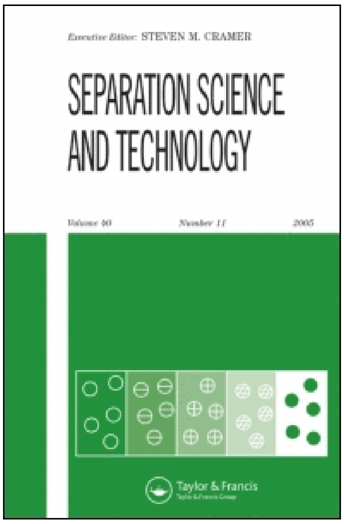

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A New Method for Recovering Fe(II) Sulfate, Copper, and Cobalt from Converter Slag

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Abstract

The aim of this study was to recover copper and cobalt from the stock-piled converter slags at the Ergani Mining Co. in Turkey. Copper and cobalt are present in various chemical forms in the slag. For that reason, copper and cobalt were first converted to Cu_2S and CoS by passing H_2S gas through a slurry of ground slag in H_2SO_4 solutions. In the second stage, the slurry was filtered and it was determined that 30–40% of the iron and trace amounts of copper and cobalt passed into the solution as Fe^{2+}, Cu^{2+}, and Co^{2+} ions. The slag residue was then dried at 105°C for 2 h and roasted in a muffle furnace at about 600–700°C for different time periods. In the third stage, the mass obtained at the end of the roasting process was boiled with distilled water and filtered. The final solution was brought to volume and analyzed for copper and cobalt. It was determined that practically all of the Cu and 70.7% of the Co passed into the solution.

INTRODUCTION

The converter slag from Ergani Copper Works contains copper and cobalt in various concentrations (about 2–8% copper, 0.2–0.8% cobalt). It also contains about 45–55% iron, 20–30% silicon dioxide, and 6–20% calcium and magnesium (*1*).

The methods related to the recovery of copper and cobalt from solidified converter slags can be classified under three headings: flotation electromagnetic separation, and hydrometallurgical methods.

In the enrichment carried out by the flotation technique, the amount of copper in the sample can be increased from 5 to 20%, which corresponds to 85% efficiency, but cobalt cannot be floated in this way . This may be attributed to the homogeneous distribution of cobalt in the lattices of copper and iron in magnetite (Fe_3O_4) and fayalite ($2FeO{\cdot}SiO_2$) (*1*).

In the electromagnetic separation method, cobalt can be collected in the concentrate (*2*), but it is not possible to collect all the copper in this phase. It is then possible to recover copper and cobalt from the concentrate by either pyrometallurgical or hydrometallurgical methods.

The means which are used for the recovery of copper and cobalt by hydrometallurgical methods are as follows: Leaching with H_2SO_4 solution at atmospheric pressure (*3*); leaching with H_2SO_4 under oxygen pressure (*4*); pyrolysis with $(NH_4)_2SO_4$ and H_2SO_4 at high temperature and then leaching in water (*5*); pyrolysis of the mixture of converter slag and pyrite and then dissolving of the sample in H_2SO_4 solution (*6*); pyrolysis of the converter slag by using reducing agents such as coal, bituminous coal, fuel oil, and leaching with Fe^{3+} and H_2SO_4 solutions (*7*); recovery of copper and zinc by chlorination roasting (*8*); and leaching in cyanide solution which results in the recovery of copper to a certain extent, but it was not possible to recover any cobalt by this procedure (*9*).

Furthermore, there are some methods concerning the recovery of copper and other elements which can be reduced together with copper in this medium from molten converter slag by pulverization of the reducing material such as dust coal together with air (*10, 11*).

In this study, a new method for recovering copper and cobalt was attempted. The first step of the procedure consists of dissolution of part of the iron compounds present in the insoluble slag as Fe_3X_4 (X: O^{2-}, SiO_3^{2-}). In the second step, the filtered residue is dried and then subjected to pyrolysis. The mass obtained at the end of the pyrolysis is leached in distilled water; thus, copper and cobalt are brought into the solution phase.

