

# The Recovery of Copper and Cobalt from Oxidized Copper Ore and Converter Slag

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The aim of this study was to develop a method for obtaining copper and cobalt from oxidized copper ore and converter slag. In order to convert the copper and cobalt into sulfate compounds the main step was to roast the samples obtained by sulfurization and transfer the samples into solution.

First the oxidized copper ore was roasted, followed by the mixture of converter slag and oxidized copper ore. Since the levels of copper and cobalt were low, the sulfurization process was carried out under autoclave conditions. The samples obtained were roasted. The yields of copper and cobalt passed into the solution under optimum conditions were 96.7% and 86.1%, respectively.

## Introduction

Metallurgical methods are usually used to treat ores, in addition to the enriching process by flotation techniques and magnetic separation. A previous article reported that floatation and magnetic separation methods, using slag, did not result in satisfactory extractions from converter slag (1). The means which are used for the recovery of copper and cobalt by hydrometallurgical methods are as follows: leaching with  $H_2SO_4$  under oxygen pressure (2); pyrolysis with  $(NH_4)_2SO_4$  and  $H_2SO_4$  at high temperatures and then leaching with water (3); pyrolysis of the mixture of converter slag and pyrite then dissolving the sample in  $H_2SO_4$  solution (4); pyrolysis of the converter slag with reducing agents such as coal, bituminous coal, fuel oil and then leaching with  $Fe^{+3}$  and  $H_2SO_4$  solutions (5); recovery of copper and zinc by chlorination roasting followed by leaching in cyanide solution (6).

In addition to the methods mentioned above, leaching was also done on oxidized copper ore. It was found that in 240 days, using  $H_2SO_4$  at pH 2 only 20% copper dissolved, and this solution was put into a liquid-liquid extraction column with Lix 622, Acorga M 5397 and 5460. With Acorga M 5640, 95% of the dissolved copper was recovered but was contaminated with cobalt (7). The objective of the study was to separate the copper and cobalt from pyrite residue with chlorine gases. It was determined that 96% of the copper and 46% of the cobalt was dissolved (8). Experiments by some researchers on the direct roasting of converter slag and pyrite mixture showed that 96% copper and 60% cobalt passed into solution (9). From the experiments, it was concluded that getting copper and cobalt using the sulfurizing method would increase the recovery of cobalt providing a closed system in used (10).

In this study, a mixture of oxidized copper ore and converter slag was sulfurized under autoclave

conditions and the samples obtained were roasted. The copper and cobalt passed into solution as sulfate compounds.

## Materials and Method

The oxidized copper ore and converter slag used in this study were obtained from the Ergani Mining Co. in Turkey. These samples were ground to 90 mesh Tyler and dried at 110°C for one day.

The composition of Cu, Co, Fe and S in converter slag were determined to be 2.14%, 0.376 %, 50.3 % and 2.92%, respectively. The oxidized slag contained 1.98% Cu, 0.142% Co and 21.33% S. All analyses were carried out by using an atomic absorption spectrometer (Varian Techtron 1200). The sulfur was determined by oxidizing it to sulfate and precipitating the sulfate as BaSO<sub>4</sub> (11). The following procedures were used to extract copper and cobalt from oxidized copper ore and converter slag.

**1♣.** Roasting the oxidized copper ore

**2♣.** Roasting with different ratios of converter slag and oxidized copper ore

**3♣♣.** Sulfurizing the samples (Oxidized copper ore and converter slag) under autoclave conditions, followed by roasting and then leaching with water.

The sulfurization process was carried out in a 1-L Teflon reactor which was placed in a 1.3-L autoclave.

♣ Direct roasting process

♣♣ Roasting the samples obtained by sulphurization in the autoclave.

## Result and Discussion

### Direct Roasting Process♣

Oxidized copper ore and mixtures in different ratios of oxidized copper to converter slag were roasted at 600°C for different lengths of time and consequently the ratios copper and cobalt which passed into solution were determined. For the roasting process, 10g samples were taken. The mass obtained at the end of the roasting process was dissolved in water and the solution was diluted to 250mL. The percentages of Cu and Co which passed into solution after roasting were determined to be 84% and 70%, respectively. Then, different ratios of converter slag and oxidized copper ore mixture were roasted and the percentages of copper and cobalt which passed into solution were determined to be 94% and 43% respectively.

