

Technical Note
**Development of a Flowsheet for Recovering Copper and Tin
from Copper Refining Slags**

F. Arslan^{1*}, K. Giray², G. Önal¹, V. Gürkan¹

¹ *Istanbul Technical University, Mining Faculty, Mining Engineering Department
Mineral and Coal Processing Division, 80626 Maslak, Istanbul, Turkey*

² *Sarkuysan A.S., Kocaeli, Turkey*

Received 15 April 2002; accepted 5 June 2002

ABSTRACT

Slags produced during the refining of blister copper contain considerable amounts of copper and tin. The purpose of this experimental study was to investigate the possibilities of recovering Cu and Sn present in the slags before their disposal. After determining chemical and structural properties of the slags, size reduction, classification, flotation and leaching tests were carried to establish the optimum conditions for Cu and Sn recoveries. As a result of this experimental study, an overall flowsheet for the recovery of Cu and Sn from the copper refining slags has been developed. © 2002 SDU. All rights reserved.

Keywords: Copper refining slags; Size reduction; Flotation; Leaching; Copper and tin recovery

1. INTRODUCTION

The large growth observed in free world metal consumption was accompanied by corresponding increase in world mine production. The increased growth in all major metal productions results in a gradual loss of reserves of mine deposits. Therefore, additional metal resources need to be explored by finding new ore bodies recycling and investigating new technologies for the beneficiation of ore processing tailings, metallurgical slags, flue dusts, etc. Thus, natural resources would be utilized more efficiently from the economical and environmental viewpoints.

During the production of metallic copper from copper concentrates through pyrometallurgical route, different types of products (slags, dusts, fumes, etc.) are accumulated and they contain considerable amounts of metallic values besides copper. Mineral processing, pyro-, hydro-, and pyro-hydrometallurgical processes are applied in order to recover these values.

Flotation process plays an important role in beneficiation of metal values from slags and is utilized in many copper smelting processes (Cankut, 1973; Bota *et al.*, 1995). As a result a copper concentrate with 20-40% Cu content is produced with 90-95% efficiency from copper slags and a tailing with 0.2-0.35% Cu is either disposed or dissolved with sulfuric acid at 70°C and then Cu in leachate is recovered with iron powder (Cankut, 1973).

In some plants, flash smelting furnace slag (1.6-2% Cu) and converter slag (5-7% Cu) are cleaned in electric arc furnace, where coke is used as reductant and copper content of waste slag decreases to 0.5-0.8% (Kim, 1982; Suziki *et al.*, 1982). Ausmelt top entry submerged lance technology is also used to recover Cu, Ni and Co from slags (Hughes, 2000; Vernon and Burks, 1997).

* Corresponding author. E-mail: arslanf@itu.edu.tr

Leaching with nitrate, perchloride, hydrochloride, and sulfuric acids, ferric chloride, ferric sulfate, cyanide, SO₂ and ammonia solutions and pressure leaching processes are mostly studied ones among the hydrometallurgical processes (Lindblad and Dufresne, 1974; Anand *et al.*, 1980a; Anand *et al.*, 1980b; Anand *et al.*, 1985; Jia *et al.*, 1999; Shelley, 1975; Ahmed *et al.*, 2000). A study on the recovery of Cu, Co, Ni, and Zn from copper converter slags by roasting with ferric sulfate or pyrite is reported (Altundogan and Tumen, 1997; Tumen and Bailey, 1990). Pyro-hydrometallurgical methods are also used for the treatment of copper converter flue dusts and copper refining slags (taken from Sarkuysan A.S., Turkey) (Geveci *et al.*, 2000; Yildiz *et al.*, 2000). Alkali roast-acid leach process is reported in the literature for recovering metals from converter slag (Das *et al.*, 1999). Hot digestion and acid curing processes were also reported for the treatment of some ores, anode slimes and slags (Habashi, 1986; Lindblad and Dufresne, 1974; Arslan, 1982).

The aim of this experimental study is to investigate the possibilities of recovering copper and tin from the slags produced during the refining of blister copper (taken from Sarkuysan A.S., Turkey) and develop a conceptual flowsheet.