MATERIALS AND METHOD

The converter slag used for this study was obtained from the Ergani Mining Co. The sample was ground to −100 mesh and dried at 110°C for one day.

The composition of the sample was 2.9% Cu, 0.2% Co, and 50.03% Fe. All analyses were carried out by using an atomic absorption spectrometer (Varian Techtron 1200). Furthermore, the percentage of sulfur in the sample was found to be about 2.3%. The sulfur was determined by oxidizing it into sulfate and precipitating it as $BaSO_4$ (*12*). The other elements are calcium, magnesium, and silicon (*1*).

All the chemicals used in this study were reagent grade and obtained from Merck Scienfitic Co. H_2S gas was prepared by the addition of technical H_2SO_4 to FeS. All the experiments were conducted in a 1-L glass reactor. A ground slag sample (300.00 g) and 750 mL of H_2SO_4 solution at various concentrations were placed in the reactor, and then H_2S gas was passed through this solid–liquid mixture.

The reactions taking place in this section can be summarized as follows:

$$Fe_3X_4 + H_2S + 6H^+ \rightleftharpoons 3Fe^{2+} + S + 4H_2X \tag{1}$$

$$Cu_2O + H_2S \rightleftharpoons Cu_2S + H_2O \tag{2}$$

$$Cu + H_2S + \tfrac{1}{2}O_2 \rightleftharpoons Cu_2S + H_2O \tag{2'}$$

$$Co_3X_4 + 4H_2S \rightleftharpoons 3CoS + S + 4H_2X \tag{3}$$

where X = O^{2-} or SiO_3^{2-}.

The transfer of Fe^{2+} into solution in the first step can be explained by Reaction (1). In the second step Cu^{2+} and Co^{2+} transfer into solution by leaching of the sample (obtained after pyrolysis) with water. This can be attributed to the conversion of Cu_2S and CoS into $CuSO_4$ and $CoSO_4$ during pyrolysis according to Reactions (2) and (3).

The pH of the solution obtained after the first step was about 4. The percentages of Cu and Co transferred into solution at this pH were approximately the same as the solubilties of Cu_2S and CoS.

RESULTS AND DISCUSSION

Initially the experiments were conducted at 30 and 60°C. It was observed that the amount of iron passed into the solution and the percentage of copper and cobalt taken into the solution after pyrolysis were higher in the experiment performed at 30°C. Therefore, all the experiments were carried out at this temperature.

The first 10 experiments were carried out in a 1-L reactor where 300.00 g slag was placed and then 750 mL of H_2SO_4 solution at various concentrations was added.

The first experiment was carried out at 30°C and the second at 60°C. 36 mL of 96% H_2SO_4 was added to the above-mentioned solid–liquid mixture.

The acid was added in 12 mL portions in three stages, and the solution was bubbled with H_2S gas obtained from 15 g FeS after each addition. The total amount of H_2S passed through the solution was obtained from 45 g FeS. The solution was mixed with a mechanical stirrer throughout the experiment. The mixture obtained at the end of the first experiment was filtered off, and the solution was made up to 250 mL. It was determined that the concentrations of Fe^{2+}, Cu^{2+}, and Co^{2+} ions that passed into the solution, prepared by using the above procedure, were 50.8, 2.93×10^{-2}, and 2.84×10^{-2} g/L, respectively. The residue was dried at 105°C (~2 h) until it reached constant weight.

For the roasting process, 10.00 g samples were taken. The mass obtained at the end of the roasting process was boiled with 100 mL water and the final solution was diluted to 250 mL. The percentages of copper, cobalt, and iron passed to the solution were analyzed by taking samples from this solution. The pH values of these solutions were found to be around 4. The analysis of the final residue obtained at the end of the first experiment showed that it consisted of 8.4% S and 43.97% Fe.

The percentages of copper, cobalt, and iron extraction from the mass formed as the result of roasting the residue obtained at the end of the first experiment are given in Table 1.

