

*Received April 16, 2014; reviewed; accepted May 29, 2014*

## RECOVERY OF COPPER FROM COPPER SLAG AND COPPER SLAG FLOTATION TAILINGS BY OXIDATIVE LEACHING

Daniela M. UROSEVIC<sup>\*</sup>, Mile D. DIMITRIJEVIC<sup>\*\*</sup>, Zoran D. JANKOVIC<sup>\*\*\*</sup>,  
Dejan V. ANTIC<sup>\*\*</sup>

<sup>\*</sup> Mining and Metallurgical Institute, Zelene Bulevar 35, 19210 Bor, Serbia

<sup>\*\*</sup> University of Belgrade, Technical Faculty at Bor, P.O. Box 50, 19210 Bor, Serbia: mdimitrijevic@tf.bor.ac.rs

<sup>\*\*\*</sup> University of Toronto, CFIE, 33 St. George Street, Toronto, Ontario, Canada M5S 2E3

**Abstract:** Copper smelter slag and copper smelter slag flotation tailings were leached using sulphuric acid solutions, without or with the addition of either ferric sulphate or hydrogen peroxide. Copper extraction from the slag was typically found to be twice as high as that from the slag flotation tailings. Hydrogen peroxide was determined to be the best lixiviant. Thus, copper and iron extractions were 63.4% and 48.6%, respectively, when leaching the slag with 3 M H<sub>2</sub>O<sub>2</sub>, after 120 minutes of reaction at room temperature. Copper dissolution was generally found to be the dominant process within the first 60 minutes of reaction, whereas iron dissolution dominated afterwards.

**Keywords:** copper slag, copper slag flotation tailings, leaching, sulphuric acid, ferric sulphate, hydrogen peroxide

### Introduction

The pyrometallurgical processing of copper concentrates generates large amounts of copper-containing slag. Management options for this slag include recycling, recovery of metal values, production of value added products and disposal (Gorai and Jana, 2003). However, there are no universal methods to recover copper from copper-bearing slags as the chemical and phase composition of a slag depend on factors such as the type of ore mined and the type of pyrometallurgical process utilized (Shen and Forssberg, 2003).

The reverberatory furnace slag that has been dumped in the vicinity of the Bor Copper Smelter, Serbia, is currently processed by flotation using an existing production line at the nearby Bor Copper Concentrator. However, the copper recovery

obtained has been rather low (about 40%). Previous research indicated that such a low recovery was due to the presence of copper oxides in the slag, as well as to the fact that copper sulphides were predominantly found in particle size fractions below 38  $\mu\text{m}$ . Accordingly, the objective of the present work was to investigate whether implementation of the hydrometallurgical processing of the slag or the slag flotation tailings could result in an increase in copper recovery.

A number of studies have been conducted on the hydrometallurgical recovery of base metals from various copper-containing slags. Thus, the lixivants investigated include sulphuric acid (Banza et al., 2002), ferric chloride (Anand et al., 1980), chlorine (Herreros et al., 1998), aqueous sulphur dioxide (Gbor et al., 2000), hydrogen peroxide (Banza et al., 2002), mixed nitric-sulphuric acid (Xie et al., 2005), potassium dichromate (Altundogan et al., 2004) and sodium chlorate (Yang et al., 2010). In addition, research has been done into pressure leaching (Anand et al., 1983, Papangelakis and Perederiy, 2009), bioleaching (Carranza et al., 2009, Kaksonen et al., 2011) and the effect of ultrasound on acid leaching (Bese, 2007). In the present paper, the results obtained for the leaching experiments with the copper smelter slag and the slag flotation tailings in sulphuric acid solutions, in the absence as well as in the presence of either ferric sulphate or hydrogen peroxide, will be presented.

## Materials and experimental methods

The experiments were performed using either reverberatory furnace slag or reverberatory furnace slag flotation tailings from the Bor Copper Concentrator. The slag was sampled from the crushing line before entering the milling section of the concentrator, whereas the slag flotation tailings were sampled from the tailings disposal line. The slag sample was ground to pass through a 75  $\mu\text{m}$  sieve. The tailings sample was used as received because its particle size was finer than 75  $\mu\text{m}$ . Quantitative determination of elements in the samples was performed by gravimetric and volumetric analysis and atomic absorption spectrophotometry (FAAS/GFAAS). The chemical compositions of the two samples are given in Table 1.

The samples of the copper slag and leach residue were characterized by using X-ray diffraction (XRD). Figure 1 shows XRD data for the slag sample. The XRD peaks indicate the presence of magnetite, olivines (among which fayalite was found to be the most abundant), pyroxene and granate.