2. MATERIAL AND METHOD

Samples used in the experiments were taken from the slags produced during the refining of blister copper in Sarkuysan A.S., one of the major electrolytic copper producers in Turkey. Chemical analysis of slag showed that slag contained about 22% Cu and 2.3% Sn. Microscopic examinations of cross-sections prepared from slag samples illustrated different structural properties (Giray *et al.*, 1996; 1997). The reason for this was the stockpile, from where the sample was taken, was accumulated during different times of refining. Therefore, it was not possible to obtain a uniform structure for the slag samples since those were a mixture of acidic and basic types of slag. As a result of microscopic examinations it was found that some of the heavy metals (Pb, Sn, Bi, Sb, As) were encapsulated in metallic copper, especially in the acidic type of slags, and others were in the silicate matrix. Cassiterite, cuprite, tenorite, magnetite and zinc silicate were also observed. The presence of fayalite, magnetite, cuprite, and mervinite was also observed in the basic type of slag samples.

3. RESULTS AND DISCUSSION

In the earlier studies on recovery of copper from Sarkuysan copper refining slags using pyro-hydrometallurgical method (sodium sulfate roasting-sulfuric acid leaching) only 65% of copper could be recovered (Yildiz *et al.*, 2000). In this present study, in order to achieve better recoveries of Cu and Sn from refining slags, size reduction, flotation, and leaching tests were performed and results are given in the following sections:

3.1. Size reduction experiments

The maximum particle size of the slag was around 150mm, as received. They were first crushed below 19mm by using primary and secondary crushers. Later, these were crushed below 2mm using jaw, cone and roll crushers. As seen from Table 1, 3.3% of the sample retained on the 2mm screen contained 44.2% Cu and 1.69% Sn, thus, this could be circulated in copper production. Since metallic copper shows plate like shapes during the crushing, it was possible to separate Cu by classifying according to the particle sizes as seen from the screen analysis after crushing.

After separating samples over 2mm in size, the rest of the material was subjected to grinding for different times and classified according to the particle size. The results with respect to Cu and Sn grade and % distribution in various size fractions are given in Table 2. Samples over 150µm contained about 82.7% Cu and 0.66% Sn. The non-uniformity in % distribution of Cu and Sn indicates their presence in different phases.

Table 1
 Distributions of Cu and Sn in various size fractions for the samples crushed below 2mm in size

Particle size mm	Amount %	Cu %	Sn %	Cu Distribution %	Sn Distribution %
+2	3.3	44.42	1.69	6.67	2.20
-2+1.41	10.4	23.04	2.30	10.89	10.57
-1.41+1	20.8	21.38	2.32	20.20	21.16
-1+0.5	28.9	22.31	2.27	29.28	29.08
-0.5+0.2	20.0	20.36	2.30	18.48	20.27
-0.2+0.1	11.3	18.80	2.28	9.62	11.45
-0.1+0.038	3.1	20.64	2.26	2.91	3.08
-0.038	2.2	9.03	2.24	1.95	2.20
Total	100	22.03	2.27	100	100

Table 2
 Distributions of Cu and Sn in various size fractions for the samples ground for 45 minutes

Particle size μm	Amount wt/wt, %	Cu %	Sn %	Cu Distribution %	Sn Distribution %
+150	4.2	82.70	0.66	17.07	1.03
-150+106	9.0	20.43	2.10	9.03	7.65
-106+38	40.2	16.79	2.41	33.15	39.24
-38	46.6	17.81	2.76	40.76	52.08
Total	100	20.36	2.47	100	100

3.2. Flotation experiments

Flotation experiments were performed to recover Cu and Sn present in the samples after separating the fractions over 150 μm . During these experiments, effects of collector type, amount of collector addition, grinding time, and Na₂S addition on the flotation were investigated

3.2.1. Nature of collector

Different types of collectors such as K-amyl xanthate, Na-isobutyl xanthate, and Hostafloat X-231 were used in order to determine the most suitable one. Three flotation stages of tests were conducted at neutral pH and Hostafloat X-231 seems to give the best results as it can be observed from Table 3. A concentrate containing 30.31% Cu and 2.03% Sn was produced with 82.26% Cu and 42.73% Sn recoveries.

