



Cleaning of high antimony smelting slag from an oxygen-enriched bottom-blown by direct reduction

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Abstract Cleaning of high antimony smelting slag from an oxygen-enriched bottom-blown was tested by direct reduction in a laboratory-scale electric furnace. The effects of added CaO, mass ratio of coal (experimental) to coal (theoretical) (ω) and the slag type on the reduction procedure were considered. The contents of Sb and Au were investigated. Iron contamination of the metal phase was analyzed as this may impede the economical viability of this process. The initial slag, coal and CaO were mixed and homogenized before charging into the furnace, and the residual slag averagely contains $1.26 \text{ g}\cdot\text{ton}^{-1}$ Au and 1.17 wt% Sb. However, the iron contamination of antimony alloy becomes unacceptably high in this case as the metal phases contain up to 10 wt% Fe. In the slag system with mass ratio of $\text{SiO}_2\text{:FeO:CaO} = 45\text{:}27\text{:}18$, the residual slag obtained after reduction under these conditions averagely contains $<1 \text{ g}\cdot\text{ton}^{-1}$ Au and $<1 \text{ wt}\%$ Sb, and the metal phase contains $<7 \text{ wt}\%$ Fe. The recoveries of Au in the metal phase are $>98 \%$ in all experiments which is proved to be an economic and cleaning process.

Keywords High antimony slag; Direct cleaning reduction; Gold

1 Introduction

Extractive metallurgy of antimony from stibnite is mainly achieved through pyrometallurgical processes [1–3]. The

traditional commercial route involves roasting of concentrate, volatilization of antimony trioxide in a blast furnace and carbon-based reduction of antimony trioxide to metallic antimony in a reverberatory furnace. In these processes, however, antimony smelting at high temperature causes (1) serious environmental pollution during roasting and smelting, since abundant antimony sulfide, some relevant low-boiling-point metals (e.g., lead, arsenic and cadmium), and a little SO_2 are emitted through volatilization, and (2) large energy consumption, since abundant high-quality coal is consumed to sustain the pyrochemical process (1100–1400 °C). Currently, more than three tons of standard coal is required to produce one ton of antimony in China.

An oxygen-enriched bottom-blown stibnite (Fig. 1) pilot plant at the oxidation smelting stage was successfully operated for direct recovery of antimony from stibnite concentrate by Central South University, China, and was proved to have advantages such as high feasibility. Steady-state pilot operation of $10 \text{ ton}\cdot\text{day}^{-1}$ was normally observed within 100 days. The oxygen autogenous smelting was realized without the addition of any other fuels. The amount of limestone added as flux greatly decreased compared with the blast furnace, and the fluidity of slag was improved. Through detection and calculation, SO_2 (above 8 wt%) was efficiently captured as sulfuric acid. This process has significant environmental and economic benefits compared with previous processes. However, the gold is mainly liquated in the slag, which contains 30 wt% antimony concentrate. Further reduction is needed to recover antimony and gold from the slag.

The slag dumped from oxygen-enriched smelting of a bottom-blown furnace or antimony smelting of a blast furnace is a valuable source of antimony, but without treatment, it may cause enormous waste of resources and

