSO<sub>4</sub>·7H<sub>2</sub>O and then placed the mixed material on silicon carbide (SiC) refractory bricks and fix the material layer at 10 mm. When the resistance furnace temperature reached the demanded data, and put the material inside for roasting in the required time. After roasting process finishing and cooling at room temperature. Grind material into around -74μm of particle size. The material leached by using demanded sulfuric acid. After leaching finishing, the residue and leaching solution was separated by filtration and washing. The concentration of In is measured by a

WFX-310 flame atomic absorption spectrophotometer (FAAS) and the leaching rate of In is calculated by Eq. (14).

$$\eta = \frac{c \times V}{m \times \alpha} \times 100\% \quad (14)$$

where  $\eta$  presents the leaching rate of In, %; c-refers to the concentration of In in leaching solution, g/L; v- volume of leach solution, L; m-mass of lead matte, g;  $\alpha$ - the composition of In in lead matte, g/t.

## RESULTS AND DISCUSSION

### Phase Changes during Sulphation Roasting

In order to investigate the phase changes, roasting products are characterized XRD, the results are shown in **Fig. 3**. It can be seen from **Fig. 3** (a) and (b), the roasting material mainly contains Fe<sub>2</sub>O<sub>3</sub>, PbSO<sub>4</sub>, CuSO<sub>4</sub>, ZnSO<sub>4</sub> which are not decomposed in roasting. Fe<sub>2</sub>O<sub>3</sub> peaks are stronger than other peaks in XRD pattern. Decomposition temperature of PbSO<sub>4</sub>, CuSO<sub>4</sub>, and ZnSO<sub>4</sub> are 1000 °C, 650°C and 680 °C, respectively. In the process of roasting, FeSO<sub>4</sub>·7H<sub>2</sub>O added reacts with metal sulfide to produce Fe<sub>2</sub>O<sub>3</sub> and SO<sub>2</sub>. Meanwhile, parts of FeSO<sub>4</sub>·7H<sub>2</sub>O added is decomposed into Fe<sub>2</sub>O<sub>3</sub>, SO<sub>2</sub> and SO<sub>3</sub>. The main reason is that FeSO<sub>4</sub> starts to decompose at 500 °C. Therefore, there was no FeSO<sub>4</sub> phase and new phase of Fe<sub>2</sub>O<sub>3</sub> appears in roasting products. Moreover, indium and ferrous sulfate presented in material reacts to form In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, which initial decomposition temperature is 650°C and decomposition rate rises to the top at 800°C (Swain et al. 2015). Under this roasting condition, indium in roasting products is in the form of In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. **Table 4** shows the chemical composition of roasting products mainly containing Pb, Cu, Zn, S, etc.

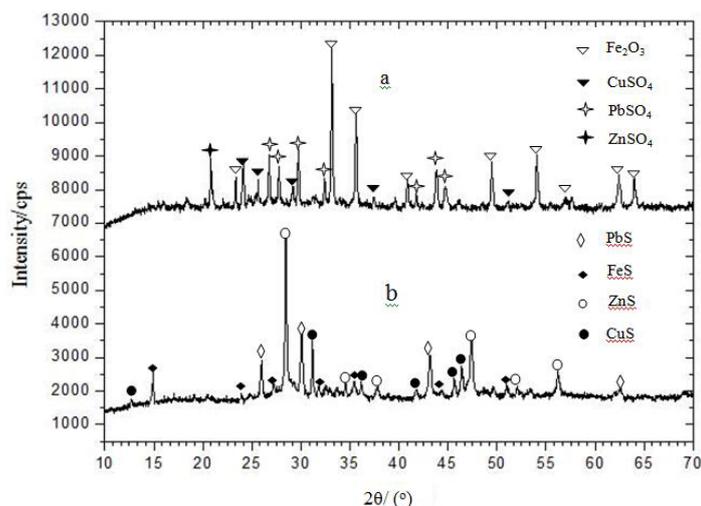


Fig. 3. XRD patterns of roasting products (a: Roasting residues; b: Raw materials)