The leaching experiments were conducted in a 250  $\text{cm}^3$  glass reactor at atmospheric pressure. Five grams of the sample was leached with 150  $\text{cm}^3$  of the lixiviant. Most of the experiments performed at room temperature at a stirring speed of 350  $\text{min}^{-1}$  by using a magnetic stirrer. The experiments performed at set temperatures were conducted in a three-necked glass reactor fitted with a glass stirrer, condenser and thermometer, which was immersed in a thermostated water bath. The reaction

Table 1. Chemical compositions of the copper smelter slag and the slag flotation tailings

Constituent	Content (wt.%)	
	Copper Slag	Slag Flotation Tailings
Cu – total	0.97	0.59
Cu – oxides	0.15	0.06
Cu – sulphides	0.82	0.53
SiO <sub>2</sub>	33.75	34.62
Al <sub>2</sub> O <sub>3</sub>	3.78	3.93
Fe <sub>2</sub> O <sub>3</sub>	8.05	1.10
FeO	33.80	34.44
Fe <sub>3</sub> O <sub>4</sub>	9.39	10.60
Fe – total	39.09	35.19
CaO	6.00	4.79

time was either 120 minutes or 180 minutes. Sampling was performed at regular time intervals by taking 1 cm<sup>3</sup> of the leach liquor with a pipette. The leach liquor sample was filtered and the filtrate was transferred to a 50 cm<sup>3</sup> volumetric flask. The flask was filled with distilled water to the mark. The diluted solution was analyzed by atomic absorption spectrophotometry. All the experiments were performed in duplicate and some were repeated several times to establish the reproducibility of the results.

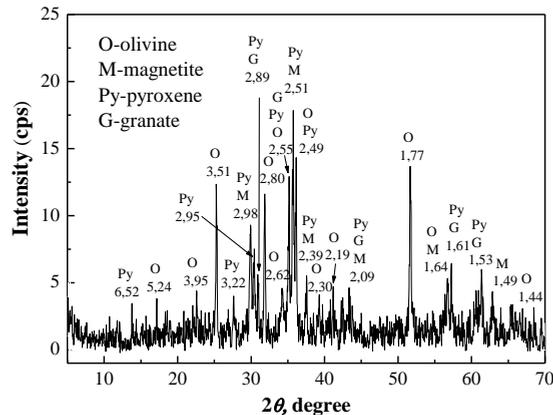


Fig. 1. XRD pattern for the copper slag sample

## Results and discussion

### Leaching with sulphuric acid

The effect of sulphuric acid concentration on metal dissolution from the slag and the slag flotation tailings was investigated at initial sulphuric acid concentrations ranging from 0.5 M to 3.0 M. The results are illustrated in Figure 2 and 3.

A common feature of the slag and the slag flotation tailings is higher iron dissolution compared to that of copper. Further, as seen in Figure 2 and 3, higher copper dissolution is accompanied with higher iron dissolution. That is, higher copper and iron extractions were observed with the slag rather than slag flotation tailings. Thus, the maximum copper and iron extractions achieved with the slag were 26.0% and 62.5%, respectively, as opposed to the slag flotation tailings where the maximum copper and iron extractions were 13.5% and 48.0%, respectively. Carranza et al. (2009) found that most of the copper-bearing species in slag flotation tailings were occluded in the slag phase and thus unable to interact with the collector. Therefore, the slag flotation tailings are inferior in terms of leaching when compared to the slag because most of the liberated copper phases have been removed by flotation.

Based on the chemical compositions of the slag and the slag flotation tailings (Table 1), it can be concluded that the copper dissolved from the slag flotation tailings mainly originates from the copper oxide phases (about 10 wt.%), which are not amenable to flotation. Low copper extractions both from the slag and the slag flotation tailings indicate that sulphuric acid is not a suitable reagent for leaching these materials, at room temperature. This conclusion is in line with the study by Banza et al. (2002) where the leaching of copper smelter slag with sulphuric acid (500 kg/Mg slag) resulted in copper and iron extractions of 20% and 52%, respectively, at 20°C, whereas the maximum copper and iron extractions were 60% and 90%, respectively, at 90°C. Also, based on the results depicted in Figure 2 and 3, it can be concluded that the iron minerals are dissolved more easily in sulphuric acid than the copper minerals, both from the slag and the slag flotation tailings, which is in accord with Banza et al. (2002).

