

# SULPHATIZING ROASTING OF Cu-Zn AND MULTIMETAL COMPLEX SULPHIDES<sup>①</sup>

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## ABSTRACT

The studies on sulphatizing roasting of Cu-Zn and complex sulphides are presented. The effects of roasting temperature and duration on the extraction of copper and zinc and volatility of sulphur and arsenic are discussed. The associations of some chalcopyrites and sphalerites with pyrites make it difficult to achieve high recoveries and high grades of the individual concentrate by beneficiation. Because of the high contents of Cu, Zn, Fe and S and the low contents of Ca and Mg in the ores, direct metallurgical treatments of the ores were carried out. There are some openings and fissures outside and inside the leaching residues, this is beneficial for the extraction of gold and silver from the residues, which can also be used as hematite concentrate after removal of lead and zinc by reducing roasting.

**Key words:** complex sulphide ore concentrate roasting

## 1 INTRODUCTION

For the last twenty years period, pronounced developments and improvements have taken place in the selective solvent extraction of copper, and many progresses have been made in the treatment of complex sulphides. The NESAC Company and the MECHIM Company have done some roasting experiments of complex sulphides. The minerals used in their experiments contain a great quantity of arsenic except nonferrous metals and precious metals. The Roasting-Leaching-Solvent Extraction process has been chosen for the treatment of the complex sulphides<sup>[1]</sup>. Demarthe and Georgeaux have advanced a new process in which cupric chloride was used as a medium to leach low-grade zinc, copper and lead sulphide compounds<sup>[2]</sup>. Limpo and Figueredo have presented the CENIM-LNETI process, which is based on an oxidizing leach of the

complex sulphides in the ammonium chloride solutions<sup>[3]</sup>.

The minerals used in our experiments were mined out from a large scale copper mine in the northeast of China. The research aim is to appraise the deposit and carry out some earlier works in mineralogy, beneficiation and metallurgy for the comprehensive utilization of the mineral resources. Roasting-Leaching-Solvent Extraction process has been adopted in the metallurgical process.

## 2 SAMPLE

The samples were obtained with a coring bit on the site of the mine. On the bases of the composition of the ores and the ore horizon, in which the ores were originally distributed, the ores are classified into two kinds; copper-zinc sulphides and multimetal sulphides. Table 1 shows the mineral phases

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of the ores.

**Table 1 Mineral phases of the ores (%)**

Mineral	Cu-Zn Sulphides		Multimetal Sulphides	
	Vol.-%	wt.-%	Vol.-%	wt.-%
Pyrite	63.90	71.08	31.50	38.63
Chalcopyrite	11.60	10.84	4.40	4.56
Tetrahedrite	1.40	1.40	1.60	1.75
Sphalerite	11.90	9.75	54.50	47.44
Galena	0.10	0.21	2.00	3.68
Gangue	11.10	6.72	6.00	3.94
Total	100.00	100.00	100.00	100.00

The mixed ores were made by mixing copper-zinc sulphides and multimetal sulphides in the ratio of nine to one. On the bases of the ratio, those are distributed in the ore horizon, the concentrates were obtained by floating the copper-zinc sulphide ores. Table 2 gives the composition of the samples.

**Table 2 Composition of the samples (%)**

Element	Cu-Zn Sulphides	Multimetal sulphides	Mixed ores	Concentrates
Cu	4.20	3.84	4.18	6.85
Zn	2.28	19.75	4.14	3.79
S	46.22	39.70	45.57	45.30
Fe	39.49	25.70	38.11	42.86
Pb	0.058	1.70	0.22	0.16
Cd	0.012	0.14	0.025	0.021
Co	0.002	0.002	0.002	0.0019
Ni	0.001	0.002	0.0011	0.0014
Bi	0.016	—	—	0.018
As	0.22	0.21	0.22	0.34
SiO <sub>2</sub>	4.48	—	—	2.17
Al <sub>2</sub> O <sub>3</sub>	1.4	—	—	—
MgO	0.08	0.08	0.08	—
CaO	0.01	0.012	0.01	—
Au(g/t)	0.84	1.28	0.88	0.97
Ag(g/t)	64.40	144.00	72.36	47.20

The experiments have been carried out for the mixed ores and the concentrates.