Examination of Table 1 shows that the highest yield was obtained by roasting the mixture of 10.00 g residue and 0.20 g sulfur at 600°C for 3 to 4 h. In this case the ratio of iron passed to the solution is relatively low compared with the other experiments. Since the percentages of copper and cobalt passed to the solution showed a significant decrease in the roasting process carried out at 700°C, no experiments were conducted at this temperature. The decrease in the percentages of copper and cobalt that passed into the solution at 700°C was attributed to the formation of highly insoluble species such as Co_3O_4, $CuO \cdot CuSO_4$, and $CuO \cdot Fe_2O_3$ (*13*).

The conditions of the second experiment were the same as these of the first one except that H_2S gas was passed through the solution at 60°C. The results of this experiment are given in Table 2.

The residue was found to contain 7.8% S and 42.75% Fe. When the results in Table 2 are compared with those in Table 1, a decrease in the ratios of copper and cobalt extracted are seen. This can be explained by the shift of Reactions (2) and (3) to the left since saturated H_2S solutions contain less dissolved H_2S at a working temperature of 60°C. Therefore, since the percentages of Cu_2S and CoS formed in the second experiment were less than those of the first experiment, the percentages converted to $CuSO_4$ and $CoSO_4$ after roasting were also less than those of the first experiment. If the roasting process is prolonged further following the sulfatization process, due to the formation of insoluble $CuO \cdot CuSO_4$ and Co_3O_4 species, the copper and cobalt extractions also decrease. This decrease is even higher in copper. The roasting process was therefore limited to 4 h.

The third experiment was carried out at 30°C. Here 36 mL of 96% H_2SO_4 was added at once. The experimental conditions were unchanged. The residue was filtered off and brought to constant weight. Analysis of the residue showed that it consisted of 8.9% S and 44.9% Fe. The percentages of copper, cobalt, and iron taken into solution following the roasting and leaching processes are given in Table 3.

When Table 3 is compared with Table 1, no significant difference is observed. However, when the sulfur ratio in the residue was increased,

TABLE 1
The Effect of Roasting Time on the Percentages of Cu, Co, and Fe Extraction

Sample	Temperature (°C)	Roasting time (h)	Percentages of Cu, Co, and Fe that passed into the solution			
			% Cu	% Co	Fe (mg/250 mL)	% Fe
Sulfidized slag residue	600	1	39.19	30.52	83.3	1.89
		2	85.48	49.59	33.3	0.76
		3	85.48	45.78	25.0	0.57
		4	80.58	41.97	13.3	0.30
Mixture of 10.00 g slag residue + 0.20 g S	600	1	28.36	41.97	120.0	2.73
		2	79.03	49.59	93.3	2.12
		3	98.37	58.04	50.0	1.14
		4	99.92	54.94	40.0	0.91
Mixture of 10.00 g slag residue + 0.40 g S	600	1	30.18	33.36	124.3	2.83
		2	65.39	45.14	102.4	2.33
		3	93.94	49.59	80.6	1.82
		4	95.79	49.59	64.0	1.45
Mixture of 10.00 g slag residue + 0.60 g S	600	1	26.80	27.65	130.7	2.97
		2	41.26	43.28	110.2	2.50
		3	90.25	49.59	90.5	2.06
		4	94.45	50.58	71.0	1.61
Sulfidized slag residue	700	1	7.74	8.93	17.0	0.39
		2	16.12	10.91	—	—
		3	10.31	7.93	—	—
		4	7.74	7.93	—	—

TABLE 2
The Percentages of Cu, Co, and Fe Extracted after Sulfidizing at 60°C and Roasting at 600°C

Roasting time (h)	Percentages of Cu, Co, and Fe that passed into the solution			
	% Cu	% Co	Fe (mg/250 mL)	% Fe
1	24.00	33.30	69.7	1.63
2	72.64	36.76	26.5	0.62
3	71.96	35.29	17.0	0.40
4	69.95	35.29	14.5	0.34
5	65.90	33.82	3.0	0.07
6	61.88	33.82	2.7	0.06

the ratio of copper passing into solution after extraction of the roasted mass with water was seen to increase. Also, the roasting process carried out at 650°C caused a decrease in the ratios of copper and cobalt, just as the roasting process carried out at 700°C did. Since the most appropriate roasting temperature was found to be 600°C, subsequent experiments were carried out at that temperature. Other researchers also found 600°C to be the optimum roasting temperature (*6*).