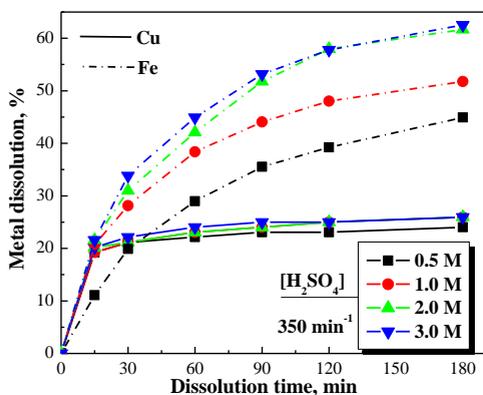


Fig. 2. Copper and iron extractions from the slag as a function of time at different initial sulphuric acid concentrations

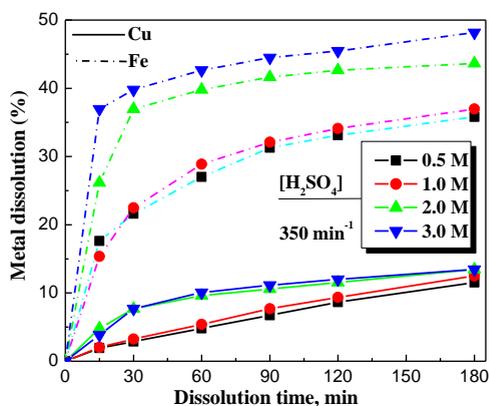


Fig. 3. Copper and iron extractions from the slag flotation tailings as a function of time at different initial sulphuric acid concentrations

## Leaching with ferric sulphate

The slag and the slag flotation tailings were leached with ferric sulphate in 1 M sulphuric acid. The ferric iron concentration was varied in the range from 5 g/dm<sup>3</sup> to 40 g/dm<sup>3</sup> and from 5 g/dm<sup>3</sup> to 20 g/dm<sup>3</sup> for the slag and the slag flotation tailings, respectively. The results are shown in Figure 4. It can be seen that copper extractions from the slag were low and similar for all the ferric iron concentrations studied, that is, between 26% and 29% after 180 minutes of reaction. Most of the copper was dissolved in the first 30 minutes of reaction. In addition, copper extractions from the slag flotation tailings were slightly lower than those from the slag (between 22% and 24%). Finally, the dissolution curves obtained with both materials have a similar shape.

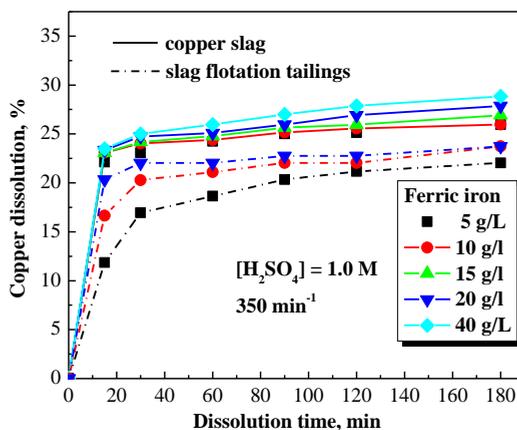


Fig. 4. Copper extractions from the copper smelter slag and the copper smelter slag flotation tailings as a function of time at different initial ferric iron concentrations

By comparing Figure 2 and 4, it can be seen that both the copper extractions and the copper dissolution curves were similar in sulphuric acid alone and in the presence of ferric iron. This observation suggests that these two lixivants have a similar, low potential for leaching copper from the slag and the slag flotation tailings at room temperature.

## Leaching with hydrogen peroxide

### Effect of hydrogen peroxide concentration

As copper extractions in the leaching experiments performed with sulphuric acid and ferric sulphate were low, a series of leaching experiments was conducted with hydrogen peroxide which is a strong oxidant. To this end, the slag and the slag flotation tailings were leached in 1 M sulphuric acid with the addition of different initial concentrations of hydrogen peroxide (0.5–3 M). The results are shown in Figures 5 and 6.

As seen in Figure 5, copper dissolution from the slag increases with increasing hydrogen peroxide concentration. The final copper extractions attained were 57.7% and 63.4% at initial hydrogen peroxide concentrations of 2 M and 3 M, respectively. These extractions are twice as high as those obtained in the leaching experiments with sulphuric acid and ferric iron. Copper extractions from the slag flotation tailings leached with hydrogen peroxide (Fig. 6) were approximately half as high as those achieved when the slag was leached with hydrogen peroxide. Thus, a copper extraction of 32.7% was obtained for the highest hydrogen peroxide concentration. However, this value is still about twice as large as those reported when the slag was leached with sulphuric acid and ferric iron.