### 3 EXPERIMENT AND ANALYSIS

The roasting experiments used laboratory pipe-furnace (ϕ18 mm × 180 mm) as a device. The flow of air was measured by capillary flowmeter. The leaching experiments were carried out in a 100

mL capacity beaker fitted with a magnetic stirrer. Atomic absorption spectrophotometer was used to analyse copper and zinc. Polarograph was used to analyse arsenic. The photos were taken through microscope. Mineral phases were identified by X-ray diffractometer.

## 4 RESULTS AND DISCUSSION

### 4.1 Effects of Roasting Temperature

#### 4.1.1 On Extraction of Copper and Zinc

When temperature changed from 680 °C to 770 °C in the experiments, the effects of roasting temperature on the extraction of copper and zinc from the mixed ores and the concentrates are shown in Fig. 1.

Fig. 1 (a) indicates that suitable roasting temperatures for the mixed ores vary in the range of 680 °C to 750 °C, and Fig. 1 (b) shows that fit roasting temperatures change from 700 °C to 720 °C for the concentrates. It is obvious that better extraction of copper and zinc can be achieved at a wider temperature range for the mixed ores.

#### 4.1.2 On Dissolution of Iron

In general terms, increasing temperature of roasting can decrease the dissolution of iron in leaching solutions owing to the increase of hematite formed in the roasted minerals. Table 3 shows the effects of roasting temperature on the dissolution of iron in leaching solutions.

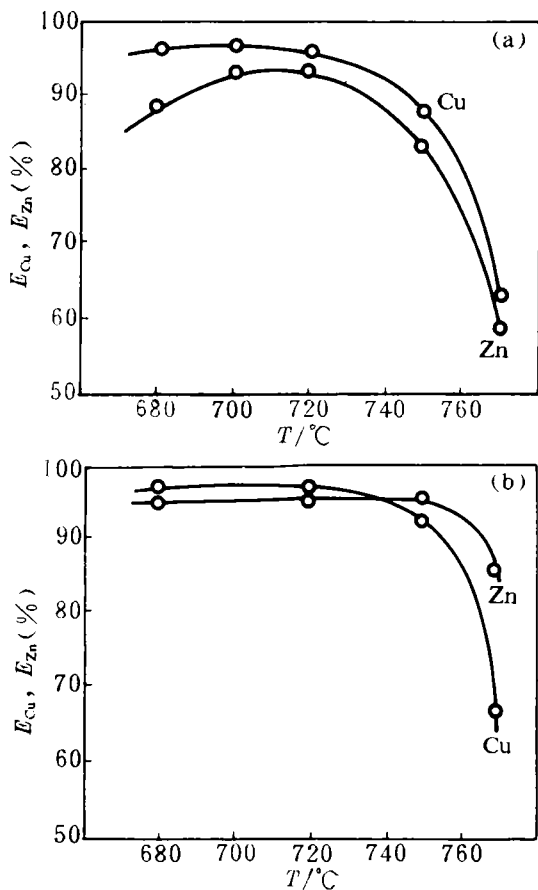
**Table 3 Effects of roasting temperature on the dissolution of iron in leaching solutions**

Temperature / °C	Leaching solutions from the mixed ores		Leaching solutions from the concentrates	
	Fe/kg·m <sup>-3</sup>	Extraction (%)	Fe/kg·m <sup>-3</sup>	Extraction (%)
680	1.52	2.32	3.32	1.60
700	—	—	2.36	1.11
720	1.61	0.86	2.21	1.09
750	1.11	0.85	2.01	0.99
770	1.11	0.85	1.18	0.72

As seen in Table 3, the contents of iron in the leaching solutions decreased with the increase of roasting temperature.

