Recovery of Copper and Cobalt from Converter Slag with a New Flotation Method Using H₂S

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Abstract: In this study, two different samples were obtained from Küre Copper factory. It was determined that the samples contain: the sample of K.C.F. (Küre Copper Factory), 0.70% Cu and 0.5% Co. This sample was firstly grounded at -100 mesh dimension. Flotation was done according to previously obtained optimum flotation conditions. The flotation yield of Cu and Co in concentrate phase was found to be low by collective flotation. Even when the samples were grounded at -160 mesh, no change was observed in the flotation result. Especially, Co could not float under the flotation conditions of the non-sulfurized samples. There, a new flotation method was applied which was not applied until now. For this aim, the samples were firstly sulphurized under the steam of H₂S + H₂O. By this method, the amount of Cu and Co in the samples get rich. According to the obtained results, the optimum reactions for flotation and sulphurization were determined. In the first sulphurization conditions for the sample of K.C.F., the yield of flotation for the Co and Cu were found to be 98.27% and 68.07%, respectively. The results indicate that Cu can be floated at low yield in the original samples. On the other hand, Co cannot float under these conditions.

Key words: Converter slag, flotation, copper, cobalt, sulphurization.

1. Introduction

Copper slag is produced in large amounts in seven copper smelter plants in Chile, and it is estimated that around 4 million tons of slag are disposed every year and another 40 to 45 million tons are historically cumulated [1]. Different slags need aid transformed as by-products clinched alongside metallurgical methods alternately as residues on incineration methods. As stated by the sources and the characteristics, those fundamental slags might be ordered under three categories, in particular, ferrous slag, non-ferrous slag furthermore incineration slag. Slags generally hold numerous amount of profitable metals. They would really be an auxiliary asset from claiming metals, instead of an end-waste, what's more, they would be connected as an asset material in numerous zones. Clinched alongside addition, to a portion application,

slags bring tantamount alternately indeed better properties over their focused materials. The third characteristic may be that some slags hold an outstanding amount of hurtful alternately overwhelming metals. Those discharge about these metals might cause natural issues [2, 3].

Metallurgical strategies would as a rule used to treat ores, what's more, of the enriching procedure by flotation strategies, are attractive division. A past article accounted that floatation what's more, attractive detachment methods, utilizing slag, didn't bring about acceptable extractions starting with converter slag [4].

Much exploration needs to be been conveyed out on the recuperation of copper from slags. Suggested strategies for cleaning the slag are flotation [5, 6], leaching, electric heater and so on [7].

Copper smelting techniques may be used [5, 8-11]. There are also some hydrometallurgical methods given in the literature for the treatment of slags, such as leaching in nitrate, perchloride, chlorate and

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sulfuric acids [12, 13] with and without pressure [13], ferric chloride [8, 14, 15], ferric sulfate [7], cyanide, thiosulphate leaching [16], ferric sulfate and ammonia sulfate solutions [7, 12, 17, 18].

In this study, the flotation of converter slag was attempted. When this was unsuccessful, a sulfurization process developed in the previous studies was used. As a result of this process, a new surface forms on the converter slag particles and flotation experiments were carried out using these samples [19-21]. As seen in the previous studies, successful results cannot be obtained by direct flotation of the original converter slag. However, in this study, significant results were obtained by flotation of a sample obtained from an appropriate sulfurization process.

2. Experimental

2.1 Reagents and Instrumentation

In this study, the converter slag used was supplied from the Kastamonu-Küre, Turkey. Küre is in the Western Black Sea region of Turkey, are a leading copper and pyrite ore production area. Analyses show that the ore obtained from the Küre Region contains

0.70% copper, 0.50% cobalt and 21.98% sulfur. The K-Amyl xanthate and Dowfroth 250 used in flotation were taken from the Ergani Copper Mining Co in Turkey. The chemicals used in these studies such as 96% (w/v) H₂SO₄, 37% (w/v) HCl, 65% (w/v) HNO₃, FeS and KClO₃ were purchased from Merck. The sample crushing was broken in a crusher belonging to Unal Engineering as -100 mesh size. The experiments were conducted in a laboratory equipped with facilities for carrying out hydrometallurgical operations such as autoclave leaching. Denver mark flotation apparatus and Nel 890 Model pH meter were used for flotation and determination of pH of samples, respectively. Sulfur in various forms was oxidized to sulfate form and precipitated as BaSO₄ and the precipitate with fixed weighing was analyzed by gravimetric method [22]. The compositions of all samples were determined using a Unicam 929 Model AAS. The spectral wavelength selected for the metal analyses is shown in Table 1.

In this study, the solutions used were prepared with concentrations of 25-100 ppm for copper and 20-60 ppm for cobalt. Calculation of flotation yield was made according to Eq. (1).

$$F. Y. \% = \frac{\text{Amount of substance required to float in Floating Substance}}{\text{The total amount of substance required to floate within the substance used in the flotation}} \times 100 \quad (1)$$

2.2 Method

The converter slag sample was first crushed and then ground to -100 mesh sizes, sieved and dried at 110 °C. These samples were used in chemical analyses and flotation studies. H₂S was produced by addition of H₂SO₄ to FeS [6, 21] obtained from pyrite. The sulfurization process was performed in an autoclave of 1.3-liter internal volume, with 60 minutes residence time at 100 °C. Different ratios of a gas mixture of H₂S + H₂O were performed. Then, samples obtained from autoclave were floated by using potassium amyl xanthate and Dowfroth 250. After the obtained concentrates and wastes are solubilized with

acid, analyzes are read in AAS.