Table 4. Chemical composition of roasting residues (mass fraction, %)

Element	As	Fe	Cu	Zn	Pb	Sb
Content	2.58	20.99	4.21	5.72	27.88	0.76
Element	Bi	Sn	S	In	Ag	Au
Content	0.44	1.75	15.23	857.67	170.95	0.52

Note: Unit of In, Au, Ag is g/t

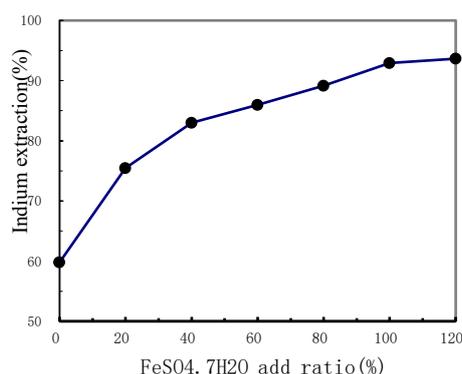
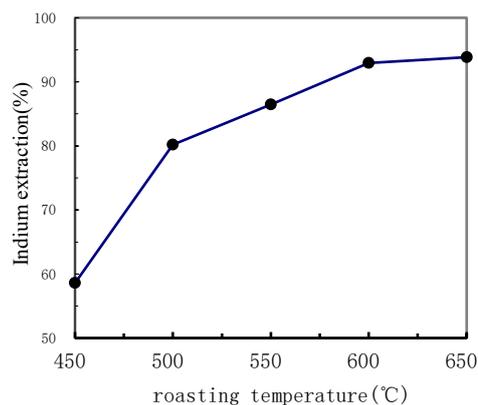


Fig. 4. Effect of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  add ratio on the indium extraction (experimental conditions: roasting temperature 600 °C, roasting time 2h, material thickness 10 mm)

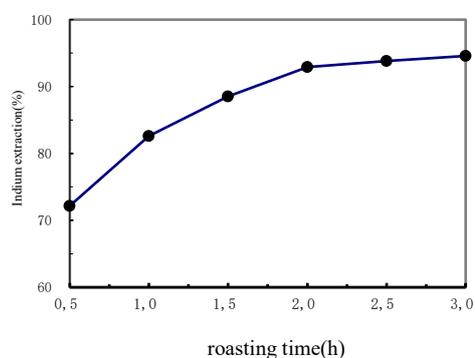
#### Effect of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /LCCM mass ratio

To study effect of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /LCCM mass ratio on the leaching of indium, a series of roasting experiments were carried out under the following roasting conditions, roasting temperature 600 °C, roasting time 2h, material thickness 10 mm, meanwhile, all the other leaching conditions are kept as a constant of (the leaching conditions: sulphuric acid concentration 1.5mol/L, Liquid-solid ratio 4:1, leaching temperature 95°C, leaching time 2.0h, stirring speed 250rpm). Effect of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /LCCM mass ratio on the leaching rate of In is shown in Fig. 4. It can be obviously seen that the leaching rate of indium increases gradually with an increase of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /LCCM mass ratio from 0 to 120%.

Without adding  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in the LCCM, only 61.05% of In could be leached into the sulfuric acid solution. However, as the  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /LCCM mass ratio is 100%, the leaching rate of indium can achieve 92.92%. Further increasing in the  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /LCCM mass ratio has a lightly changes in the leaching rate of In. It should be included that the leaching rate of indium increased by 33.12% from 0 to 100% mass ratio of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /LCCM. It means that the present of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in the roasting process has a critical influence on the leaching rate of indium. In view of subsequent extracting the lead and without reducing the content of Pb in leaching residue, the  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  adding ratio for LCCM mass ratio was determined at 100%.



