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Recirculation of high arsenic content copper smelting dust to smelting and converting processes

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ABSTRACT

Flue dusts generated in Chilean copper smelters are partly recycled to smelting units, such as flash smelters and Teniente Converters, and partly processed separately by hydrometallurgical methods, in order to recover copper and stabilize arsenic in the waste. Flue dust generation is increasing due to increasing copper production and arsenic content in the copper concentrates, thus creating environmental problems. Additionally, the flue dusts contain associated metals, such as zinc and lead, which can be potentially recovered. Tests on concentrate smelting and matte converting, with various additions of flue dust, allowed the determination of the distribution coefficients of arsenic, zinc and lead among the products, and, as a result of flue dust addition, oxygen enrichment and temperature. The distribution coefficients permit determination of impurities in blister copper, which affect the quality of cathodic copper produced.

1. Introduction

The removal of impurities is critical in copper metallurgy for the production of high quality copper, but it is also of great importance from an environmental aspect. Due to the constant increase in impurities in copper ore over the years, an even more critical situation can be reasonably expected in the future. It is essential to keep impurities below the levels accepted by national and international standards for the copper industry, and to decrease the total emission of harmful components. Currently, the majority of smelters around the world face this problem.

Impurity removal in copper smelting process is carried out through oxidation, followed by slagging and volatilization during smelting, conversion and refining (Yazawa and Azakami, 1969). A combination of intensive reactors, using oxygen or oxygen-enriched air as the blowing gas, has provided a number of improvements in copper smelter processes, such as that of the Teniente Converter, Inco Flash, Outokumpu Flash and Mitsubishi processes. However, the method of removing impurities has not changed, but has instead become a serious limitation in the modern process of copper smelting and converting (Utigard et al., 1997).

Copper processes generate gaseous emissions that contain SO_2, N_2, O_2, water vapor, heavy metals and other impurities. Metallurgical dust is generated as a result of the gas cleaning process; the gas contains condensate matter and fine particles from the semi-melted concentrate, which are transported with the off-gas. The mass of the dust produced in smelting and converting processes varies mainly according to the type of reactor. The dust usually contains copper (Cu), iron (Fe) and other minor elements, such as lead (Pb), arsenic (As), cadmium (Cd), antimony (Sb), zinc (Zn), bismuth (Bi) and selenium (Se), but the form of the elements depends on the conditions and the operating parameters of the smelting and converting processes. Arsenic is the main impurity of concern in the dust and during the smelting process around 15% of the total input of As from the concentrate is transferred to the matte and 22% to the slag phase, but the main part is eliminated through the gas phase, creating the copper smelter flue dust (Alguacil et al., 1996).

The flue dust generated by the Chilean copper smelters is partly recycled to the smelting units, such as the Flash smelter and the Teniente Converter, and partly processed separately by hydrometallurgical methods, in order to recover copper and stabilize the impurities (Maldini et al., 2006). The final residue is stored in a special landfill. In recent years, increase in copper production and degradation of the quality of copper ore, have resulted in higher amounts of dust from the process. In addition, environmental regulations have become stricter. Due to environmental concerns the amount of disposed dust must be reduced. Moreover, flue dust contains associated metals, such as zinc and lead, which can be potentially recovered. In this study, simulated scale tests of

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concentrate smelting and matte conversion with addition of flue dust, allowed the determination of the distribution coefficients of As, Zn, Sb and Pb among the products, as a result of dust recycling, matte grade, temperature variation and oxygen enrichment. The outcome also permits evaluation of the effect of dust addition on the quality of the matte and blister copper.

2. Experimental methods

Industrial matte, slag, copper concentrates and flue dust from a Chilean smelter were used as the test materials. Table 1 shows the chemical composition of the samples. X-ray diffraction analysis (XRD) of the dust samples showed that the main components are $CuSO_4$, Cu_2O, As_2O_3, ZnO and $PbSO_4$ (see Fig. 1).

Simulated tests of dust addition were conducted in an electric furnace, as shown in Fig. 2. The furnace was heated to a fixed temperature (1523–1573 K) under a continuous flow of nitrogen 200 $cm^3\ min^{-1}$. A Pt/Pt–Rh thermocouple in an alumina sheath was introduced into the furnace to monitor the temperature.

Two types of experiments were conducted, in order to simulate the smelting and converting processes, respectively. In the smelting test, 13 g of slag, 10 g of matte and 20 g of charge (concentrate, dust and silica mixed in different ratios) were initially charged in an alumina crucible (12 mm ID, 100 mm H) and placed in an alumina reaction tube, closed by a water-cooled brass flange. After the melting and temperature stabilization, an alumina tube was introduced to start the gas blowing. The ratio of matte/slag used in the test was the same as in the industrial Teniente Converter. The silica addition was adjusted, so that the ratio Fe/SiO_2 in the slag was constant at about 2.