Table 3
 Effect of collector type on flotation of copper refining slags

Collector type	Products	Amount wt/wt, %	Cu %	Sn %	Cu recovery %	Sn recovery %
K-amyl xanthate	Concentrate	40.3	28.56	2.10	70.05	36.75
	Tailings	59.7	7.84	2.50	28.35	63.25
	Total	100.0	16.20	2.34	100.0	100.0
Na-isobutyl xanthate	Concentrate	39.0	32.26	2.16	73.27	34.15
	Tailings	61.0	7.52	2.66	26.73	65.85
	Total	100.0	17.17	2.46	100.0	100.0
Hostafloat X-231	Concentrate	47.09	30.31	2.03	82.26	42.73
	Tailings	52.21	6.01	2.50	17.74	57.27
	Total	100.0	17.65	2.27	100.0	100.0

3.2.2. Effect of grinding time

Experiments were carried out with the samples ground for 45, 60, and 75 minutes using Hostafloat X-231 at neutral pH in order to determine the effect of grinding time on flotation and the results are shown in Figure 1. Since grinding time had no significant effect on the metal

contents of concentrates and flotation recoveries, 45 minutes of grinding time was found sufficient for the liberation of Cu and Sn compounds.

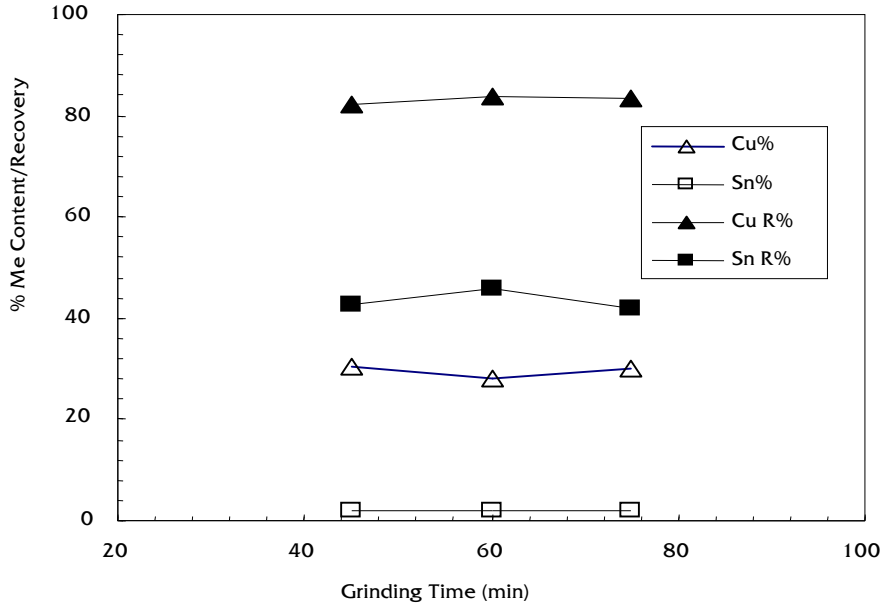


Figure 1. Effect of grinding time on flotation of slag

3.2.3. Effect of collector amount

In order to see the effect of collector amount on the flotation, experiments were carried out with the samples ground for 45 minutes using Hostafloat X-23 1 as a collector at neutral pH and the results are shown in Figure 2. The best results were obtained at the collector addition of 100g/t.