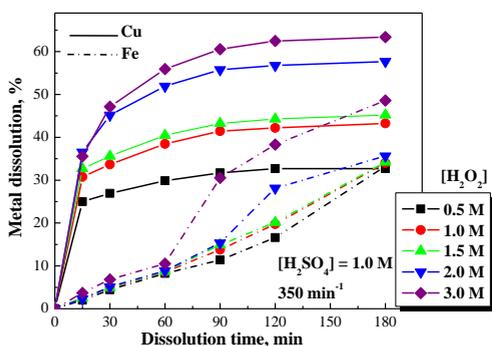


Fig. 5. Copper and iron extractions from the slag as a function of time at different initial hydrogen peroxide concentrations

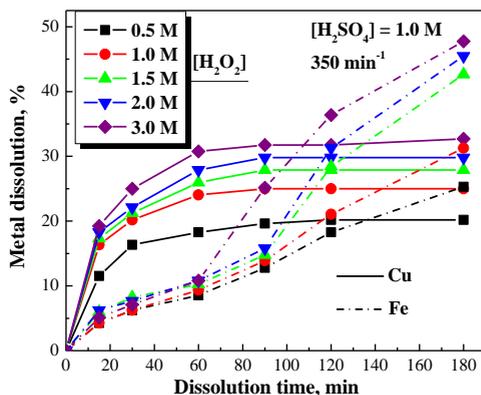
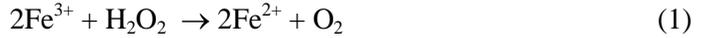


Fig. 6. Copper and iron extractions from the slag flotation tailings as a function of time at different initial hydrogen peroxide concentrations

With regard to iron dissolution, it is significantly lower than that of copper for both the slag and the slag flotation tailings in the first 60-90 minutes of leaching. Following that, iron dissolution increases, in particular in the case of the slag flotation tailings, but also in the case of the slag at the highest hydrogen peroxide concentration. Thus, after 60 minutes of reaction, iron extractions from the slag and the slag flotation tailings are 10.5% and 10.8%, respectively, whereas the corresponding values are 48.6% and 47.8%, respectively, after 180 minutes of leaching (at 3 M  $H_2O_2$ ). A possible explanation for this phenomenon could be that hydrogen peroxide has a greater affinity towards copper than towards iron, that is, the copper may be present as a phase that is more amenable to oxidation with hydrogen peroxide than the form in which the iron exists. Once most of the available copper from the slag (or from the slag flotation tailings) has been dissolved (i.e., after about 60 min), hydrogen peroxide is consumed primarily for iron oxidation. The more iron there is in solution, the faster the dissolution. This acceleration is due to the catalytic decomposition of hydrogen peroxide to oxygen and water through a redox process caused by the  $Fe^{3+}/Fe^{2+}$  redox couple (Eqs. 1, 2 and 3).



The higher the decomposition of hydrogen peroxide, the higher the dissolution of iron (Dimitrijevic et al., 1999). As copper dissolution from the slag flotation tailings is much lower than that from the slag, the sharp increase in iron dissolution is significantly higher in the case of the former.

It can be seen that even the application of a strong oxidant such as hydrogen peroxide ( $E^\circ = 1.776 \text{ V}$ ) does not result in complete copper dissolution, with the attained copper extractions being 60% and 30% from the slag and the slag flotation tailings, respectively. This observation indicates that much of the copper that is locked within the slag matrix was not liberated prior to leaching. As shown in Table 2, the finest fraction (-38+0  $\mu\text{m}$ ) of the slag comprises in excess of 60% of the sample and contains almost 1.1% copper. However, further particle size reduction would probably be economically unjustified.

Table 2. Particle size distribution for the copper smelter slag sample and the copper content of the various size fractions

Size fraction ( $\mu\text{m}$ )	Weight (%)	Cu content (wt. %)
-75+53	13.60	0.75
-53+38	17.80	0.81
-38+0	68.60	1.07

XRD analysis of the leach residue showed the same mineral phases as those found in the slag, but with more pronounced peaks. The crystallinity of the residue was higher than that of the slag, but nevertheless low.