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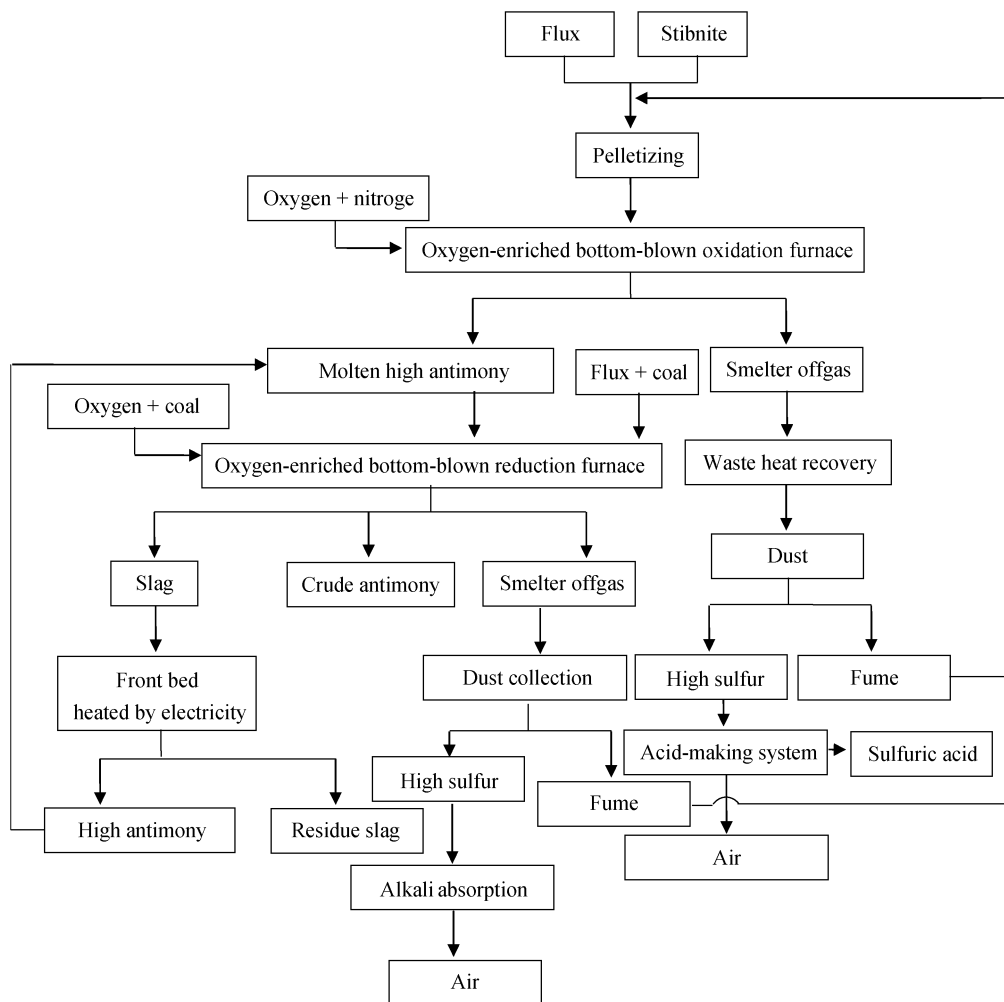


Fig. 1 Schematic flow of direct recovery of antimony from stibnite concentrate

constitute an ecological threat to the surrounding environment. Hence, slag cleaning is important from both economical and environmental perspectives.

The removal of metals from this slag can be conducted via a pyrometallurgical or hydrometallurgical route [4]. A pyrometallurgical route mainly uses reduction of metal oxides in the slag, and this process has been investigated extensively. Banda et al. [5] separately utilized CaO, CaF₂ and TiO₂ as slag modifiers during carbothermic reduction of waste smelter slag to reduce the activity of FeO under vacuum and argon, and TiO₂ effectively reduced the activity coefficient of FeO owing to the strong affinity between the two oxides. Zhai [6] used activated carbon as a reducing agent with CaO and TiO₂ as modifiers to recover cobalt from converter slag of Chambishi Copper Smelter.

Many empirical equations [7–12] were proposed to estimate the solubility of nonferrous metals in the slag as

functions of their chemical composition especially the contents of SiO₂, FeO and CaO, which will prominently affect the recovery of valuable metals from the slag. The possibility of slag cleaning via the hydrometallurgical route by roasting with sulfuric acid or ferric sulfate [13] was proposed, and the recovery rates of copper, cobalt and zinc were higher than 80 %. However, contamination by Fe appeared to be a major handicap as more than 80 % Fe was simultaneously extracted from the slag.