3. Results and Discussion

3.1 Effect of pH on the Flotation of Converter Slag

Converter slag sample was floated at different pHs and the results are given in Fig. 1 [21].

This study was carried out under the conditions indicated in Table 2.

As seen in Fig. 1, the best flotation yield was at pH 11.0.

For flotation, 100 g of the ore sample was fed and 28.56 g of converter slag was floated. The flotation yields of Cu and Co were determined as 57.81% and

Table 1 The spectral wavelength of metal for AAS.

Metal	Wavelength (nm)	Silit (nm)	Current (mA)	Oxidant-Fuel
Copper	324.75	0.5	3	Air-Acetylene
Cobalt	240.73	0.2	10	Air-Acetylene

Table 2 Flotation condition at different pHs.

Parameter	Flotation condition
Particle dimension	-100 mesh
Solid/liquid ratio	100 g/L
Collector	0.2 g Z ₅ (KAX) 3 minute mix
Frother	0.5 mL Dowfroth 250 (1%) 2 minute mix
Mix speed	900 periods/minute
Flotation time	3 minute

Fig. 1 The effect of pH on the flotation yield.

34.38% respectively, and their concentrate grades of Cu and Co have ascertained as 1.17% and 0.43% Co. At the end of the flotation process, the results aimed were not attained, and flotation yield was low. Converter slag samples were first sulfurized at 100 °C by using various ratios of H₂S + H₂O. Then, these samples were floated.

3.2 The Flotation of Sulfurized Converter Slag

Firstly, the converter slag samples were ground, sieved to -100 mesh size, dried at 110 °C and then reacted with gas mixtures containing different amounts of H₂S + H₂O for 1 hour at 100 °C. For this purpose, the six samples each of which was 1000 g, were reacted with mixtures of H₂S and H₂O separately

as seen in Table 3.

After sulfurization, the sulfurized samples were floated at pH 11 under the conditions indicated in Table 2.

Eight sulfurized sample was floated at different sulfurization condition and the results are given in Fig. 2 and Table 4.

As seen in Table 4, the best result was obtained from a seventh sulfurized sample by flotation. In order to be understood better these results; they are given in Fig. 2 with respect to different H₂S values.

3.3 The Effect of the Activator

In this step, the flotation process on the seventh sulfurized sample was performed to test the effect of

Table 3 The used amount of gas mixtures of H₂S and H₂O.

Sulphurization number	H ₂ S amount (g)	Water amount (g)
1	3.83	20
2	5.74	30
3	7.66	40
4	9.57	50
5	13.40	70
6	15.32	80
7	17.23	90
8	19.14	100

Fig. 2 The effect of sulfurization on the flotation yield of sulfurized samples (at pH 11).**Table 4** The values obtained by flotation of the sulfurized sample.

Sulphurization number		1	2	3	4	5	6	7	8
pH		11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00
Froth (g)		22.28	23.93	26.70	40.51	37.05	62.67	47.86	61.23
Tailing (g)		76.03	76.13	72.70	59.40	62.32	37.07	51.96	38.18
Recovery (%)	Cu%	48.45	43.36	60.72	71.51	68.52	83.93	77.89	81.66
	Co%	26.26	24.96	30.57	42.46	39.46	65.78	71.10	61.05
Concentrate	Cu%	1.31	1.25	1.68	1.37	1.42	0.86	1.38	0.70
Assay (%)	Co%	0.45	0.42	0.67	0.64	0.66	0.44	0.74	0.43
Unfloated	Cu%	0.43	0.43	0.40	0.37	0.38	0.24	0.36	0.25
Assay (%)	Co%	0.38	0.40	0.57	0.58	0.59	0.39	0.28	0.23
Time (Min)		2.50	3.20	4.40	4.30	5.00	3.00	2.07	2.30

activator amount. The studies were carried out at pH 11.0 and by using 10 mg, 30 mg, 50 mg, 60 mg, 80 mg, 125 mg, 150 mg and 200 mg CuSO₄ and results are given in Fig. 3.

Flotation studies were conducted using CuSO₄, it can be seen that there is not a significant difference in flotation yield as activator and depressant changes. Thus, the results were not given.

Fig. 3 The effect of activator amount on the floatability of the result obtained from seventh sulfurized samples.

Fig. 4 The effect of collector amount on the floatability of the result obtained from a seventh sulfurized sample.

3.4 The Effect of Collector Amount

In this step, the flotation process on the seventh sulfurized sample was performed to test the effect of collector amount. The studies were carried out at pH 11.0 and by using 0.20 g, 0.25 g, 0.30 g and 0.35 g KAX (K-amyl Xanthate) and results are given in Fig. 4.

4. Conclusions

The findings of this study are as:

- Enrichment cannot be achieved with the flotation of original ore;
- For enrichment with flotation, it was understood that a new surface is required;
- It was determined that the efficiency increased with the flotation of the sample obtained from sulfurization of converter slag samples, sized to -100 mesh with the appropriate amount of H_2S . e.g. For sulfurization of one kg of sieved ore, 17.23 g H_2S +

90.00 g H₂O gas mixture is enough. The sulfurization was finished in 1 hour in the autoclave for 100 °C;

- When the flotation of converter slag is performed at pH 11.00, maximum efficiency of copper and cobalt was obtained;

- Increase in the efficiency in the flotation of sulfurized samples is not only limited to the converter slag; the amount of H₂S used according to the composition of copper ore must be determined experimentally.

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