In contrast to the results of this study, where iron dissolution from the slag and, in particular, from the slag flotation tailings sharply increases after 60 min of leaching, Banza et al. (2002) found, when leaching slag with hydrogen peroxide ( $\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$ , pH 2.5, 70 °C), that iron extraction drops from about 95% to 5%, with copper extraction being 85%, at hydrogen peroxide concentrations in excess of 62  $\text{dm}^3/\text{Mg}$  slag.

### Effect of stirring

It is well known that the decomposition of hydrogen peroxide is catalysed by a number of elements and their ions, as well as by stirring, shaking and similar operations (Dimitrijevic et al., 1999). For this reason, the effect of stirring on copper and iron extractions was studied. Two experiments were performed, namely one without stirring the slag slurry and the other one at a stirring speed of 350  $\text{min}^{-1}$ . The results are shown in Figure 7.

It can be seen that stirring has a beneficial effect on copper and iron extractions. This effect may be due to a better contact between the peroxide and the slag which has a high density (i.e.,  $3600 \text{ kg m}^{-3}$ ).

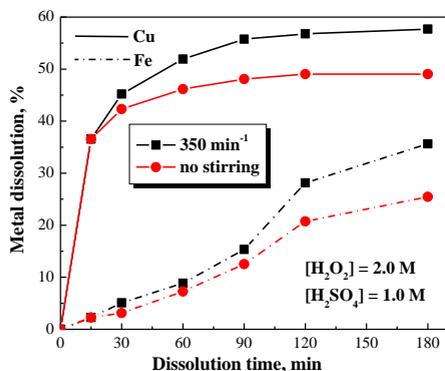


Fig. 7. Copper and iron extractions from the slag with and without stirring

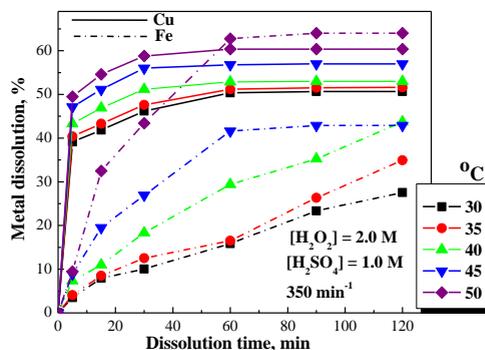


Fig. 8. Copper and iron extractions from the slag as a function of temperature

### Effect of temperature

The effect of temperature was investigated in a narrow temperature range from  $30 \text{ }^{\circ}\text{C}$  to  $50 \text{ }^{\circ}\text{C}$  as hydrogen peroxide is unstable at temperatures above  $40 \text{ }^{\circ}\text{C}$ . The temperatures were kept constant in a thermostated water bath. The reaction time was reduced to 120 minutes because shapes of the dissolution curves suggested that copper dissolution ceases after that time. The results are shown in Figure 8.

From Figure 8, it can be concluded that temperature has no significant effect on copper dissolution from the slag in an acidic solution of hydrogen peroxide. However, the effect of temperature is greater in the case of iron. Thus, at  $50 \text{ }^{\circ}\text{C}$ , iron extraction becomes greater than that of copper, that is, 64%. The copper extractions were in the 50-60% range between  $30 \text{ }^{\circ}\text{C}$  and  $50 \text{ }^{\circ}\text{C}$ , whereas 57.7% of Cu was dissolved at room temperature. As this value was close to that found at  $45 \text{ }^{\circ}\text{C}$  (i.e., 57%), a possible reason was sought why this was the case. To this end, a series of experiments was conducted where changes in the slurry temperature were recorded at different hydrogen peroxide concentrations. The results are given in Table 3.

It was observed that the leaching reaction was more vigorous and accompanied with loud hissing sound due to hydrogen peroxide decomposition and oxygen effervescence at hydrogen peroxide concentrations equal to or in excess of 2 M. In addition, the temperature was measured to be the highest after 90-120 minutes of reaction, which is the time when iron dissolution was found to increase sharply. This means that increasing  $\text{Fe}^{3+}/\text{Fe}^{2+}$  concentration results in an increase in the catalytic decomposition of hydrogen peroxide. As hydrogen peroxide decomposition is exothermic, there is an increase in temperature, which in turn accelerates hydrogen peroxide decomposition.

The effect of temperature on the leaching of slag flotation tailings was not studied as copper extractions from the slag flotation tailings were rather low.

Table 3. Change in slurry temperature with time as a function of hydrogen peroxide concentration ( $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$ ,  $350 \text{ min}^{-1}$ ).