Pyrometallurgical treatment of the slag obtained during smelting of the antimony sulfide ores saves great energy, as the slag can be treated at its melting temperature when it was trapped from the furnace before cooling down and losing thermal energy in the air [14, 15]. In this study, the antimony smelting slag was directly reduced from oxygen-enriched bottom-blown stibnite concentrate, thus resulting in ‘cleaned’ slag by the removal of antimony and gold from the dumped slag.

2 Thermodynamic analyses

The chemical compositions of the slag used in this study are presented in Table 1. The slag, essentially a mixed oxide phase, contains antimony oxide, such as Sb_2O_3 and Sb_2O_4 . The Gibbs energy (ΔG) of antimony oxide compounds reacting with carbon at varying temperature was calculated (Fig. 2). Obviously, these reactions can occur spontaneously when temperature is maintained above 1200 °C because of their $\Delta G < 0$. Therefore, it can be concluded that antimony oxide can be reduced to Sb by carbon while these reduction reactions are endothermic reactions.

3 Experimental

Carbon-based direct reduction of the antimony smelting slag was conducted in an electric furnace. Powder solid slag (1 kg) and coal and slag modifier (CaO) at corresponding weights were premixed and loaded in a graphite crucible which was then put in the electric furnace. Carbon used in the reduction process was added in the form of metallurgical coal. The weight of metallurgical coal was calculated considering the antimony in the slag as Sb_2O_3 and 85 wt% carbon in the coal. The crucible was taken out and naturally cooled to room temperature in air after 100 min of smelting. The depleted slag and antimony alloy in the crucible were manually separated, weighed, ground

Table 1 Chemical compositions of slag from oxygen-enriched bottom-blown stibnite concentrate (wt%)

Sb	SiO ₂	FeO	CaO	Pb	As	S	Au ^a
32.00	23.00	20.00	6.00	0.30	0.63	2.00	58.00

^a Au unit being $\text{g}\cdot\text{ton}^{-1}$

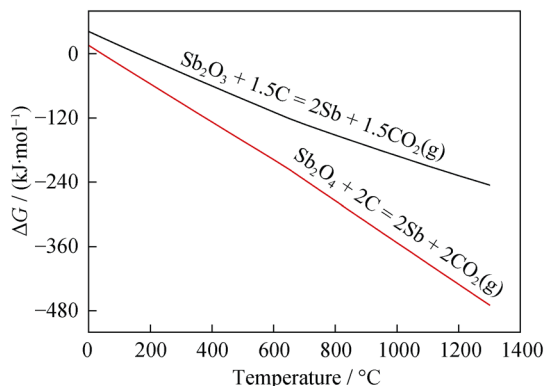


Fig. 2 Relationships between ΔG and temperature in antimony compound reactions

in a vibrating mill and sampled. The contents of antimony, iron and gold in the depleted slag and antimony alloy were detected by chemical analysis.

4 Results and discussion

4.1 CaO added to slag

The slag is FeO–CaO–SiO₂ slag system, and the contents of iron and silicon in the slag are 20 wt% FeO and 23 wt% SiO₂. To save energy and fully use the slag's thermal energy in industry at the same smelting temperature, the same slag system was chosen. With such high content of SiO₂, however, polymerization occurs readily between the silicate anions, thus producing three-dimensional structures with high viscosity that may lead to reduced fluidity and slow separation of the alloy from the slag. In addition, high corrosion of the MgO-based refractory may also result from the increased acidity of the slag. For these reasons, any possibility of increasing the SiO₂ content during the reduction process should be considered. FeO can be added for that purpose as it helps to lower the slag's surface tension and viscosity by breaking the polymerized chains. However, the FeO content in the starting slag is already at a high level and cannot be increased further during the cleaning process, and thus, iron is not reduced into the metal phase. Another option is to introduce lime into the slag. Lime is a strong base that can reduce the solubility of weak bases in the slag, therefore improving their activities by substitution. The ternary diagram suggests the mass ratio of SiO₂ to CaO for the slag fusible at 1200 °C, and the ratio was chosen as $\text{CaO}/\text{SiO}_2 = 0.4$.