**Fig. 5.** Effect of roasting temperature on the leaching rate of indium (experimental conditions:  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{LCCM}$  mass ratio 100%, roasting time 2h, material thickness 10 mm)



**Fig. 6.** Effect of roasting time on the leaching rate of indium ( experimental conditions:  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{LCCM}$  mass ratio 100%, roasting temperature 600 °C, material thickness 10 mm)

#### Effect of Roasting Temperature

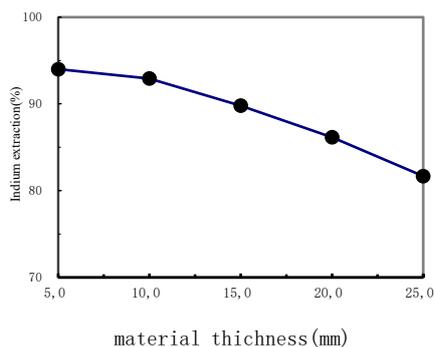
Normally, roasting temperature has an important role on the behaviors of metals in the process of roasting. For this purpose, the experiments of roasting temperature were employed at the range of 450 °C~ 650 °C. Other experimental conditions remain a constant.

**Fig. 5** manifests the effect of roasting temperature on the leaching rate of In by using sulfuric acid. As shown in **Fig. 5**, the leaching rate of indium has a remarkable increasing with an increase of roasting temperature from 450 to 600 °C. Only 58% of In could be leached into acid solution at 450 °C. Especially, as the roasting temperature increases to 600°C, 92.92% of indium could be obtained by sulfuric acid leaching. However, further more increasing of roasting temperature to 650 °C, the leaching rate of In nearly keeps a stable level. It can be explained by the reasons that  $\text{CuSO}_4$  and  $\text{In}_2(\text{SO}_4)_3$  start to decompose at 650 °C. In the course of the decomposition, the increasing acid consumption results from the production of copper oxide. Meanwhile, the produced indium oxide is easy to volatile into the gas resulting in indium dispersion.

Therefore, the optimum roasting temperature is determined to be 600°C.

#### Effect of Roasting Time on the Indium Extraction

In order to improve the recovery rate of In from the LCCM, roasting time is an important condition in the recovery process. Thus, the experiments of roasting time were carried out by controlling the range of time from 0.5 h to 3 h, while other conditions remain a constant. Effect of the different roasting time on the leaching of indium is illustrated in **Fig. 6**. As shown in **Fig. 6**, when roasting time in 0.5 ~ 2.0 h, the leaching rate of indium increases greatly with the increasing roasting time. Further prolong the roasting time extend to 3.0 h, the increasing trend of leaching rate of In nearly remain a stable. The results show that the roasting time has an important influence on the indium leaching within 2.0 h. Consequently, the roasting time was determined to be 2.0 h.



**Fig. 7.** Effect of material thickness on the leaching of indium (experimental conditions:  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{LCCD}$  mass ratio 100%, roasting temperature 600 °C, roasting time 2h)

**Table 5.** The main composition of the leaching residue by using sulfuric acid (mass fraction, %)

<b>Element</b>	<b>As</b>	<b>Fe</b>	<b>Cu</b>	<b>Zn</b>	<b>Pb</b>	<b>Sb</b>
<b>Content</b>	0.36	6.42	0.21	0.26	70.58	70.58
<b>Element</b>	<b>Bi</b>	<b>Sn</b>	<b>S</b>	<b>In</b>	<b>Ag</b>	<b>Au</b>
<b>Content</b>	1.12	4.19	6.13	21.09	432.78	<b>1.32</b>

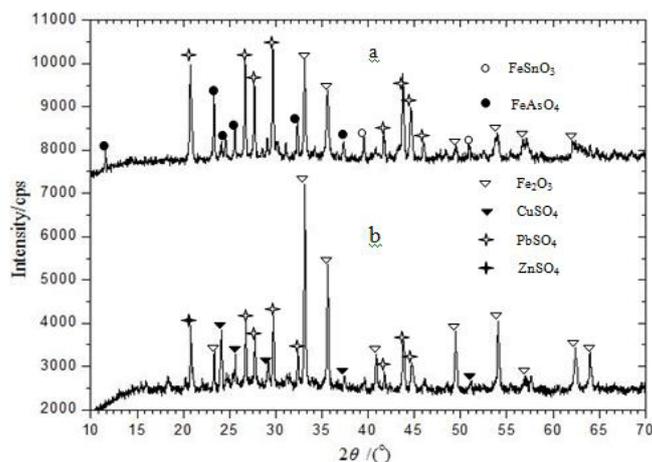
#### Effect of Material Thickness on the Indium Extraction