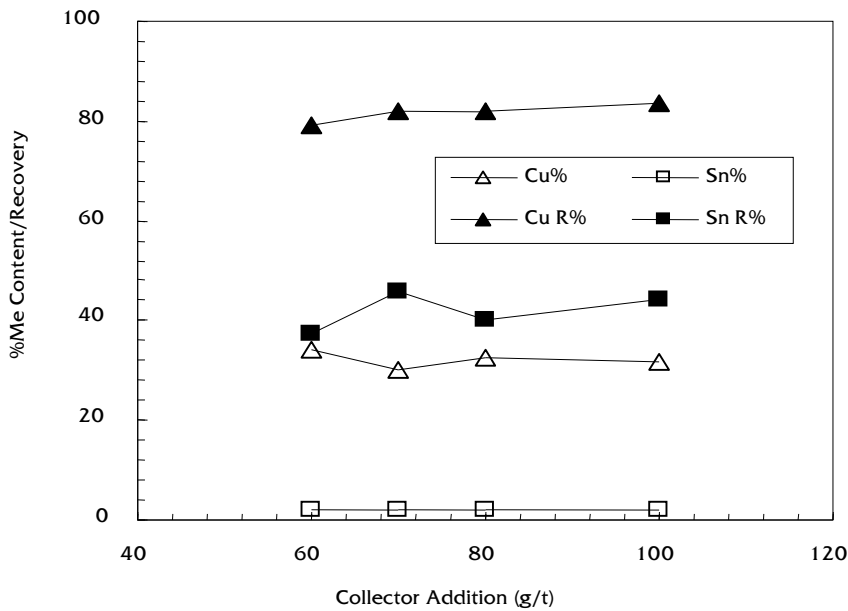


Figure 2. Effect of collector addition on flotation of slag

3.2.4. Effect of Na₂S addition

Figure 3 shows the effect of Na₂S addition on flotation of slags and experiments were performed with the samples ground for 45 minutes using 100g/t Hostafloat X-231 as a collector at neutral pH. As it can be seen from the figure that slight increase in Cu recovery and slight decrease in Sn recovery were observed till Na₂S is increased to 300g/t.

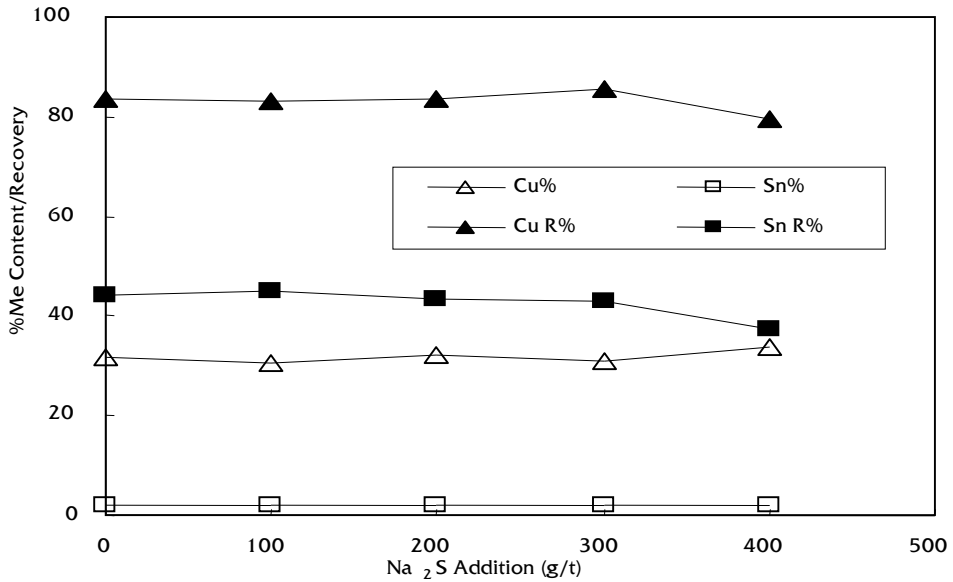


Figure 3. Effect of Na₂S addition on flotation of slag

3.2.5. Combined results on size reduction-classification-flotation

Table 4 shows the results of size reduction and classification tests together with flotation experiments. Results given in Table 5 were obtained when the products over 2mm and 150µm were added to flotation concentrate and middlings was distributed between flotation concentrate and tailings. As seen from that table, a flotation concentrate containing 49.67% Cu and 1.69% Sn was produced with 81.12% Cu and 27% Sn recoveries while 73% of Sn remained in the tailings.

