

# NON-POLLUTION PROCESS FOR COMPLEX REFRACTORY SILVER-GOLD ORES<sup>(1)</sup>

Xu Shengming, Zhang Chuanfu, Zhao Tiancong, Li Zuogang

Department of Nonferrous Metallurgy,  
Central South University of Technology, Changsha 410083

**ABSTRACT** Chemistry of lime roasting process for complex sulfided concentrate was described briefly, the chemical phases of gold, silver and carbonaceous substances in the concentrate were also investigated, and the influences of roasting temperature, time and stoichiometric ratio of hydrated lime on sulfur retention and silver extraction of the calcine were studied finally. Under the optimized conditions, gold-silver extractions exceeded 93% and 83%, respectively.

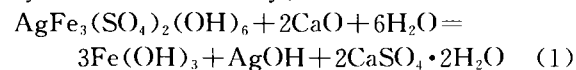
**Key words** complex ore carbonaceous substances silver-gold concentrate lime roasting

## 1 INTRODUCTION

After Tongbei silver mine, the first single silver ore in China, constructed in 1986, about 20 silver mines have been established in China; they produce large amounts of flotation concentrates amounting to hundreds of tons of silver by the end of 1995. The markets of these concentrates, however, are limited because of existing poorly recoverable accompanying elements and/or minor hazardous elements such as arsenic, carbon and antimony. Moreover, large number of carbonaceous gold ores in southwestern China also face with similar problems. Therefore, it is of great significance to develop a non-pollution process for refractory gold and complex silver ores.

The concentrate in this study is a silver-gold sulfide concentrate containing many carbonaceous materials. Because of "pre-robbing" reaction of them and silver being "locked" inside base metal sulfides, a pretreatment prior to cyanidation or acid-thiourea leaching is necessary. With regard to pretreatment for carbonaceous gold ores, authors in reference<sup>[1]</sup> reviewed all kinds of processes. As the case of the concentrate, chlorination

operation and acid pressure oxidation are not suitable, the former is due to high chlorine consumption, the latter is due to poor decarbonizing effect and the formation of silver-jarosite, and the pulp discharged must be further treated with heated lime slurry prior to cyanidation<sup>[2]</sup>, namely:



Though arseno/redox process seems to be appropriate, there is no practical plant in the world. Thus, roasting process is still a profitable pretreating measure in many cases, especially in recent years, lime roasting process for refractory precious metals ores described by Taylor *et al.*<sup>[3-7]</sup> has not only overcome the disadvantages of conventional roasting, eliminated pollution of SO<sub>2</sub> and As<sub>2</sub>O<sub>3</sub> emission, but also can utilize existing equipments and so on. Therefore, this paper will describe the lime roasting process (LRP) for the concentrate.

## 2 CHEMISTRY OF LIME ROASTING

Lime roasting of refractory sulfide/arsenide containing gold ores was investigated

① Received Dec. 1, 1994; accepted May 17, 1995

by Taylor *et al*<sup>[3-7]</sup>. The basic requirement for the technology is that the lime sulfation reaction be much faster than the sulfide oxidation or the formation of volatile arsenic oxides, so that as the sulfur and arsenic are volatilized from the sulfide mineral surface, they are immediately captured by the lime. The gas-solid reactions occur in succession are presented in Table 1.

**Table 1 Major reactions during lime-silver concentrate roasting**

Reactions	Num.
$FeS_2 = FeS + 1/2S_2$	(2)
$S_2 + 2O_2 = 2SO_2$	(3)
$3FeS + 5O_2 = Fe_3O_4 + 3SO_2$	(4)
$3FeS_2 + 8O_2 = Fe_3O_4 + 6SO_2$	(5)
$2Fe_3O_4 + 1/2O_2 = 3Fe_2O_3$	(6)
$Ca(OH)_2 = CaO + H_2O$	(7)
$CaO + SO_2 = CaSO_3$	(8)
$CaSO_3 + 1/2O_2 = CaSO_4$	(9)
$4CaSO_3 = CaS + 3CaSO_4$	(10)
$CaS + 2O_2 = CaSO_4$	(11)
$C + O_2 = CO_2$	(12)
$Ag_2S + 2O_2 = Ag_2SO_4$	(13)
$2Ag + SO_2 + O_2 = Ag_2SO_4$	(14)