In the roasting process, the material thickness is another condition to affect the reaction rate. Therefore, the influence of material thickness (as **Fig. 7**) on the leaching of indium was examined using five different material thickness: 5 mm, 10 mm, 15 mm, 20 mm and 25 mm while keep all other conditions constant. **Fig. 7** indicates that leaching rate of In decreases gradually with increasing thickness of material layer. When the thickness of material layer is 10 mm, the leaching rate of In has a significantly decrease with the thickness of material layer increasing. This is resulted from the thickness of material would improve the contact time between oxygen and bottom material in the course of roasting. Therefore, some parts of indium contained in the bottom material cannot react with oxygen. However, when the material thickness is fixed at 5 mm, compared with that at 10 mm, only more 1.09% of In can be obtained. Meanwhile, less thick material layer would cause high energy consumption during roasting. Thus, the material thickness was determined at 10 mm.

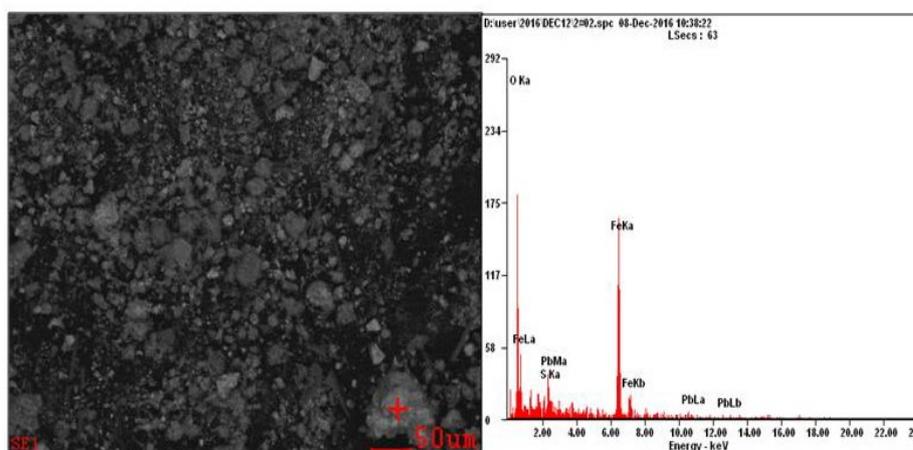
#### Repeatability Experiment

Based on analysis of experimental results mentioned above, it is proved that the experimental conditions of roasting temperature,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{LCCM}$  mass ratio, roasting time and thickness of material layer have significant effects on the indium leaching. Under the optimal conditions and fixed leaching condition, 93.10% of the indium extraction and 39.50% of slag ratio are obtained, respectively. These experimental results are agreed well with that of condition experiments. The main composition of leaching residue

is shown in **Table 5**. The leaching residue is characterized both with X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The results shown in **Fig. 8** and **Fig. 9** demonstrate that the new generated phases in residue contain not only  $\text{FeSnO}_3$  and  $\text{FeAsO}_4$  but also  $\text{PbSO}_4$  and  $\text{Fe}_2\text{O}_3$ . Phase peak was stronger, and no other phases in the leaching residue, such as  $\text{CuSO}_4$  and  $\text{ZnSO}_4$ .  $\text{CuS}$  and  $\text{ZnS}$  contained in the LCCM are converted into  $\text{CuSO}_4$  and  $\text{ZnSO}_4$ , respectively, and dissolve into sulfuric acid solution in the leaching process. As shown in **Fig. 9**, the leaching residue mainly include Fe, Pb, O, S, etc. Particle size of leaching residue is mostly within 10 ~ 30  $\mu\text{m}$ , few of particle are bigger than 30 $\mu\text{m}$  ~75 $\mu\text{m}$ . Combined with phase analysis in **Fig. 8**, leaching residue is mainly consist of  $\text{Fe}_2\text{O}_3$  and  $\text{PbSO}_4$ .