Table 4
 Products of size reduction and flotation tests

Products	Amount wt/wt. %	Cu %	Sn %	Cu Recovery %	Sn Recovery %
+2mm	3.3	44.42	1.84	6.67	2.65
+150µm	4.1	82.70	0.66	15.38	1.33
Flot. Conc.	26.7	45.49	1.85	55.12	21.68
Flot. Middl.	7.1	17.08	2.34	5.49	7.52
Tailing	58.8	6.50	2.57	17.33	66.82
Total	100.0	22.04	2.26	100.00	100.00

Table 5
 Combined results of concentration tests

Products	Amount wt/wt. %	Cu %	Sn %	Cu Recovery %	Sn Recovery %
Concentrate	36.0	49.67	1.69	81.12	27.0
Tailing	64.0	6.50	2.58	18.88	73.0
Total	100.0	22.04	2.26	100.0	100.0

3.3. Leaching experiments

Leaching experiments were performed in order to recover Cu and Sn in the tailings. For this purpose, the effects of reagent type, reagent concentration, temperature and time on leaching recoveries of Cu and Sn were investigated. Solid/liquid ratio was kept constant at 1/10 for all the experiments.

3.3.1. Effect of nature of leachant

In order to determine the effect of reagent type, $\text{Fe}_2(\text{SO}_4)_3$ (80g/L) + H_2SO_4 (20g/L), HNO_3 (100g/L), and HCl (150g/L) were used in the experiments and tests were carried out at room temperature for one hour. As it is seen from the results given in Table 6, using HCl gave better results than other leachants, therefore, HCl was used for varying other leaching parameters.

Table 6
 Results of leaching experiments by using different types of reagent

Type of reagent	Cu recovery, %	Sn recovery, %
$\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$	29	12
HNO_3	38	4
HCl	80	40

3.3.2. Effect of leaching time and temperature

For studying the effect temperature, 150g/L HCl was used during the experiments carried out at different temperatures (25, 50, 80°C) for 8 hours. The samples were withdrawn at known time intervals and analyzed for Cu and Sn to determine the effect of time on the metal leaching recoveries. Figure 4 shows the time and temperature effects on Cu recovery of increased up to 2hrs of leaching and stabilized after that. Increasing temperature shifted Cu recovery-time curves to the higher values. Complete dissolution of Cu was observed at the end of 2hrs leaching at 80°C.

The effect of time and temperature on leaching recoveries of Sn is shown in Figure 5. Sn recovery increased with the increase in leaching time up to 6 hours. Sn leaching recovery-time curves were shifted to the higher values with increasing temperature. Complete dissolution of Sn was observed at 80°C after 6hrs of leaching.