#### 4.1.3 On Volatility of Sulphur and Arsenic

Effects of roasting temperature on the volatility of sulphur and arsenic are shown in Table 4.



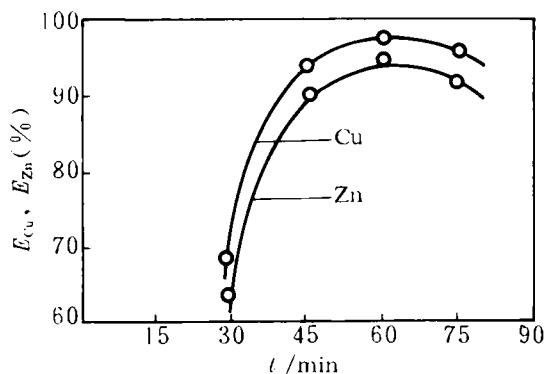
**Fig. 1 Effects of roasting temperature on the extraction of copper and zinc**

(a)—for the mixed ores; (b)—for the concentrates  
 Roasting conditions;  $t = 1.0$  h. Coefficient of excess air = 1.86. Leaching conditions; Initial  $H_2SO_4 = 20$  kg/m<sup>3</sup>,  $T = 80$  °C,  $t = 1.5$  h, Ratio of liquid to solid = 2.4:1

Table 4 indicates that increasing temperature of roasting is beneficial for the escape of sulphur and arsenic.

**4.2 Effects of Roasting Duration**

Tests were only done for the mixed ores. effects of roasting time on the extraction of copper and zinc and effects of roasting time on volatility of sulphur are shown in Figs. 2 and 3 respectively. Fig. 2 shows that one hour period of roasting can satisfy the extraction of copper and zinc from the mixed ores. As seen in Fig. 3, sulphur reacted rapidly with oxygen given by blowed air within the initial fifteen minutes. The escape of sulphur nears end at the point of sixty minutes. Fig. 2 and Fig. 3 suggest that an hour roasting can satisfy both the extraction of copper and zinc and the escape of sulphur.



**Fig. 2 Effects of roasting time on the extraction of copper and zinc**

**Table 4 Effects of roasting temperature on the volatility of sulphur and arsenic(%)**

Temperature /°C	The roasted mixed ores				The roasted concentrates			
	Content		Volatility		Content		Volatility	
	S	As	S	As	S	As	S	As
650	4.67	0.202	91.87	27.16	—	—	—	—
680	—	—	—	—	6.52	0.20	88.08	51.37
700	—	—	—	—	6.46	0.123	88.89	68.16
720	4.38	0.091	92.37	67.18	—	—	—	—
750	4.62	0.035	91.96	87.38	5.06	0.076	90.62	81.22
800	0.66	0.012	98.84	95.89	1.71	0.033	97.33	92.10

Roasting conditions;  $t = 1.0$  h, Coefficient of excess air = 1.86

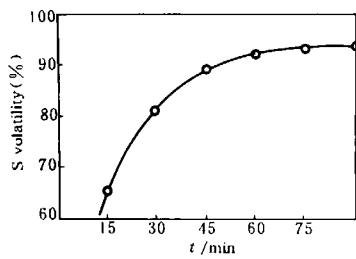


Fig. 3 Effects of roasting time on volatility of sulphur

### 4.3 Phase Studies

Microphotographs of ores, roasted ores and leaching residues are shown in Fig. 4.

It can be seen in microphotographs in Fig. 4 that:

(1) Chalcopyrites and sphalerites are found both in the roasted mixed ores and the leaching residues, and the reason was that some mineral particles were not got in touch completely with the blown air. The copper and zinc in the form of sulphides can not be dissolved in the sulphuric acid.

(2) Iron exists mainly in the form of hematite in the residues.