**Fig. 8.** XRD patterns of leaching residue (a: Leaching residue; b: Roasting product)



**Fig. 9.** SEM image of leaching residue & area spectrum

### CONCLUSION

- (1) LCCM as an intermediate product of blast furnace smelting is characterized by XRD, SEM and XRF. The material of LCCM mainly contains Pb, Cu, Fe, Zn, S and small amounts of In and Ag. The compounds of those metals are mainly in the form of sulfide.
- (2)  $\text{PbSO}_4$ ,  $\text{CuSO}_4$ , and  $\text{ZnSO}_4$  are produced during the course of oxidation roasting. Under the optimum conditions such as 100% of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /LCCM mass ratio, 2.0 h of roasting time, 10 mm of material layer and  $600^\circ\text{C}$  of roasting temperature, 93.10% of the indium extraction and 39.50% of slag ratio are obtained.

- (3) Ecological phase analysis of leaching residue indicates that main phase of leaching residue consist of  $\text{PbSO}_4$  and  $\text{Fe}_2\text{O}_3$ . The products of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  in roasting process are disappeared and dissolve into the leaching solution.

### ACKNOWLEDGEMENTS

This research was supported by Yunnan Copper Co., Ltd Foundation of Yunnan, China (No. 2016-01F-348). The author thanked the research and development center of Yunnan Copper Metallurgy Research Institute.

## REFERENCES

- Bakhtiari F, Atashi H, Zivdar M, Seyedbagheri S, et al. (2011) Bioleaching kinetics of copper from copper smelters dust. *Journal of Industrial and Engineering Chemistry*, 17(1): 29-35.
- Fu Y, Li B-C, Fan C-L, Zhai X-J, et al. (2010) Selective leaching of nickel from low-sulfur Ni-Cu matte at atmospheric pressure. *Transactions of Nonferrous Metals Society of China*, 20(Sup1): 71-76.
- Grimes SM, Yasri NG, Chaudhary AJ (2017) Recovery of critical metals from dilute leach solutions – Separation of indium from tin and lead. *Inorganica Chimica Acta*, 461: 161-166.
- He J, Tang M-T, Zhou C, Wu S-N, et al. (2011) Extracting indium and preparing ferric oxide for soft magnetic ferrite materials from zinc calcine reduction lixivium. *J. Cent. South Univ. Technol.*, 18: 1074-1079.
- He J, Wang R-X, Liu W (2008) Recovery of indium and lead from lead bullion. *J. Cent. South Univ. Technol.*, 15: 835-839.
- Hiroyuki Y, Shamsul I, Yasuhiko U, Nobuaki K, et al. (2014) Recovery of indium from TFT and CF glasses in LCD panel wastes using sub-critical water. *Solar Energy Materials & Solar Cells*, 125: 14-19.
- Huang C, Shen Q-H, Zhang X, Li F, et al. (2016) Study novel technology of Cu-Pb matte reduction smelting with kiln slag. *Mining & Metallurgy*, 25(3): 58-60.
- Jiang J, Liang D, Zhong Q (2011) Precipitation of indium using sodium tripolyphosphate. *Hydrometallurgy*, 106(3/4): 165-169.
- Jin B, Yang X, Shen Q (2009) Kinetics of copper dissolution during pressure oxidative leaching of lead-containing copper matte. *Hydrometallurgy*, 99(1/2): 119-123.
- Jin B, Yang X, Shen Q (2009) Pressure oxidative leaching of lead-containing copper matte. *Hydrometallurgy*, 96(1-2): 57-61.
- Ladenberger A, Demetriades A, Reimann C, Birke M, et al. (2015) GEMAS: Indium in agricultural and grazing land soil of Europe - its source and geochemical distribution patterns. *Journal of geochemical exploration*, 154: 61-80.
- Li X, Deng Z, Li C, Wei C, et al. (2015a) Direct solvent extraction of indium from a zinc residue reductive leach solution by D2EHPA. *Hydrometallurgy*, 156: 1-5.
- Li X, Wei C, Deng Z, Li C, et al. (2015b) Extraction and separation of indium and copper from zinc residue leach liquor by solvent extraction. *Separation and Purification Technology*: 348-355
- Ni Y, Yu X, Hua H, Shu B, et al. (2014) Experimental Study of Pressure Leaching on Lead Matte. *Conservation and utilization of mineral resources*, (6): 33-37.
- Nusen S, Chairuangstri T, Zhu Z, Cheng CY (2016) Recovery of indium and gallium from synthetic leach solution of zinc refinery residues using synergistic solvent extraction with LIX 63 and Versatic 10 acid. *Hydrometallurgy*, 160: 137-146.
- Park K-H, Mohapatra D, Reddy BR, Nam C-W (2007) A study on the oxidative ammonia/ammonium sulphate leaching of a complex (Cu-Ni-Co-Fe) matte. *Hydrometallurgy*, 86(3-4): 164-171.
- Pereira EB, Suliman AL, Tanabe EH, Bertuol DA (2018) Recovery of indium from liquid crystal displays of discarded mobile phones using solvent extraction. *Minerals Engineering*, 119: 67-72.
- Raghavan R, Mohanan PK (2000) Hydrometallurgical treatment of copper matte generated at a lead smelter for simultaneous recovery of copper, lead and silver. *Bull. electrochem.*, 16(1): 44-48.
- Rocchetti L, Amato A, Fontia V, Ubaldini S, et al. (2015) Cross-current leaching of indium from end-of-life LCD panels. *Waste Management*, 42: 180-187.
- Sawai H, Rahman IMM, Tsukagosh Y, et al. (2015) Selective recovery of indium from lead-smelting dust. *Chemical Engineering Journal*, 277: 219-228.
- Shen X-M, Li L-S, Wu Z-J, et al. (2013) Ultrasonic-assisted acid leaching of indium from blast furnace sludge. *Metallurgy and materials transactions B*, 44B: 1324-1328.
- Swain B, Mishra C, Kang L, Park K-S, et al. (2015) Recycling process for recovery of gallium from GaN an e-waste of LED industry through ball milling, annealing and leaching. *Environmental Research*, 138: 401-408.
- Yao J, Li X, Pan L, Mo J, Wen Z (2013) Kinetics of leaching zinc and indium from indium-bearing zinc ferrite mechanically activated by tumbling mill. *Minerals & metallurgical processing*: 45-52.
- Yin F, Xing P, Li Q, et al. (2014) Magnetic separation-sulphuric acid leaching of Cu-Co-Fe matte obtained from copper converter slag for recovering Cu and Co. *Hydrometallurgy*, 149: 189-194.