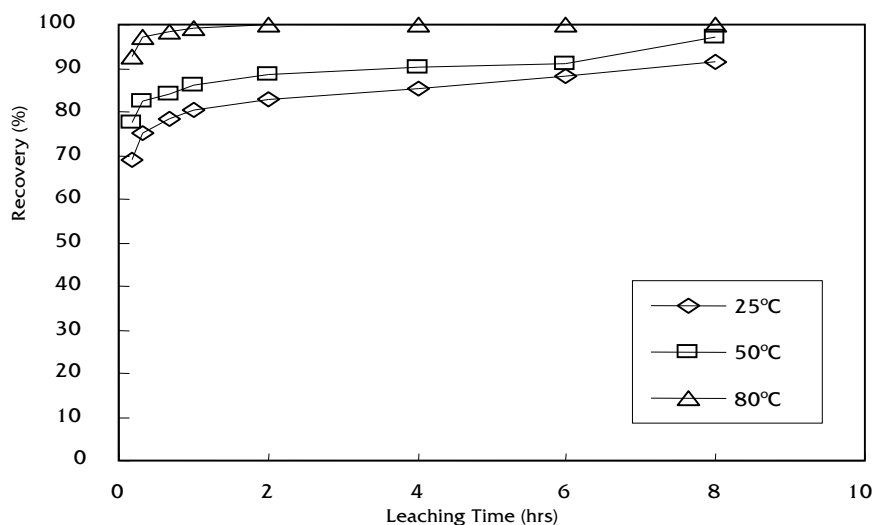


Figure 4. Effect of time and temperature on the leaching recovery of copper

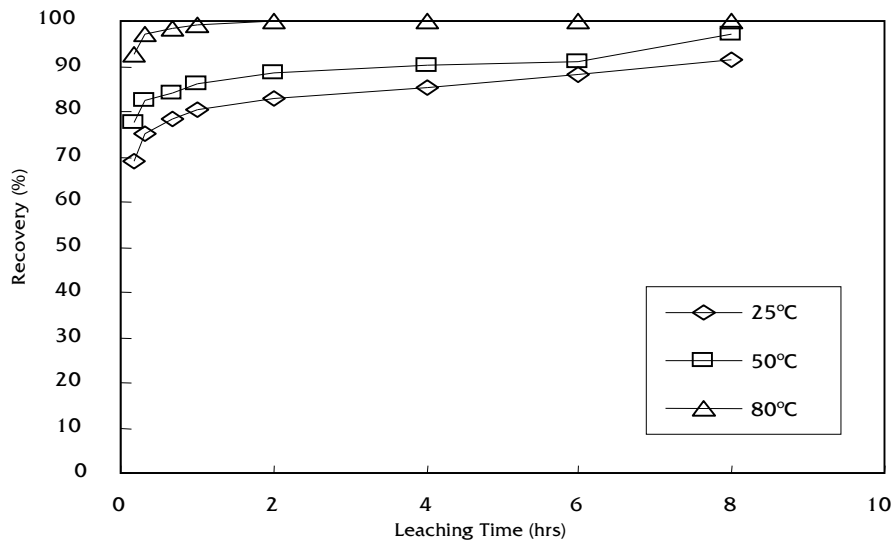


Figure 5. Effect of time and temperature on the leaching recovery of tin

3.3.3. Effect of HCl concentration

In order to investigate effect of HCl concentration, experiments were carried out at 80°C for 2hrs using different HCl concentrations and the results are shown in Figure 6. Increasing HCl concentration resulted in increases of Cu and Sn recoveries.

As a result of investigating the effects of different parameters for Cu and Sn recoveries, the following optimum leaching conditions were found: HCl concentration 150g/L, temperature 80°C, time 2 hours, and solid/liquid ratio 1/10, almost all Cu and Sn were extracted under these conditions.

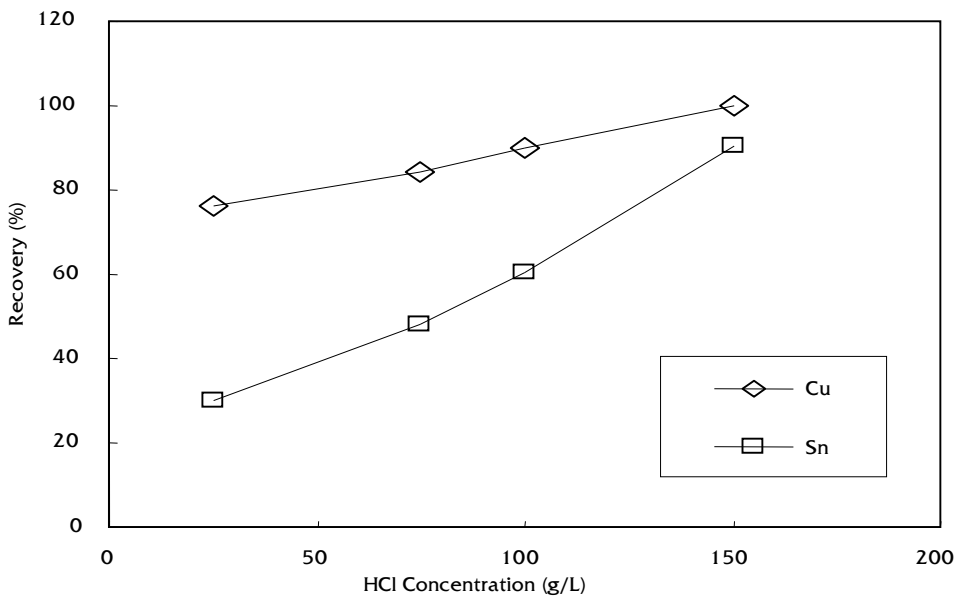


Figure 6. Effect of HCl concentration on the leaching recoveries of copper and tin

Based on the studies summarized above, a schematic flowsheet, given in Figure 7, is proposed for total recoveries of Cu and Sn from copper refining slags.