Then, the experiments were carried out by increasing the ratios of oxidized copper ore. The percentages of Cu and Co were determined to be 85% and 50% respectively.

It was observed that the yield of copper decreased while the yield of cobalt increased.

### Roasting the Samples Obtained by Sulfurization in the autoclave



In this part of the study, various amounts of the mixture of oxidized copper ore, converter slag, FeS and H<sub>2</sub>SO<sub>4</sub> were reacted under autoclave conditions and the solid samples obtained were roasted. Then, the values of copper and cobalt which passed into solution were determined. The amounts of substance used in

the sulfurization process are shown in Table 1 and the values of copper and cobalt transferred solution after roasting the samples obtained by sulfurization are shown in Table 2.

**Table 1.** The Amounts Used In Sulfurization Process

Experiment	Oxidized Copper Ore(g)	Converter Slag(g)	FeS(g)	96% H <sub>2</sub> SO <sub>4</sub>	Solution(mL)
E <sub>1</sub>	300.00	-	10.00	65	425
E <sub>2</sub>	175.00	225.00	20.00	130	750
E <sub>3</sub>	175.00	200.00	20.00	130	750
E <sub>4</sub>	100.00	100.00	10.00	65	400
E <sub>5</sub>	125.00	100.00	10.00	65	400
E <sub>6</sub>	150.00	100.00	10.00	65	400
E <sub>7</sub>	150.00	100.00	15.00	65	400
E <sub>8</sub>	150.00	100.00	20.00	65	400
E <sub>9</sub>	150.00	100.00	20.00	65	600
E <sub>10</sub>	150.00	100.00	15.00	65	500
E <sub>11</sub>	150.00	100.00	15.00	65	500
E <sub>12</sub>	150.00	100.00	10.00	65	500
E <sub>13</sub>	150.00	100.00	10.00	65	600

In the first experiment the oxidized copper ore was sulfurized under autoclave conditions. Even from the data of experiment 1 shown in Table 2, it can be seen that sulfurization compared with direct roasting causes about a 10% increase. In the following experiments, the mixture of oxidized copper ore and converter slag were sulfurized under autoclave conditions. In the second and third experiments the amount of converter slag was changed. A comparison of the data in A<sub>2</sub> (see table 1 for conditions) with those in E<sub>3</sub> shows that greater amounts of copper and cobalt passed into solution with processes applied in E<sub>3</sub> than with those in E<sub>2</sub>. In E<sub>4</sub>, E<sub>5</sub> and E<sub>6</sub> experiments the amount of oxidized copper ore was changed. While E<sub>4</sub>, E<sub>5</sub> and E<sub>6</sub> are compared, it is clear than E<sub>6</sub> conditions are more effective for cobalt to be passed into solution.

Then, the studies were carried out with 150g of oxidized copper ore and 100g of converter slag. In E<sub>7</sub> and E<sub>8</sub>, H<sub>2</sub>SO<sub>4</sub> and the solid/liquid ratio were kept constant but the amount of FeS was changed. When E<sub>7</sub> and E<sub>8</sub> are compared, it can be seen that there was no significant difference between copper and cobalt. Then, the solid/liquid ratio was changed as in E<sub>9</sub>, causing an increase in the amount of copper which passed into solution but that of cobalt did not change. The values of iron were also given in this experiment. Although the amount of Fe is only shown in E<sub>9</sub>, it is the same in all other experiments. Since the greater amount of copper passed into solution in E<sub>9</sub>, E<sub>10</sub> and E<sub>11</sub> only solid/liquid ratios and 15g of FeS were employed for sulfurization. When E<sub>7</sub>, E<sub>10</sub> and E<sub>11</sub> were compared, as the amount of liquid in the sulfurizing process was increased, there was also an increase in the amounts of copper and cobalt passed into solution. In E<sub>12</sub> and E<sub>13</sub> 10g of FeS was used in the sulfurization process and when the results of the other experiments were compared with E<sub>13</sub>, the amounts of copper and cobalt were highest in E<sub>13</sub>. The autoclave process was repeated twice and the roasting process was repeated three times in E<sub>13</sub>. The results the amount of FeS was less than 10g and the experiments were performed under autoclave conditions. The samples obtained by sulfurization were roasted and it was determined that there was no increase in the amount of copper and cobalt passed into solution. These results are not given in the table.