In the absence of lime, examination of phase-stability diagram<sup>[8]</sup> for the system Fe-S-O at 602 C shows that pyrite always goes through an intermediate pyrrhotite stage during its breakdown to iron oxide. So it would appear that low temperatures, e. g. 402 C, would favour the direct transformation of pyrite to hematite or possibly magnetite; this conversion is even more apparent for smaller particles, which are exposed to a higher  $p_{SO_2}$ <sup>[9, 10]</sup>. However, in the presence of hydrated lime, lime reacts with surrounding  $SO_2$  into anhydrite ( $CaSO_4$ ), oldhamite ( $CaS$ ) and calcium sulfite, which extremely decreases  $SO_2$  partial pressure in the layer of the charge. Consequently, lime-roasting process of pyrite will tend to pass through an intermediate pyrrhotite stage, the pyrrhotite produced then recrystallizes, and diffusion becomes grain-boundary controlled. Further oxidation of the

pyrrhotite will be slowed down, thus partial sintering of the particle and the formation of insoluble silver compounds will be prevented. Oxidation of the carbonaceous material is also favourable for the conversion through pyrrhotite stage.

The equilibrium diagram of Ca-Ag-S-O system illustrates that lime has no favourable effect on sulfation of argentite. It also shows that if oldhamite is a stable phase in calcine, argentite may be major silver species. The results reported by Hagni *et al*<sup>[11]</sup> on lime-roasting for pyrite shows that oldhamite is a stable phase in the temperature range of 500 ~ 800 C. Therefore, it is necessary to investigate further the behavior of silver in lime-roasting process for the concentrate, and the results will be published in another paper.

### 3 EXPERIMENTAL

#### 3.1 Raw Materials and Analytical Methods

The raw materials used in this study is a flotation concentrate of silver and gold from Jilin province. It mainly consists of pyrite, silica and carbonaceous substances, the rest are galena, sphalerite and chalcopyrite, etc. The screening assay shows that the particles with minus 0.074 mm account for 95%, in which 85% is below 0.042mm, whose mainly chemical composition and phases of gold and silver are presented in Tables 2 to 4.

Analytically pure chemicals were used in all experiments. Combustion and weighing methods with  $BaSO_4$  were used for assays of total carbon and sulfur, respectively. Gold

**Table 2 Mainly chemical composition of the concentrate**

Component	Ag <sup>1)</sup>	Au <sup>1)</sup>	Cu	Pb	Zn	Fe
Content	4400	17.3	0.39	2.05	2.27	26.49
Component	S	Ca	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	C <sub>T</sub> <sup>2)</sup>	C <sub>OR</sub> <sup>3)</sup>
Content	25.29	0.99	25.29	3.89	6.71	6.69

Note: 1) -g/t;

2) -total carbon content;

3) -carbon content except for carbonate salt.

**Table 3 Chemical phases of gold in the concentrate**

Gold types	Content /g·t <sup>-1</sup>	Distribution /%
free and partially exposed	15.87	95.09
encapsulated in sulfides	0.72	4.31
encapsulated in silicates	0.10	0.60
total	16.69	100.00

**Table 4 Chemical phases of silver in the concentrate**

Silver types	Content /g·t <sup>-1</sup>	Distribution /%
nature	20	0.50
argentite	1730	43.13
encapsulated in galena	263	6.56
encapsulated in other sulfides	1944	48.47
cerargrite	22	0.55
encapsulated in rest minerals	32	0.80
total	4011	100.0

and silver analyses in the concentrate, calcine and residues are pyrogenic process and atomic absorption spectrophotometry method, respectively. In this study, sulfur retention is calculated by the total content of sulfur in the calcine without considering its phases.

### 3.2 Procedure

The concentrate and stoichiometric lime are mixed for 1 min in a XZP-100 vibration mill; 80 g mixture was placed on a 120 mm × 160 mm boat, and then put into a preheated muffle furnace, whose door opened slightly. Record the time as soon as the temperature reach the scheduled one. The calcine produced was ground and used as raw material of thiourea leaching.

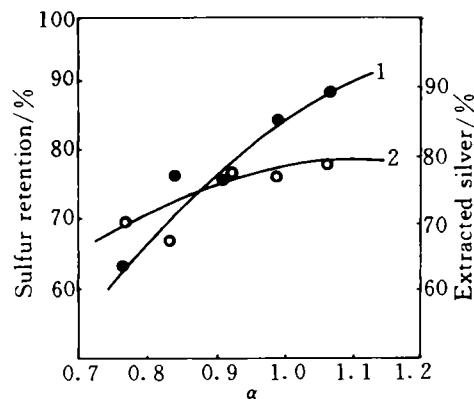
The conditions of verifying tests are as

follows: temperature ( $T$ ) 55 °C, thiourea (Tu) 20 g/L; initial ferric ion ( $\text{Fe}^{3+}$ ) 1.15 g/L; ratio of liquid to solid (L/S) 5:1; resident time ( $t$ ) 3 h and pH below 1.5.