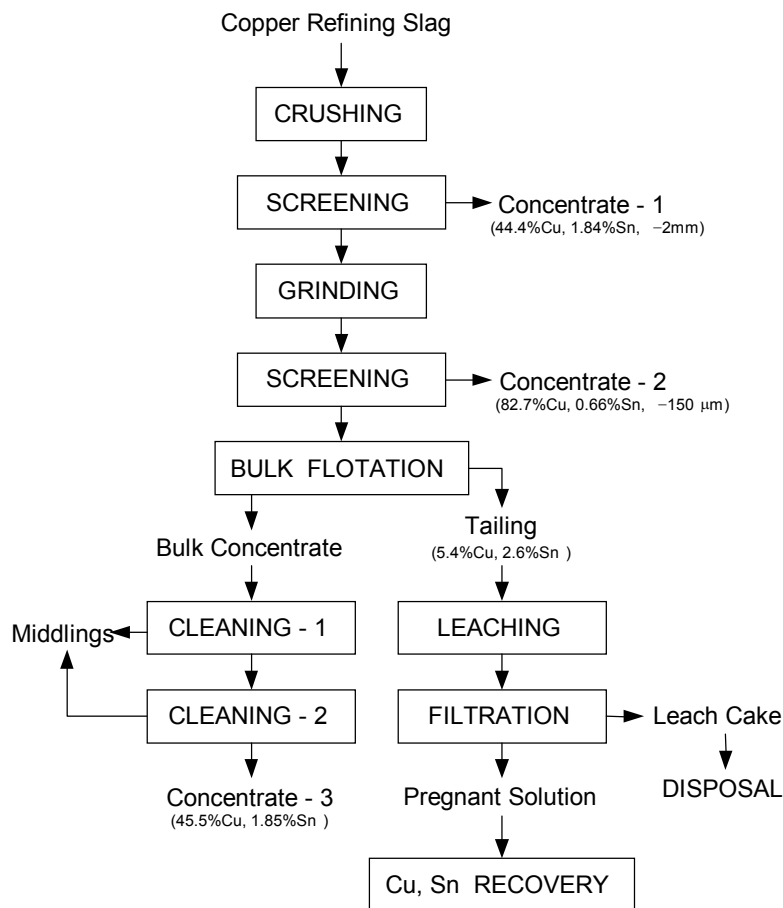


Figure 7. A proposed flowsheet for recovering copper and tin from copper refining slags produced as a result of this experimental study

4. CONCLUSIONS

Samples taken from the slags produced during the refining of blister copper in Sarkuysan A.S. contain 22% Cu and 2.3% Sn. As a result of size reduction, classification and flotation tests a concentrate containing 49.67% Cu and 1.69% Sn could be produced with 81.12% Cu and 27% Sn efficiencies. This concentrate could be reused in the copper production. All Cu and Sn in the flotation tailings were leached with HCl. As a conclusion of this experimental study, it was shown that all Cu and Sn in the refining copper slags could be recovered efficiently and this could be considered a success from the viewpoint of recycling. In the light of these experimental results, a flowsheet for recovering copper and tin from copper refining slag has been proposed.

ACKNOWLEDGEMENT

Authors would like to thank Sarkuysan A.S., Turkey for supplying the raw material used in this experimental study and helping on the chemical analysis.

