Original Research Article

Hydrometallurgical recovery of lead from direct-to-blister copper flash smelting slag

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ARTICLE INFO

ABSTRACT

Furnace slag from direct-to-blister smelting of copper concentrates contains 12–15% of copper and 2.5–4% of lead. In this form it cannot be deemed as waste material, and thus it is subjected to a high-temperature process of slag decopperization; after this, converting process is performed on the Cu–Pb–Fe alloy being the product of decopperization process in electric furnace. An interesting alternative to the presently used processing of flash smelting slag would be its hydrometallurgical processing and selective recovery of Pb and Cu. This paper presents the results of laboratory tests on flash smelting slag leaching with acetic acid solutions and acetic acid with urea additive. The experiments performed allowed to optimize the process parameters to such an extent that Pb content in the post-leaching sediment is practically equal to the value obtained through the high-temperature process performed in electric furnace.

1. Introduction

Feed materials for direct-to-blister smelting furnace mainly contain chalcocite (Cu_2S) and bornite (Cu_5FeS_4) [1]. The quality of copper produced in flash smelting furnace is defined by its lead content, which should be below 0.3% for the product to conform to blister copper quality requirements. The obtaining of the required lead content in copper necessitates significant oxidation of the concentrate components in the reaction shaft of flash furnace, and to transfer the lead into slag. This procedure introduces significant amounts of copper (12–15%) into slag, which the copper mainly occurs in the form of copper oxide [2,3]. The level of oxidation of flash smelting process products, defined by Cu_2O content in slag and oxygen content in copper, is mainly dependent on lead content in the concentrate. The content of the main components of flash smelting slag may fluctuate within the following ranges [4]: 10–15% Cu, 2.5–4% Pb, 4–6% Fe, 32–36% SiO_2, 12–17% CaO, 8–11% MgO, 9–12% Al_2O_3, 2.5–4% K_2O.

Due to high content of copper in slag, the decopperization process is performed. Decopperization consists in reducing copper oxide and other metals, mainly lead and iron, in liquid

state in electric furnace in the presence of coke and basic technological additive being calcium carbonate [5–8].

The following is obtained as a result of the decopperization process of flash smelting slag in electric furnace:

- Cu–Pb–Fe alloy (69–80% Cu), which is subjected to converting process,
- waste slag (0.5–0.6% Cu, ~1.2% Pb), which – in granular form – is mostly utilized for constructing embankments of tailings reservoir, or for producing abrasive,
- dust, containing on average 35% Pb and 20% Zn, being a raw material used for producing these metals,
- gases, which, after CO oxidation in after combustion chamber and dedusting in jet filter, are directed to the chimney.

In this paper it was decided to firstly analyze the properties of flash smelting slag in terms of the possibility of its processing in a manner alternative to high-temperature electric furnace processing, and then to perform laboratory-scale evaluation of the possibility of hydrometallurgical extracting of lead from slag.

2. Experimental procedure

2.1. Physical and chemical properties of flash smelting slag

Prior to all slag testing, an averaging procedure to large mass of slag was performed to produce samples characterized by the same composition in each volume element. Slag composition analysis was performed using atomic absorption spectrometry. The results are presented in Table 1, after converting to oxides.

The slag was examined in fragmented form. Therefore, it was subjected to size composition test. The measurement of particle-size distribution of flash smelting slag was performed using sieve analysis. After screening, the share of individual fractions of slag was determined, and then they were analyzed for copper and lead content. The results of the above mentioned tests are presented in Table 2.

For individual size grades, the sieve analysis, along with Cu and Pb content analysis indicate clearly the existence of fractions (1.00 ÷ 0.63 mm) with significantly increased Cu and decreased Pb content compared to overall slag mass. The content of these elements is 46.2% and 1.95%, respectively. The

Table 1 – Composition of flash smelting slag examined.

Compound	Content [%]
Na_2O	0.75
K_2O	2.39
SiO_2	33.94
CaO	15.60
MgO	4.94
Al_2O_3	10.00
Fe_2O_2	6.81
ZnO	1.40
FeO	5.23
CuO	15.58
PbO	3.28

Table 2 – Results of sieve analysis and Cu and Pb content in individual fractions.

Grain size [mm]	Mass share of fraction [%]	Cu content [%]	Pb content [%]
1.00 ÷ 0.63	1.56	46.2	1.95
0.63 ÷ 0.32	22.61	15.2	3.02
0.32 ÷ 0.16	51.89	12.1	2.96
0.16 ÷ 0.10	13.71	10.2	2.96
0.10 ÷ 0.071	9.41	10.7	3.49
0.071 ÷ 0.056	0.38	11.5	3.50
0.056 ÷ 0	0.45	15.6	3.40

content of analyzed elements in the other size grades is similar (Cu: 10.2–15.6%, Pb: 2.96–3.5%).

Another test that was performed on a sample of flash smelting slag was determining phase composition of flash smelting slag, which was carried out using X-ray diffraction method. The results of phase analysis are presented in Fig. 1 in the form of X-ray pattern.

The XRD analysis indicates that copper occurs in the slag in the form of Cu_2O and $CuFeO_2$ compounds, and lead occurs as PbO.

2.2. Test methodology applied

This paper presents research concerning the procedure of leaching lead and copper from slag obtained from one-stage flash smelting process. The research was performed in two variants. First, experiments were made with the purpose to leach lead from slag using acetic acid. In the second variant, acetic acid solutions with urea additive were used as the lead leaching agent. The parameters analyzed in this paper and having an important impact on the leaching process included: time, temperature, acetic acid concentration, mass ratio of solid phase to liquid phase, and urea concentration. Based on the examinations performed, conditions were determined in which the level of release of lead into the solution is the highest.

Leaching solutions of specific concentration were prepared using distilled water and appropriate reagents. Then, appropriate volumes of the solution were measured and poured into a beaker in which the slag leaching was performed. The beaker was placed in a measuring system, and the solution was heated to predetermined temperature using a hob. An analytical sample of slag of specified mass was weighed on analytical balance. After reaching the intended temperature by the solution, a slag sample was added, mechanical stirrer was started, and the process was performed for specific time. Each experiment was performed at fixed mixing speed, enabling the lifting of slag. After completing the leaching process, the slurry was filtered, and the sediment obtained was washed with distilled water, dried and weighed.

Post-leaching slag was subjected to chemical analysis using atomic absorption spectrometry (AAS) in order to evaluate lead and copper content. The change in sample mass and the known Pb content in the sample before and after leaching allowed for determining the efficiency of lead leaching process according to the following formula:

$$\eta = \left(1 - \frac{c_{Pb} \cdot m}{c_{Pb_0} \cdot m_0}\right) \times 100\% \tag{1}$$