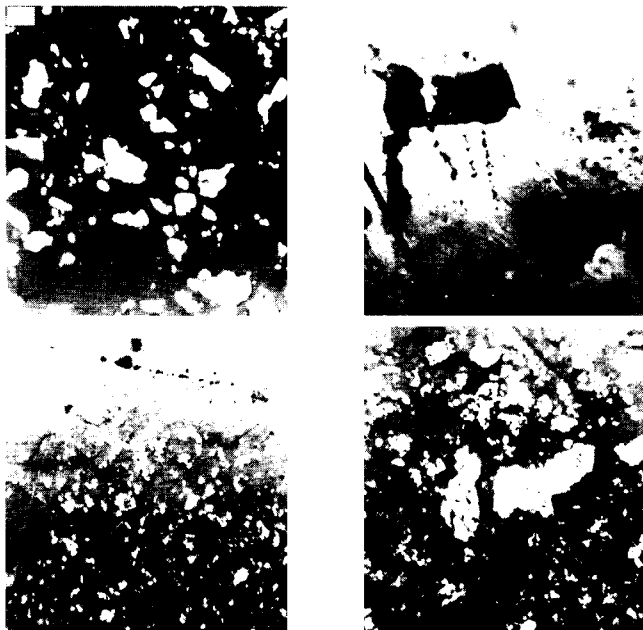


Fig. 4 Microphotographs of the mixed ores, the roasted mixed ores and the leaching residues

(a) mixed ores; (b) roasted mixed ores;  
(c) leaching residues pyrite; (d) leaching residues chalcoprite

(3) Small openings and fissures were found outside and inside some mineral particles in the leaching residues.

X-ray diffractograms show that phase transformation took place in the minerals of pyrite, chalcopyrite and sphalerite after roasting. Iron in the pyrite and chalcopyrite was mainly changed into hematite. The main content of the leaching residues is hematite. Investigations were also made for the concentrates, and the conclusions are the same as that of mixed ores.

#### 4.4 Discussion

The roasted mixed ores and concentrates were leached under moderate acidity. The compositions of the residues are given in Table 5.

**Table 5 Analysis of the leaching residues (%)**

	Cu	Zn	S	Fe	Pb	Cd	Co
1	0.26	0.28	0.16	63.64	0.22	0.003	0.001
2	0.22	0.43	0.19	61.60	0.46	0.003	0.001
	Ni	As	SiO <sub>2</sub>	MgO	CaO	Au /g·t <sup>-1</sup>	Ag /g·t <sup>-1</sup>
1	0.000	0.090	4.58	0.127	0.045	1.70	85.90
2	0.001	0.034	6.55	0.141	0.026	1.51	124.11

Note: 1—The leaching residues from the roasted mixed ores;  
2—the leaching residues from the roasted concentrates

The main content of the two kinds of residues is iron. The percent of iron in the residues from the mixed ores satisfies the demand for iron content of H<sub>62</sub> grade hematite concentrate. The content of iron in the residues from the concentrates reaches the standard of H<sub>59</sub> grade hematite concentrate. The sulphur in the two kinds of residues is both below the limit for sulphur in hematite concentrate<sup>[4]</sup>. Silver content in the residues from the mixed ores arrives industry grade<sup>[5]</sup>. Therefore, the recovery of precious metals and iron in the residues is the main goal of comprehensive utilization.

In the field of extraction of precious metals from leaching residues, Laoshan Company has studied and developed the method of recovering precious metals from leaching residues of roasted zinc concentrates since 1970. A special method of thiourea leaching has been established by the company and a plant of annual output of 25 tons precious

metals was built with this method in Viviez in 1978<sup>[1]</sup>. Schulze presented a method that acidic thiourea solutions were used to extract silver from silver-bearing materials from zinc hydrometallurgy<sup>[6]</sup>. Yu, Bingquan pointed out that 70 to 80 percent of silver in the leaching residues was transferred into slag and the rest of the silver was enriched in zinc oxide during reducing roasting in rotary furnace<sup>[7]</sup>.

On the bases mentioned above, it seems reasonable that gold and silver are first extracted by thiourea leaching and then rotary furnace is adopted to volatilize lead and zinc in the leaching residues through reducing roasting. Lead, zinc and water can be cut down to lower levels so that qualified hematite concentrate can be obtained.