The initial slag, coal and CaO were mixed and homogenized before charging into the furnace. The heating of the loaded furnace up to 1200 °C took 100 min. To reduce all Sb_2O_3 in the initial slag into antimony alloy, the corresponding coal mass was 1.4 times the theoretically calculated value. This consideration yields a ratio $\omega = \text{coal mass}/\text{coal mass by theoretical calculation}$. The same experiment was conducted six times.

The corresponding gold and antimony chemical compositions of the residual slag after reduction and the metal phases are shown in Fig. 3a and b, respectively. The slag averagely contains $1.26 \text{ g}\cdot\text{ton}^{-1}$ Au and 1.09 wt% Sb. The slag contains $0.60\text{--}3.00 \text{ g}\cdot\text{ton}^{-1}$ Au, and 0.60 and 1.90 wt% Sb. The average recovery of Au in the metal phase is 98.69 %. These results show a good advantage to recover the gold and antimony from the slag. However, the iron contamination of antimony alloy becomes unacceptably high in this case as the metal phases contain iron up to 10 wt% iron.

4.2 Effect of coal amount

To reduce iron contamination in the antimony alloy, $\omega = 1.2, 1.4$ and 1.6 were considered to elucidate the effect of coal values on metal recovery and iron contamination. Each test was conducted twice, and the chemical compositions are their average.

The corresponding chemical compositions of gold and antimony in the residual slag after reduction and in the metal phases are shown in Fig. 4a and b, respectively. Clearly, the metal phases contain less Fe than those in previous experiments, 1.23 wt% Fe in the case of $\omega = 1.2, t = 80$ min. It shows a rule of coal for the containment Fe in the metal phase that the larger amount of coal results in higher iron content in the metal phase. The slag averagely contains $0.32 \text{ g}\cdot\text{ton}^{-1}$ Au and 3.12 wt% Sb. The average recovery of Au in the metal phase is 99.66 %. However, the antimony content in the slag is high with the decreased amount of coal.

4.3 Slag type

There are two contradictions: (1) the antimony and gold contents in residual slag, as low gold residual slag corresponds to high antimony; (2) the amount of coal and the containment of iron in the metal phase, as less iron metal phases need a low amount of coal but it results in an antimony rich residual slag. The contradictions result from high FeO in the slag with mass ratio of FeO/SiO₂ of 87 %. In this experiment, SiO₂, CaO and high ω of coal were added to reduce the contents of antimony and gold in the residual slag and the iron content in the metal phase. The slag system with mass ratio of SiO₂:FeO:CaO = 45:27:18 and $\omega = 1.4, 1.6$ and 1.8 were considered.

Figure 5a and b shows that after reduction under these conditions, the residual slag averagely contains $<1 \text{ g}\cdot\text{ton}^{-1}$ Au and $<1 \text{ wt}\%$ Sb and the metal phase contains $<7 \text{ wt}\%$ Fe; specially when $\omega = 1.4$, the metal phase contains 2.88

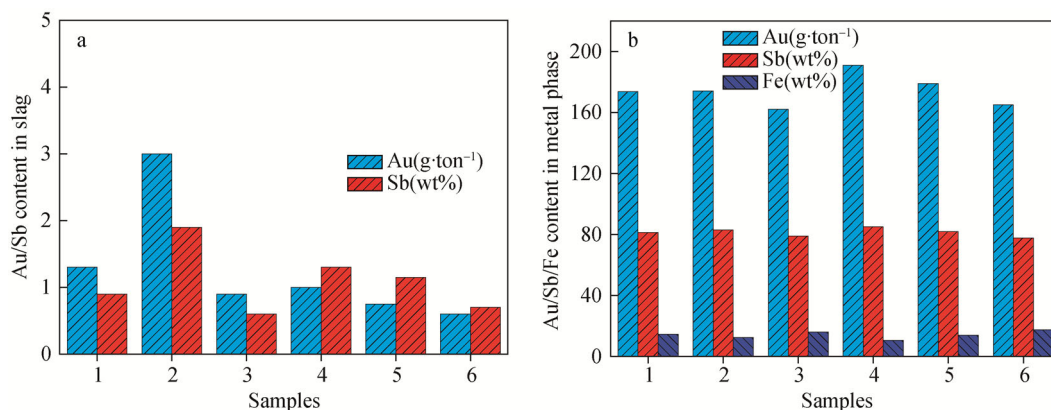


Fig. 3 Chemical compositions of a gold and antimony in residual slag and b gold, antimony and iron in metal phase after reduction

