Experimental Study of the Sulphatizing Roasting of Flotation Tailings from Copper Slag Processing Using Iron Sulfates

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Abstract. The present study focuses on the experimental investigation of sulphatizing roasting of flotation tailings from copper slag processing using iron (II) and (III) sulfates followed by water leaching. The effect of temperature, duration of sulphatizing roasting, as well as the amount of iron sulfates on the conversion of zinc, copper, iron and other components in the tailings into water-soluble sulfate compounds were studied. The experiments have shown that there is no significant difference between using of both iron sulfates. The extraction degree after more than 20 min of the roasting varied in the approximate ranges of 50-70\% for Zn, 45-70\% for Cu and 0.01-10\% for Fe. The best results were the extraction of 69.2\% Cu, 62.8\% Zn and 1.2\% Fe obtained by 180 min of the roasting at 625\°C with addition of 150\% FeSO\textsubscript{4} \cdot 7H\textsubscript{2}O to 100\% of the tailings. Based on the mineralogic and microstructure investigations of the samples, the assumptions were made for the reasons of the deficient extraction degrees of copper and zinc, as well as high sulphatizing agent consumption.

1. Introduction

Due to the depletion and grade decreasing of copper and zinc natural raw materials [1], nowadays the increasing attention devotes to wastes with a high content of non-ferrous metals. Among them, copper tailings deserve consideration because they often contain a significant percentage of copper, zinc and iron, as well as generate in large quantities [2]. In addition, copper tailings form dumps, which is harmful for the environment [3]. To reduce the adverse environmental impact, copper tailings should be recycled.

Currently, processing of copper smelting slag accumulated in dumps is widespread [4]. Froth flotation method is often used and efficient to extract copper sulfides from the slag [5]. However, significant content of zinc and copper remains in the residue after the processing. The recycling of such wastes is complicated due to low solubility of zinc and copper phases, namely ferrites and silicates, because the tailings contain a considerable percentage of iron and silicon, respectively.

Various copper tailings have different applications in the construction industry [6], but due to the high content of non-ferrous metals, especially in the residues after flotation of copper slag, extraction of zinc and copper can also be beneficial. It is reported about the methods of zinc and copper extraction by leaching in inorganic reagents [7,8], bioleaching [9,10] and their combination [11–14],
as well as by pyrometallurgical ways [15,16]. Recently, the promising method using sulphatizing roasting for processing of various materials [17–19] is used. In this method, zinc, copper and some other compounds convert into water-soluble sulfate phases, which then can pass into solution without significant iron dissolution by water leaching.

This paper studies the effect of temperature, roasting time and amount of sulphatizing agent, namely iron sulfates FeSO₄ and Fe₂(SO₄)₃, on the behavior of zinc, copper, iron and other components in the tailings obtained by froth flotation of copper slag.

2. Materials and methods

In the experiments the flotation tailings from copper slag processing from OAO SUMZ (56°51'41.7"N, 59°53'31.3"E, Revda, Sverdlovsk region, Russia) were used. The tailings and the chemically pure reagents of FeSO₄·7H₂O and Fe₂(SO₄)₃·9H₂O were grinded and sieved up to the fraction of 0.2 mm in an agate mortar. The chemical composition of the tailings was analyzed by Axios Advanced X-ray fluorescence spectrometer (Netherlands); table 1 shows the composition.

| Element | Fe   | Cu  | Zn  | S   | Si  | Ca  | Mg  | Al  | Pb  | Ba  | K   | Mn  | Cd  | As  | C   |
|---------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Composition, % | 30.3 | 0.41 | 3.11 | 1.2 | 12.36 | 2.35 | 0.38 | 1.98 | 0.26 | 0.22 | 0.72 | 0.06 | 0.02 | 0.1 | 0.08 |

Mineralogical composition was determined using X-ray diffractometer DRON-3M (Russia). The microstructure was investigated by scanning electron microscopy (SEM) using Carl Zeiss EVO LS 10 (Germany) device.

The experiments were performed as follows. Mixtures of the tailings and an agent in the selected ratios were prepared and pressed into tablets of 1 g in mass using a manual hydraulic press. The mixtures were added to the mold of 17 mm in diameter and compacted by 40 MPa pressure. Then, 3 g of the samples in a corundum crucible were placed in a muffle furnace heated to a certain temperature in the range of 600-625°C. The samples were held for 5-240 min, then pulled out and after cooling down were crushed up to the fraction of 0.054 mm.