For the converting experiments, a synthetic fayalite was used in order to assess the influence of the slag on the impurities with dust addition (slag forming stage). A total mass of 37 g of different materials was initially charged with copper and slag to reproduce the 3-phase system. To prevent the volatilization of dust during the injection, a copper tube (6 mm OD and 5.4 mm ID) was filled with 2 g of dust, which was continuously charged through an alumina tube. The number of charged tubes varied with the dust addition ratio. The temperature of the furnace was maintained at 1473 K. To control the oxygen partial pressure, a mixture of N_2–CO_2 was injected to the furnace to control the partial pressure between 10^{-3} and 10^{-5} atm. To determine the influence of converting process time, an initial test was conducted using 5% addition of dust, with a continuous gas blowing of 0.1 l/min of CO_2 for 1, 2, 4 and 8 h. The results showed that the concentration of impurities decreased remarkably in the first 2 h of the process, but after the 4th hour the concentration remained constant. From these results, the blowing time for the experimental test was fixed at 4 h.

When the gas injection for both processes was finished, the sample was kept at the same temperature for 30 min to promote settling and phase separation. The crucible was then taken out of the furnace and quenched immediately by jetting helium gas. The off-gas from the reaction tube was continuously passed through a water-cooled condenser, which collected the volatile matter, and then was directed to solutions of 1 M H_2SO_4 and 1 M NaOH to remove harmful components and to neutralize the SO_2. The condensed volatile matter, the slag and the matte phases were analyzed for their elemental content, by inductively coupled plasma atomic emission spectrometry (ICP-AES).

Table 1
Chemical composition of samples.

Element	Cu	Fe	S	Zn	Pb	Bi	As	Sb
Concentrate	36.1	22.9	32.6	0.7	0.2	0.05	0.7	0.01
Matte	76.4	1.4	19.8	0.6	0.08	ND	0.4	0.01
Slag	8.03	38.4	1.9	7.9	0.1	0.1	0.4	0.06
Dust	10.4	0.8	10.4	15.6	7.8	3.5	19.4	0.1

(Unit: mass%)

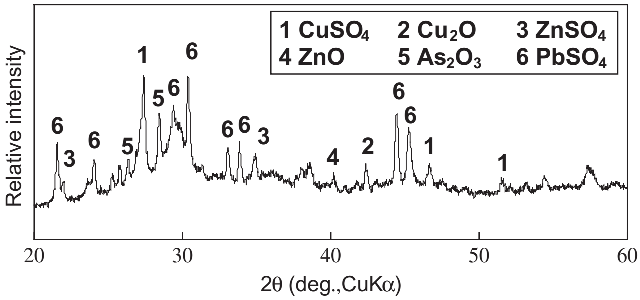

Fig. 1. XRD results of Chilean smelter copper dust.

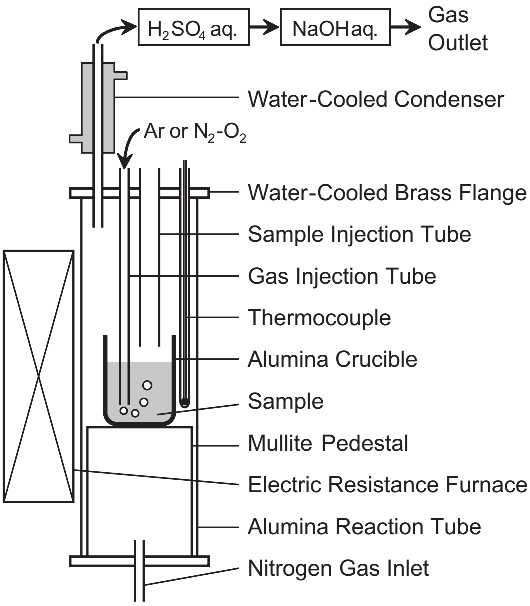

Fig. 2. Experimental apparatus.

3. Results

3.1. Smelting process

3.1.1. Distribution of minor elements

The dust addition ratio represents the amount of dust charged to the process, which is defined by the following equation:

$$\text{Addition ratio } (\%) \equiv \frac{\text{Addition of dust}}{\text{Charge (concentrate} + \text{dust} + \text{silica)}} \times 100 \qquad (1)$$

The distributions of As, Pb and Zn were evaluated by alternating the amount of dust added to the smelting process, which used 21 vol.% of oxygen in the blowing gas at 1523 K. Previous research (Yazawa and Azakami, 1969; Itagaki, 1986; Montenegro et al., 2008) showed that distributions of Sb and Bi were almost independent of the dust addition ratio, and for these reasons the impurities of concern are As, Pb and Zn in the present study.

The results are shown in Fig. 3. The terms $\langle\%X\rangle$, $(\%X)$ and $\{\%X\}$ represent the fractional distribution of the element X in the gas,