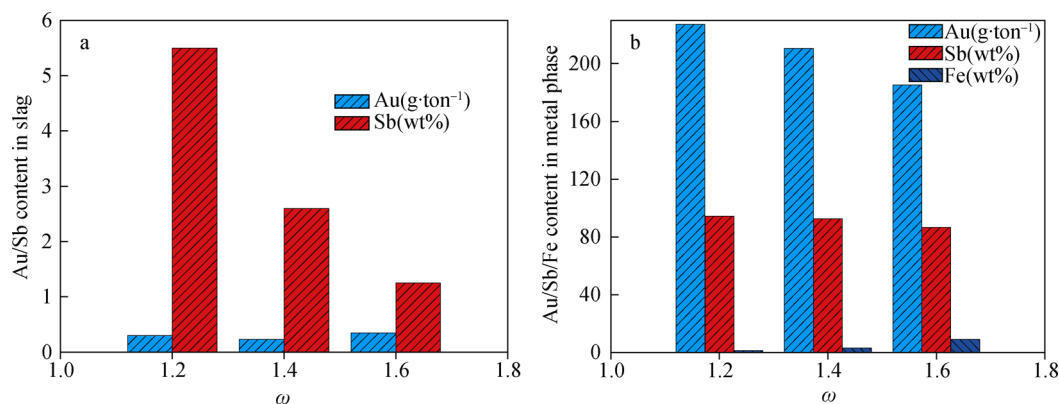


Fig. 4 Chemical compositions of a gold and antimony in residual slag, and b gold, antimony and iron in metal phase after reduction at different ratios of coal (ω) added in initial slag

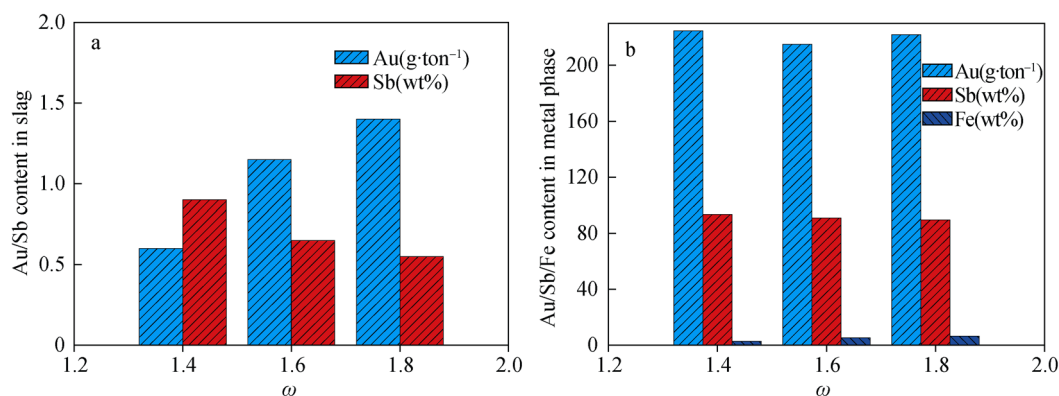


Fig. 5 Chemical compositions of **a** gold and antimony in residual slag, and **b** gold, antimony and iron in metal phase after reduction at different ω at mass ratio of $\text{SiO}_2\text{:FeO:CaO} = 45\text{:}27\text{:}18$

wt% iron. The recoveries of Au in the metal phase are more than 98 % in all experiments.