Leaching of the roasted samples was carried out by distilled water using magnetic stirrer at 70°C, 160/1 of W/S ratio, and 30 min of duration. The content of zinc, copper, iron, cadmium and arsenic in the obtained solutions after filtration was analyzed by inductively coupled plasma mass spectrometer Elan 6100 DRC (USA).

3. Results and discussion

Figure 1 demonstrates the influence of roasting duration on the extraction of zinc, copper, iron, cadmium and arsenic at the roasting with addition of 81.5% Fe₂(SO₄)₃·9H₂O at 600 and 625°C. Such amount of the sulphatizing agent and temperature was selected based on the thermodynamic calculation by HSC Chemistry 9.9 software [20] that was given in our previous paper [21]. The experiments have shown that roasting over 20 min led to the extraction of 50-70% Zn, 45-70% Cu and less than 10% Fe, while the extraction degree of Cd and As was less than 5% and 1%, respectively. The increasing of temperature up to 625°C has influenced insignificantly the extraction degrees.
Figure 1. Effect of roasting duration on extraction degree of Zn, Cu, Fe, Cd, As by water leaching after the treatment at 600°C (a) and 625°C (b) with addition of 81.5% Fe$_2$(SO$_4$)$_3$·9H$_2$O to 100% of the tailings.

Figure 2 compares the dependences of the extraction degree of the elements on the amount of two different iron sulfates at 600°C after 180 min of the roasting.

Figure 2. Effect of addition of Fe$_2$(SO$_4$)$_3$·9H$_2$O (a) и FeSO$_4$·7H$_2$O (b) to 100% of the tailings on extraction degree of Zn, Cu, Fe, Cd, As by water leaching after 180 min of the roasting at 600°C.

Therefore, the addition of more than 54% Fe$_2$(SO$_4$)$_3$·9H$_2$O or more than 100% FeSO$_4$·7H$_2$O led to the extraction of both zinc and copper in the range of 45-70%. There is no significant difference between using of both iron sulfates.

Figure 3 shows the XRD patterns of the tailings and the roasted tailings with excess of FeSO$_4$·7H$_2$O 180 min of the treatment.
Figure 3. XRD patterns of the copper tailings (a) and the roasted copper tailings (b) at 625°C after 180 min of the roasting with addition of 150% FeSO$_4$·7H$_2$O to 100% of the tailings.

It was found that the main phases of the tailings are fayalite Fe$_2$SiO$_4$, diopside CaMgSi$_2$O$_6$, frankline ZnFe$_2$O$_4$, sphalerite Zn$_{1-x}$Fe$_x$S, gibbsite Al(OH)$_3$. There is also an amorphous ring in the XRD pattern that indicates the presence of an amorphous phase. During the roasting of the tailings zinc and copper partly transformed into zinc sulfate. Zinc and copper sulphating reactions were analyzed in detail in [21]. Furthermore, it is interesting to note that aluminum, calcium and magnesium also converted to a large degree into the sulfate form as Al$_2$(SO$_4$)$_3$ and Mg$_3$Ca$_2$(SO$_4$)$_5$. 
Fayalite, which is the main phase of the tailings, decomposes into hematite probably as follows:

\[
\text{Fe}_2\text{SiO}_4 + \text{SO}_3(g) \rightarrow \text{Fe}_2\text{O}_3 + \text{SiO}_2 + \text{SO}_2(g)
\]  

(1)

Figure 4 demonstrates the temperature dependence of Gibbs free energy change of the reaction (1).

The thermodynamic data has shown that fayalite oxidation by sulfur trioxide is possible and it can occur before zinc and copper ferrites sulphatizing due to more negative values of Gibbs free energy. Consequently, although the reaction (1) is exothermic, it contributes to a considerable consumption of sulphatizing agent for the treatment of the tailings compared with other materials with high zinc and copper content [19].

Thus, the cumulative evidence suggests that the method of the sulphatizing roasting followed by water leaching has low efficiency to extract zinc and copper from the copper tailings due to high consumption of the agent and insignificant extraction degrees. In order to interpret these results unambiguously, study of the tailings was carried out by SEM. Figure 5 shows the microstructure of the tailings; table 2 presents the composition of some phases of the tailings.

Figure 5. Microstructure of the copper tailings.
5. Conclusion

The microstructure study indicated that the sample consists of fayalite slag particles, other silicates crystallized from the melt during the slag cooling down, as well as ferritic grains and sulfide inclusions. As can be seen, small zinc ferrite particles impregnate inside the slag particle that can hinder interaction between them and sulfur trioxide during sulphotizing roasting. Accordingly, to obtain higher extraction degree of zinc and copper, fine grinding can be advantageous.

4. References

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