The fourth experiment was carried out by adding an acid solution containing 40 mL of 96% H_2SO_4 in 750 mL water to the 300.00-g sample. The solution was bubbled with H_2S gas obtained from 60 g FeS. The residue, which was brought to constant weight by subjecting it to the necessary procedures, was found to contain 9.65% S and 43.9% Fe.

TABLE 3
Effect of Roasting Time on Percentages of Cu, Co, and Fe Extraction during Roasting at 600 and 650°C.

Roasting temperature (°C)	Roasting time (h)	Percentages of Cu, Co, and Fe that passed into solution			
		% Cu	% Co	Fe (mg/250 mL)	% Fe
600	1	28.5	29.0	75.0	1.67
	2	81.2	35.2	49.8	1.11
	3	93.2	37.4	28.7	0.64
	4	91.3	37.8	11.1	0.25
650	1	26.0	24.2	16.6	0.37
	2	50.7	29.0	—	—
	3	59.5	33.1	—	—

TABLE 4
The Percentages of Cu, Co, and Fe after Roasting and Extracting the Residue at 600°C as a Function of Roasting

Roasting time (h)	Percentages of Cu, Co, and Fe that passed into solution			
	% Cu	% Co	Fe (mg/250 mL)	% Fe
1.00	25.9	33.5	80.6	1.86
2.00	74.8	41.5	52.0	1.18
2.25	74.5	42.5	30.5	0.69
2.50	99.1	45.0	30.0	0.68
2.75	99.1	45.6	17.6	0.40
3.00	100.0	46.2	15.8	0.36
4.00	93.0	46.0	11.0	0.25

The ratios of copper, cobalt, and iron taken into the solution after roasting the residue are listed in Table 4.

The percentages of copper and cobalt taken into solution in the 15 minutes following the roasting process were evaluated in order to understand whether there were any changes in copper or cobalt yield between the 2nd and 3rd hours. As seen from Table 4, the yield reaches a maximum in the 3rd hour because sulfatization of the sulfurs present in various valence states takes that long.

The fifth experiment was carried out by adding 50 mL of 96% H_2SO_4 in addition to the other components of the fourth experiment. When the residue obtained was brought to constant weight after subjecting it to the necessary procedures and analyzed, it was found to contain 8.4% S and 40.46% Fe.

The percentages of copper, cobalt, and iron extracted as a result of roasting the residue at 600°C are given in Table 5.

TABLE 5
The Percentages of Cu, Co, and Fe Extracted as a Result of Roasting the Residue at 600°C for Various Times

Roasting time (h)	Percentages of Cu, Co, and Fe that passed into solution			
	% Cu	% Co	Fe (mg/250 mL)	% Fe
2.50	95.1	57.8	36.1	0.90
3.00	98.5	56.9	33.4	0.75
3.50	99.1	56.9	16.2	0.40
4.00	93.0	56.9	8.1	0.20

As seen from Table 5, there was a significant increase in the cobalt yield compared with other experiments. Accordingly, the experiments carried out in order to determine whether more cobalt would be extracted from the residue prepared by bubbling H_2S gas in a medium containing more concentrated H_2SO_4 solution showed that the yield of cobalt did not increase significantly.

All these experiments were replaced by grinding the converter slag under 160 mesh. No increase in the cobalt yield was observed.

In order to increase the yield of cobalt, some experiments were carried out qualitatively by using pure chemicals. The same experiments were also carried out on the residue obtained from the fifth experiment.

In the study carried out with pure compounds, no Co^{2+} extraction was observed when a quantity of pure Co_3O_4 was used. In an experiment performed by passing H_2S gas through two tubes each containing Co_3O_4 + H_2SO_4 and then adding $FeSO_4$ to one of them, it was observed that Co^{2+} ions formed in both solutions.