## 4 RESULTS AND DISCUSSION

### 4.1 Effect of Hydrated Lime

The results reported by Taylor *et al.*<sup>[3]</sup> demonstrated hydrated lime was the best sulfur-fixed reagent in the study, the influences of usage of hydrated lime on sulfur retention and silver extraction were illustrated in Fig. 1.



**Fig. 1 Sulfur retention and extracted silver vs  $\alpha$**

( $\alpha$ —stoichiometric ratio of hydrated lime to sulfur,  $T = 650$  °C;  $t = 1$  h)

1—sulfur retention; 2—extracted silver

Fig. 1 shows that  $\alpha$  has favourable effects on sulfur retention and silver extraction. When  $\alpha$  amounts to 1.1, sulfur retention exceeds 90%.

### 4.2 Effect of Roasting Temperature

As shown in Fig. 1, silver extraction increases little when  $\alpha$  accounts for 1.06. As a result, the effects of roasting temperature on sulfur retention and silver extraction were investigated under the conditions of  $\alpha = 1.06$  and  $t = 1$  h. The results are shown in Fig. 2.

The curves in Fig. 2 show that sulfur retention increases with elevating temperature.

but silver extraction only fluctuates in the range of 83%~85%. This phenomenon needs to be investigated further.

### 4.3 Effect of Roasting Time

The influences of roasting time on sulfur retention, decarbonation and silver extraction at 650 C and 700 C are presented in Figs. 3 and 4, respectively.

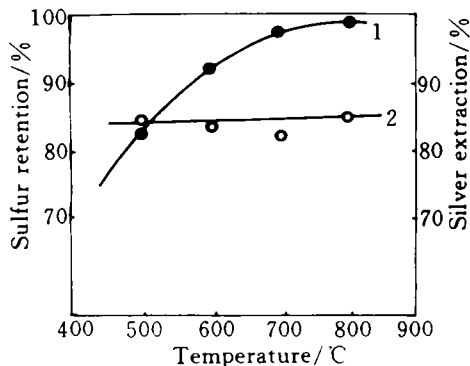


Fig. 2 Sulfur retention and silver extraction vs temperature

( $t = 1\text{h}$ ,  $\alpha = 1.06$ )

1—sulfur retention; 2—silver extraction

As the case of decarbonating, both roasting time and temperature are favourable factors, and decarbonation is proportional to roasting time. By prolonging time and elevating temperature, decarbonation can complete throughout, but too high temperature will cause partial sintering of pyrite particles to decrease gold and silver recoveries in subsequent leaching stage. Therefore, as long as the technology is rational economically and environmentally, lower temperature will be beneficial. As mentioned above, temperature has favourable effect on sulfur retention, but the retention reaches its maximum at 700 C, which can be attributed to the difference between oxidating rate of sulfides and sulfating reaction of lime. In the temperature range of 500~800 C, the lime sulfation reaction is much faster than the sulfide oxidation, so that the sulfur dioxide volatilized from the sulfide mineral

surface can be immediately captured by the lime if the charge is pelleted. At 700 C, the oxidation rate of sulfides is much faster than that at 650 C; the formation layer of anhydrite becomes thicker and thicker with time,

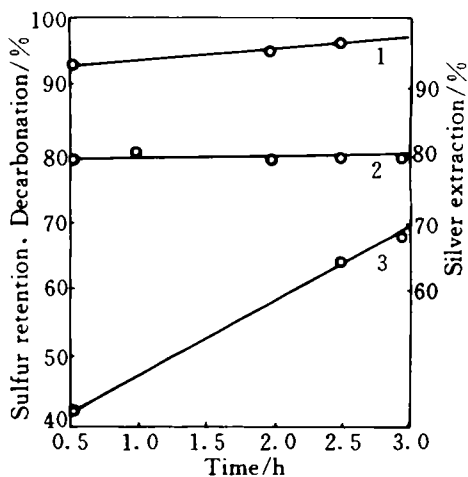


Fig. 3 Sulfur retention decarbonation and silver extraction vs time

( $T = 650\text{ C}$ ;  $\alpha = 1.1$ )