5 Conclusion

The recovery of Sb and Au through direct reduction of the slag from oxygen-enriched bottom-blown stibnite concentrate is feasible. The initial slag, coal and CaO were mixed and homogenized before charging into the furnace and the slag averagely contains $1.26 \text{ g}\cdot\text{ton}^{-1}$ Au and 1.17 wt% Sb. The average recovery of Au in the metal phase is 98.69 %. However, the iron contamination of antimony alloy becomes unacceptably high in this case as the metal phases contains up to 10 wt% iron. The iron contents in metal phases increase with mass ratio of coal (ω). The lower ratio yields a metal phase $<1.23 \text{ wt}\%$ Fe. However, a rule of coal for the containment iron in the metal phase is that a greater amount of coal results in higher iron content in the metal phase. However, the lower ratio of coal yields a high content of antimony in the residual slag. In the slag system with mass ratio of $\text{SiO}_2\text{:FeO:CaO} = 45\text{:}27\text{:}18$, the residual slag obtained after reduction under these conditions averagely contains $<1 \text{ g}\cdot\text{ton}^{-1}$ Au and $<1 \text{ wt}\%$ Sb, and the metal phase contains $<7 \text{ wt}\%$ Fe. The recoveries of Au in the metal phase are $>98 \%$ in all experiments.

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References

- [1] Lager T, Forsberg KSE. Current processing technology for antimony-bearing ores a review—part 2. *Miner Eng.* 1989; 2(4):543.
- [2] Mahlangu T, Gudyanga FP, Simbi DJ. Reductive leaching of stibnite (Sb_2S_3) flotation concentrate using metallic iron in a hydrochloric acid medium I: thermodynamics. *Hydrometallurgy.* 2006;84(3):192.
- [3] Yang J. Separation of antimony from a stibnite concentrate through a low-temperature smelting process to eliminate SO_2 emission. *Metall Mater Trans B.* 2011;42(1):30.
- [4] Shen H, Forsberg E. An overview of recovery of metals from slags. *Waste Manag.* 2003;23(10):933.
- [5] Banda W, Morgan N, Eksteen JJ. The role of slag modifiers on the selective recovery of cobalt and copper from waste smelter slag. *Miner Eng.* 2002;15(11):899.
- [6] Zhai X. Recovery of cobalt from converter slag of Chambishi copper smelter using reduction smelting process. *Trans Non-ferrous Metals Soc China.* 2011;21(9):2117.
- [7] Banda W, Morgan N, Eksteen JJ. The role of slag modifiers on the selective recovery of cobalt and copper from waste smelter slag. *Miner Eng.* 2002;15(11):899.
- [8] Kaiura GH, Watanabe K, Yazawa A. Behaviour of lead in silica-saturated, copper smelting systems. *Can Metall Q.* 1980; 19(2):191.
- [9] Mackey PJ. Physical chemistry of copper smelting slag—a review. *Can Metall Q.* 1982;21(3):221.
- [10] Heo JH, Kim B, Park JH. Effect of CaO addition on iron recovery from copper smelting slags by solid carbon. *Metall Mater Trans B.* 2013;44(6):1352.
- [11] Hu T. Reduction behavior of panzhihua titanomagnetite concentrates with coal. *Metall Mater Trans B.* 2013;44(2):252.
- [12] Padilla R, Ruiz MC, Sohn HY. Reduction of molybdenite with carbon in the presence of lime. *Metall Mater Trans B.* 1997; 28(2):265.
- [13] Altundogan HS, Tümen F. Metal recovery from copper converter slag by roasting with ferric sulphate. *Hydrometallurgy.* 1997;44(1–2):261.
- [14] Maweja K, Mukongo T, Mutombo I. Cleaning of a copper matte smelting slag from a water-jacket furnace by direct reduction of heavy metals. *J Hazard Mater.* 2009;164(2–3):856.
- [15] Li L, Chen JY, Liu YJ. Temperature stability of magnetic field for periodic permanent-magnet focusing system. *Rare Met.* 2014;33(2):180.