- Zhang F, Wei C, Deng Z, Li X, et al. (2016a) Reductive leaching of indium-bearing zinc residue in sulfuric acid using sphalerite concentrate as reductant. *Hydrometallurgy*, 161: 102-106.
- Zhang F, Wei C, Deng Z-G, Li C-X, et al. (2016b) Reductive leaching of zinc and indium from industrial zinc ferrite particulates in sulphuric acid media. *Transactions of nonferrous metals society of China*, 26: 2495-2901.
- Zhang L-Y, Mo J-M, Li X-H, et al. (2013) A kinetic study of indium leaching from indium-bearing zinc ferrite under microwave heating. *Metallurgy and materials transactions B*, 44B: 1320-1325.
- Zhang Y, Jin B, Ma B, Feng X (2017) Separation of indium from lead smelting hazardous dust via leaching and solvent extraction. *Journal of Environmental Chemical Engineering*, 5(3): 2182-2188.
- Zhang Y-J, Li X-H, Pan L-P, et al. (2010) Studies on the kinetics of zinc and indium extraction from indium-bearing zinc ferrite. *Hydrometallurgy*, 100: 172-176.
- Zimmermann Y-S, Niewersch C, Lenz M, Kül Z, et al. (2014) Recycling of indium from CIGS photovoltaic cells: potential of combining acid-resistant nanofiltration with liquid-liquid extraction. *Environmental science & technology*, 48(22): 13412-13418.