1—sulfur retention; 2—silver extraction; 3—decarbonation

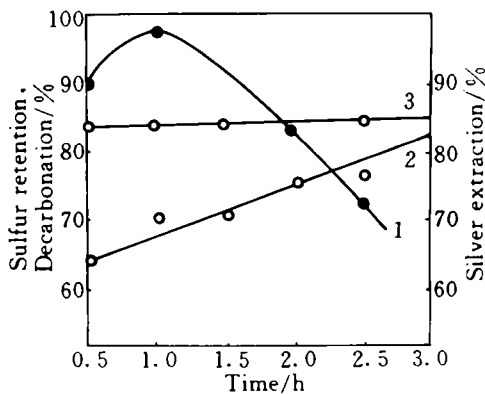


Fig. 4 Sulfur retention, decarbonation and silver extraction vs time

( $T = 700\text{ C}$ ;  $\alpha = 1.1$ )

1—sulfur retention; 2—decarbonation; 3—silver extraction

(To page 83)

**Table 1 Mechanical properties of (Ti-33Al-3Cr)-0.5Mo alloy with homogeneous and fine full-lamellar microstructure**

Temperature	$\sigma_b$ /MPa	$\sigma_s$ /MPa	$\delta$ /%	$K_{IC}$ /MPa m <sup>1/2</sup>
RT	650	494	2.4	20.0
900 °C	430	329	113	

## 5 CONCLUSIONS

(1) It is difficult to remove the coarse lamellar colonies in cast TiAl-based alloy with one-step hot working process.

(2) The thermal deformation ability of

TiAl-based alloy can be enhanced in the presence of three dimensional compressive stresses.

(3) The fine full lamellar structure obtained from MSTMT can result in very superior combined mechanical properties.

## REFERENCES

- 1 Lipsitt H A, Shechtman D, Schafrik R E. Metall Trans, 1975, 6A: 1991.
- 2 Sastry S M L, Lipsitt H A. Metall Trans, 1977, 8A: 299.
- 3 Huang S C. Metall Trans, 1992, 23A: 375.
- 4 Kim Y W. JOM, 1989, 7: 24.
- 5 Kim Y W. Acta Metall Mater, 1992, 40: 1121.

(Edited by Peng Chaoqun)

(From page 72) and bigger; thus the rate of SO<sub>2</sub> loss into the gaseous effluent increases with roasting time. When roasting time retains 1 h at 700 °C, 97% of the sulfur can be retained.

As mentioned above, the optimized roasting conditions are as follows: temperature 700 °C, time 1 h,  $\alpha$  1.1. Correspondingly, the sulfur retention and extractions of gold and silver can reach 97%, 91.3%~93% and 83%, respectively. If stoichiometry ratio ( $\alpha$ ) reduces to 0.95, the consumption of sulfuric acid in the leaching will be decreased, and gold and silver recovered is almost constant.

## 5 CONCLUSIONS

(1) The oxidation of pyrite in the presence of hydrated lime will tend to pass through an intermediated pyrrhotite stage. The behavior of silver during lime-roasting of the concentrate needs further investigation.

(2) Roasting temperature and residence time have in general favourable effects on sulfur retention and decarbonation as well as gold and silver extraction.

(3) Under the optimized conditions, the sulfur retention and leaching extractions of gold and silver in calcine can gain 97%, 93% and 83%, respectively.

## REFERENCES

- 1 Institute of Chemical Metallurgy, Chinese Academy of Science. Extractive Technology of Gold (in Chinese). Beijing: Beijing University Press, 1991: 1-9.
- 2 Thompson P, Diaz, M, Plenge C. Mining Engineering, 1993; 1195-1200.
- 3 Taylor P R, Yin Z B, Bell S L *et al.* In: Cas D R (ed). EPD Congress' 91. The Minerals, Metals and Materials Society, 1991:725-742.
- 4 Hagni, Ann M, Hagni R D, Taylor P R. JOM, 1992, 44(4): 36-38.
- 5 Taylor P R, Yin Z B, Bartlerr R W. Gold 90, SME. Littleton Co, 1990:411-419.
- 6 Yang Tianzu, Bin Wenda, Lu Yiran *et al.* Gold(in Chinese), 1994, 15(2): 31-34.
- 7 Xiao Songwen. Gold(in Chinese), 1993, 14(10): 31-35.
- 8 Jha M C, Kramar J W. In: Kudry K V *et al* (eds), Precious Metals: Mining, Extraction and Processing. TMS of AIME, Warrendale PA, 1984:337-365.
- 9 Ariagada F J Oddeo-Assare. In: Kudry K V *et al* (eds), Precious Metals: Mining, Extraction and Processing. TMS of AIME, Warrendale PA, 1984: 367-386
- 10 Swash P, Ellis P. In: Fivay C E(ed), Gold 100, Vol. 2. Extractive Metallurgy of Gold Johannesburg, SAIMM. 1986:235-257

(Edited by Li Jun)