This can be explained by the following reactions:

$$Co_3O_4 + H_2S(g) + 6H^+ \rightleftharpoons 3Co^{2+} + S + 4H_2O \qquad (4)$$

$$Co_3O_4 + 2Fe^{2+} + 8H^+ \rightleftharpoons 3Co^{2+} + 2Fe^{3+} + 4H_2O \qquad (5)$$

Since the equilibrium constant of Reaction (4) is higher than that of Reaction (5), Reaction (4) produces more Co^{2+} ions.

Following these procedures, two samples, each weighing 50.00 g, were taken, and 50 mL of H_2SO_4 containing 2 and 4 mL of 96% H_2SO_4 respectively were added. The solid–liquid mixtures were bubbled with H_2S obtained from 5 g FeS. The residue obtained was filtered off and made up to 100 mL before copper and cobalt analyses were performed. The concentrations of copper and cobalt extracted to the solution at the end of the first experiment were found to be 13.2 and 0.77 mg/100 mL, respectively. The results in the second experiment were 19.9 mg/100 mL for cobalt and a trace quantity for copper. The pH values of these solutions were 1.7 and 2.6, respectively. The percentages of total cobalt present in the sample passing to solution at the end of the first and second experiments were found to be 12.2 and 18.4.

As understood from the results of these experiments, the percentage of cobalt increases as the acid concentration is increased. This result is in complete compliance with Reaction (4). Also, the second factor, which shifts the equilibrium of Reaction (4) to the right, was found to be increased with increased pressure of H_2S. This requires a high-pressure H_2S tube and a suitable autoclave. No experiments were conducted at different H_2S pressures due to the lack of facilities.

The percentage of copper passed to the solution was found to be negligibly small in both experiments. This was due to the insolubility of Cu_2S ($K_{sp} = 1.2 \times 10^{-49}$). The residues obtained in the first experiments were found to contain 9.92 and 10.1% sulfur, respectively.

The results of the first experiment showed that the percentage of cobalt present in the residue taken into the solution after the first stage and the second stage had been roasted at 600°C for 3 h were 12.2 and 49.0%, respectively. The total percentage of cobalt taken into solution was 61.2. In the second experiment these values were observed to increase to 18.4 and 92.3%, respectively, totaling 70.7%.

In the two experiments where these residues were roasted at 600°C, the maximum extractions of copper were seen to occur at a roasting period of 3 h.

The experiments were also conducted using pure material in order to determine whether $CoSO_4$ occurred in addition to CoS and $CoSO_4$. These were carried out by weighing two samples of Co_3O_4 and adding a stoichiometric quantity of FeS according to Reaction (6) to one of them and a stochiometric quantity of sulfur according to Reaction (7) to the other. These mixtures were kept at 600°C for 3 h after being thoroughly homogenized. The resulting masses were boiled in water. The percentage of cobalt passed to the solution was found to be 20% of the Co_3O_4 originally used.

The reactions taking place were as follows:

$$Co_3O_4 + 4FeS + 8O_2 \rightleftharpoons 3CoSO_4 + 2Fe_2O_3 + SO_2 \tag{6}$$

$$Co_3O_4 + 4S + 5O_2 \rightleftharpoons 3CoSO_4 + SO_2 \tag{7}$$

As seen from these reactions, the conversion of cobalt into $CoSO_4$ not only takes place through conversion of CoS but also occurs through Reactions (6) and (7). The formation of $CoSO_4$ is the overall result of all these reactions. That is why the more the equilibria of the reactions in the first stage are shifted to the right, the higher will be the optimum roasting temperature and the sulfatization efficiency. Thus, some of the Fe present in the slag can be taken into the solution phase as Fe^{2+} if Reactions (1), (2), and (3) in the first stage are carried out in an autoclave.

In the second stage, after providing optimum conditions, cobalt in the slag residue can be extracted with high efficiency.

Because of the above results, studies using the autoclave were carried out. In the first stage, some of the iron was first extracted from the slag residue and then copper and cobalt were extracted from the sulfidized slag residue.

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