H <sub>2</sub> O <sub>2</sub> Concentration	0.5 M	1.0 M	2.0 M	3.0 M	4.0 M
Time, min	Temperature, °C				
0	24	24	24	23	23
15	25	25	25	25	25
30	28	27	27	27	27
60	30	31	31	36	42
90	32	35	37	51	71
120	34	38	44	42	42
150	32	34	36	34	34
180	32	32	33	31	30

## Conclusions

Copper smelter slag and copper smelter slag flotation tailings were leached using sulphuric acid solutions, without or with the addition of either ferric sulphate or hydrogen peroxide. The highest copper extraction was attained with hydrogen peroxide at room temperature. Copper extraction from the slag was much higher than that from the slag flotation tailings. However, the maximum copper extraction achieved was only 63.4% when using 3 M H<sub>2</sub>O<sub>2</sub>, with the iron extraction being rather high at 48.6%. The lixivants studied were not selective and consequently iron extraction was relatively high, which is unfavourable in terms of further treatment of the leach liquors. In the majority of experiments, most of the copper was dissolved in the first 30-60 minutes of reaction, whereas iron dissolution was comparatively low in the first 60 minutes (around 10% with H<sub>2</sub>O<sub>2</sub>) but sharply increased afterwards.

## Acknowledgements

The authors acknowledge financial support from the Ministry of Science and Technological Development of Serbia (Project no. BR172031 and TD33023).

## References

- ALTUNDOGAN H. S., BOYRAZLI M., TUMEN F., 2004. *A study on the sulphuric acid leaching of copper converter slag in the presence of dichromate*. Minerals Engineering 17, 465–467.
- ANAND S., KANTA RAO P., JENA P.K., 1980, *Recovery of metal values from copper converter and smelter slags by ferric chloride leaching*. Hydrometallurgy 5, 355–365.

- ANAND S., SARVESWARA RAO K., JENA P.K., 1983. *Pressure leaching of copper converter slag using dilute sulphuric acid for the extraction of cobalt, nickel and copper values*. Hydrometallurgy 10, 305–312.
- BANZA A.N., GOCK E., KONGOLO K., 2002. *Base metals recovery from copper smelter slag by oxidizing leaching and solvent extraction*. Hydrometallurgy 67, 63–69.
- BESE A.V., 2007. *Effect of ultrasound on the dissolution of copper from copper converter slag by acid leaching*. Ultrasonics Sonochemistry 14, 790–796.
- CARRANZA F., ROMERO R., MAZUELOS A., IGLESIAS N., FORCAT O., 2009. *Biorecovery of copper from converter slags: Slags characterization and exploratory ferric leaching tests*. Hydrometallurgy 97, 39–45.
- DIMITRIJEVIC M., ANTONIJEVIC M., DIMITRIJEVIC V., 1999. *Kinetics of pyrite oxidation by hydrogen peroxide in phosphoric acid solutions*, J. Serb. Chem. Soc. 753–764.
- GBOR P.K., HOQUE S., JIA C.Q., 2006. *Dissolution behavior of Fe, Co, and Ni from non-ferrous smelter slag in aqueous sulphur dioxide*. Hydrometallurgy 81, 130–141.
- GORAI B., JANA R.K., PREMCHAND, 2003. *Characteristics and utilisation of copper slag – a review*. Resources, Conservation and Recycling 39, 299–313.
- HERREROS O., QUIROZ R., MANZANO E., BOU C., VINALS J., 1998. *Copper extraction from reverberatory and flash furnace slags by chlorine leaching*. Hydrometallurgy 49, 87–101.
- KAKSONEN A.H., LAVONEN L., KUUSENAHO M., KOLLI A., NARHI H., VESTOLA E., PUHAKKA J.A., TUOVINEN O.H., 2011. *Biorecovery and recovery of metals from final slag waste of the copper smelting industry*. Minerals Engineering 24, 1113–1121.
- LI Y., PAPANGELAKIS V.G., PEREDERIY I., 2009. *High pressure oxidative acid leaching of nickel smelter slag characterisation of feed and residue*. Hydrometallurgy 97, 185–193.
- SHEN H.T., FORSSBERG E., 2003. *An overview of recovery of metals from slags*. Waste Management 23, 933–949.
- XIE Y., XU Y., YAN L., YANG R., 2005. *Recovery of nickel, copper and cobalt from low-grade Ni-Cu sulfide tailings*. Hydrometallurgy 80, 54–58.
- YANG Z., RUI-LIN M., WANG-DONG N., HUI W., 2010. *Selective leaching of base metals from copper smelter slag*. Hydrometallurgy 103, 25–29.