As seen in Fig. 4(a), although 95 percent of the mineral particles are less than 0.075 μm through grinding, some chalcopyrites and sphalerites are still in associations with pyrites. For this reason, it is difficult to take full advantage of differential flotation, as it is practically impossible to achieve high recoveries and high grades of the individual concentrate as well as mixed concentrates at the same time. But the ores have an advantage that the sum of Cu, Zn, Fe and S arrives 80% and the sum of Ca and Mg is less than 0.1%. Consequently, direct metallurgical treatment of the ores has been carried out in the experiments and satisfied results have been achieved.

## 5 CONCLUSIONS

There are no tailings and wastes in the process presented in this paper. Metallurgy and mineralogy were studied to make this research more reasonable. Advantages of the process make it particularly appropriate for the treatment of this type of ore.

The following gives out the most significant characteristics and advantages of the process:

(1) The extractions of copper and zinc from the mixed ores and concentrates exceed 96% and 94% respectively through one time leaching.

(2) Iron exists in the form of hematite in the roasted mixed ores and concentrates.

(3) Sulphur and arsenic can be volatilized  
(To page 20)

**Table 1** Checking of iso-activity

Cu-Ce-M	%M					$\bar{a}_{Ce}$
	0.1	0.3	0.5	0.7	0.9	
Cu-Ce-Sn	0.259	0.259	0.259	0.259	0.259	
Cu-Ce-Zn	0.217	0.217	0.217	0.217	0.217	0.234
Cu-Ce-Pb	0.227	0.227	0.228	0.225	0.225	

**6 CONCLUSIONS**

(1) The equilibrium products of Cu-Ce-M (M = Sn, Zn, Pb) systems were identified as  $Ce_2O_3$  at 1200 C.

(2) The activity interaction coefficients between M and Ce in liquid copper solutions at 1200 C were obtained by use of iso-activity method and conjugate gradient method of solving ill-conditioned equations.

For the Cu-Ce-Sn system;

$$e_{Ce}^{Sn} = -0.131, \gamma_{Ce}^{Sn} = 0.284, \gamma_{Ce}^{Sn \cdot Ce} = 1.660, e_{Sn}^{Ce} = -0.110, \gamma_{Sn}^{Ce} = 1.616, \epsilon_{Ce}^{Sn} = \epsilon_{Sn}^{Ce} = -57.2;$$

For the Cu-Ce-Zn system;

$$e_{Ce}^{Zn} = -0.794, \gamma_{Ce}^{Zn} = 0.162, \gamma_{Ce}^{Zn \cdot Ce} = 1.053,$$

$$e_{Zn}^{Ce} = -0.368, \gamma_{Zn}^{Ce} = 0.563, \epsilon_{Ce}^{Zn} = \epsilon_{Zn}^{Ce} = -187.9;$$

For the Cu-Ce-Pb system;

$$e_{Ce}^{Pb} = -0.680, \gamma_{Ce}^{Pb} = 0.247, \gamma_{Ce}^{Pb \cdot Ce} = 0.875, e_{Pb}^{Ce} = -1.01, \gamma_{Pb}^{Ce} = 1.483, \epsilon_{Ce}^{Pb} = \epsilon_{Pb}^{Ce} = -512.3.$$

(3) The equilibrium constant of the reaction  $3[O] - 2[Ce] = Ce_2O_3$  in liquid copper at 1200 C is  $5.08 \times 10^{20}$ , and the Gibb's standard free energy of formation of  $Ce_2O_3$  is  $-583.87$  kJ/mol.

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efficiently in the roasting operation in the temperature range of 680 C to 720 C.

(4) There are lower content of sulphur and higher porosities in the residues. As a consequence, this is beneficial for the extraction of gold and silver in the residues.

(5) The residues can be sured as hematite concentrate after the removal of lead and zinc by reducing roasting.

(6) Direct metallurgical treatment of the ores can avoid the difficulties of beneficiation and improve the comprehensive utilization.

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