**Table 2.** Percentages of Cu and Co Passed Into Solution By Roasting at 600°C of Samples Obtained By Sulfurization

Roasting Time (h)	Passed Into Solution								
	Experiment	% Cu	% Co	Experiment	% Cu	% Co	Experiment	% Cu	% Co
1	E <sub>1</sub>	0.5	9.3	E <sub>2</sub>	20.3	19.2	E <sub>3</sub>	7.3	27.4
2		1.9	29.9		67.4	35.0		54.0	47.3
3		41.4	54.0		95.1	46.5		98.0	62.9
4		83.4	69.0		95.1	47.1		98.5	64.8
5		91.5	76.0		88.1	47.0		97.2	64.8
6		86.0	74.7		84.7	46.6		94.7	64.8
1	E <sub>4</sub>	-	-	E <sub>5</sub>	-	-	E <sub>6</sub>	-	-
2		51.8	35.9		43.7	44.7		2.5	21.8
3		90.2	56.5		86.6	61.8		18.4	41.1
4		90.2	59.0		93.9	66.6		76.0	63.0
5		96.4	61.6		93.9	66.6		90.0	68.3
6		92.9	62.9		89.9	66.6		93.9	68.3
7		91.7	62.9		89.9	66.6		91.7	68.3
1	E <sub>7</sub>	7.9	20.2	E <sub>8</sub>	15.0	20.0	E <sub>10</sub>	4.5	16.0
2		34.7	42.6		30.0	40.0		35.9	46.0
3		68.3	60.6		50.0	53.0		58.6	57.5
4		93.4	75.6		78.0	71.0		90.8	75.8
5		87.0	77.2		86.0	76.0		90.9	75.8
6		85.6	78.0		86.0	83.0		91.1	77.9
1	E <sub>11</sub>	2.1	21.5	E <sub>12</sub>	15.1	20.7	E <sub>13</sub>	10.1	22.3
2		27.6	52.7		30.2	35.3		31.3	44.5
3		41.9	54.8		63.6	53.6		63.2	65.7
4		75.7	72.0		81.3	66.7		88.4	79.2
5		95.0	83.2		92.2	74.9		96.7	86.1
6		95.0	83.2		92.2	74.9		96.6	86.1
	E <sub>9</sub>			E <sub>9</sub>	Amount of Fe in solution 250 mL				
1		12.0	23.0		0.025				
2		32.0	44.0		0.05				
3		52.0	59.0		0.08				
4		92.0	78.0		0.02				
5		92.0	78.0		0.02				
6		92.0	82.0		0.02				

Since the oxidized copper ore used in this study can not be enriched by flotation, various hydrometallurgic methods are used in order to obtain copper and cobalt. As the copper and cobalt which exist in the ore can not be dissolved in acid, acidic leaching does not give a positive result. Whereas the method in this study employed to transfer copper and cobalt into solution after being roasted for 6 hours at 600°C yielded 83.8% and 70.0% respectively.

On the other hand, a good result cannot be obtained when the same experiments are performed with mixtures of oxidized copper ore and converter slag. So sulfurization was used under autoclave conditions. A

significant increase in the copper and cobalt yield was observed. The aim of this study was to evaluate the combination of oxidized copper ore and converter slag. Therefore sulfurization was done with the mixture of 100g converter slag, 150g oxidized copper ore, 10g FeS and 600 ml of 65mL-96% H<sub>2</sub>SO<sub>4</sub> solution under autoclave conditions and the sample obtained was roasted for 5 hours at 600°C and it was observed that 96.7% of the copper and 86.1% of the cobalt passed into solution. In this last autoclave experiment 42.04g of Fe<sup>+2</sup> passed into solution (600mL). The sulfurized sample was washed with water so that the volume was 1000mL. 3.57.10<sup>-3</sup>g of copper and 0.02g of cobalt passed into this solution. These values are the equivalent of 0.05% copper and 7.5% cobalt in the mass.

The aim of sulfurization is to convert sulfide compounds of copper and cobalt into spinel and different structures found in ore and converter slag. In the previous study, the cobalt transferred into solution by sulfurization was 57% under atmospheric conditions (1). In this study, since the more effective sulfurizing process was employed, the cobalt transferred into solution was 86.1%. So the yield of cobalt was increased by sulfurization, but during the sulfurization process 7-8% of cobalt passed into solution.

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