REFERENCES

- Ahmed, I.B., Gbor, P.K. and Ji, C.Q., Aqueous sulfur dioxide leaching of Cu, Ni, Co, Zn, and Fe from smelter slag in the absence of oxygen. *Canadian Journal of Chemical Engineering*, 2000, 78(4), 694-703.
- Altundogan, H.S., and Tumen, F., Metal recovery from copper converter slag by roasting with ferric sulfate. *Hydrometallurgy*, 1997, 44(1-2), 261-267.
- Anand S., Kanta Rao. P., Jena P.K., Recovery of copper, nickel, and cobalt from copper converter and smelter slag through ferric chloride leaching. *Hydrometallurgy*, 1980a, 5, 355-365.
- Anand S., Kanta Rao. P., Jena P.K., Leaching behaviour copper converter slag in sulphuric acid. *Trans. Indian Instn. Metals*, 1980b, 33(1), 77-81.
- Anand S., Sarveswaro Rao. K., Jena P.K., Pressure Leaching of copper converter slag with dilute sulfuric acid for the extraction of copper, nickel and cobalt values. *Hydrometallurgy*, 1983, 10, 305-312.
- Arslan, C., Evaluation of Black Sea Copper Works' smelter slags via acid baking method. M.S. Thesis, Istanbul Technical University, 1982, (in Turkish).
- Bota, G., Gican, I. and Poputa, G., 1995, The beneficiation of the non-ferrous metals from secondary resources at regia autonoma a Cuprului Deva-Romania. 6th Balkan Mineral Processing Symposium, 18-21 Sept. 1995, Ohrid, Macedonia, pp. 426-431.
- Cankut S., *Extractive Metallurgy Applications: Copper*. Istanbul, 1973, pp. 62-68 (in Turkish).
- Das G.K., Mishra D., Anand S., Das R.P., Recovery of metals from copper converter slag by alkali roast-acid leach process. *J. Metals, Materials and Processes*, 1999, 11(1), 43-48.
- Geveci A., Topkaya Y., Gerceker E., Recovery of Copper and zinc from copper converter flue dusts. 10th International Metallurgy and Material Congress, 24-28 May 2000, Istanbul-Turkiye, pp. 59-68.
- Giray K., Onal G., Arslan F., Gurkan V., Recovery of Copper and Tin from Copper Fire-refining Slags. *Changing Scopes in Mineral Processing*, Eds. M. Kemal, V. Arslan, A. Akar, M. Canbazoglu, A.A. Balkema, Rotterdam, 1996, pp. 301-306
- Giray K., Arslan F., Onal G., Gurkan V., Beneficiation of Copper Fire-refining Slags. 7th Balkan Conference on Mineral Processing, Volume II, 26-30 May 1997, pp. 157-161.
- Habashi, F., *Principle of Extractive Metallurgy-Pyrometallurgy*. Vol.3, 1986, Gordon & Breach, New York.
- Hughes, S., Applying Ausmelt technology to recover Cu, Ni and Co from slags. *Journal of Metals*, 2000, 52(8), 30-33.
- Jia, C.Q., Xiao, J.Z., and Orr, R.G., Behavior of metals in discard nickel smelting slag upon reacting with sulfuric acid. *J. of Env. Sci. and Health, Part A - Toxic/Hazardous Substances & Environmental Engineering*, 1999, 34(5), 1013-1034.
- Kim, T.J., Flash smelting in Korea, in *Copper Smelting - An update*. Eds. D.B. George and J.C. Taylor, 1982, TMS of AIME, pp.33-39.
- Lindblad, K.O. and Dufresne, R.E., Acid leach of copper reverberatory slag—a new approach. *Journal of Metals*, February 1974, 29-31.
- Shelley, T.R., Possible methods for recovering copper from waste copper smelting slags by leaching. *Inst.Min.Met.Trans., C*, 1975, 84(820), C1-C4.
- Suzuki, T., Yanagida, T., Goto, M., Echigoya, T. and Kikumoto, N., Recent operation of Mitsubishi Continuous Copper Smelting and Converting Process at Naoshima, in *Copper Smelting –An update*. Eds. D.B. George and J.C. Taylor, 1982, TMS of AIME, pp. 51-76.
- Tumen F., Bailey N.T., Recovery of metal values from copper smelter slags by roasting with pyrite. *Hydrometallurgy*, 1990, 25, 317-328.
- Vernon, P.N., and Burks, S.F., The application of Ausmelt technology to base metal smelting, now and in the future. *Journal of the South African Institute of Mining and Metallurgy*, 1997, 97(3), 89-98.
- Yildiz K., Alp A., Aydın A.O., Utilization of copper refining slags by a pyro-hydrometallurgical method. 10th International Metallurgy and Material Congress, 24-28 May 2000, Istanbul-Turkiye, pp. 127-132.