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Separation Science and Technology
Publication details, including instructions for authors and subscription information:
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Online publication date: 25 September 2000

To cite this Article Ziyadanoullari, Berrin(2000) 'Recovery of Copper and Cobalt from Concentrate and Converter Slag', Separation Science and Technology, 35: 12, 1963 — 1971

To link to this Article: DOI: 10.1081/SS-100100630

URL: http://dx.doi.org/10.1081/SS-100100630

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SEPARATION SCIENCE AND TECHNOLOGY, **35**(12), pp. 1963–1971, 2000

Recovery of Copper and Cobalt from Concentrate and Converter Slag

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ABSTRACT

This study was designed to recover copper and cobalt hydrometallurgically from an enriched concentrate of flotation and converter slag. Three slag samples collected from the Ergani Copper Co. of Etibank were studied. In order to convert the copper and cobalt into sulfate compounds, samples were roasted after sulfurization and leached with water. The hydrometallurgical process involves sulfurizing the slag and then roasting the samples to form $CuSO_4$ and $CoSO_4$. The roasted samples were treated with water; copper and cobalt were dissolved while any other impurities remained in the solid phase. Very little iron was dissolved; only 0.2–0.3% of the total. The sulfurization experiments were carried out in a closed system and roasted at 600°C for different times to optimize the process. Under optimum conditions almost all of the copper and cobalt were dissolved and recovered in high purity and with high yield.

INTRODUCTION

Pyrometallugic, hydrometallurgical, and electrometallurgical methods have been developed for the production of copper and cobalt from ores. The important studies on the ores can be summarized as follows: Hydrometallurgic studies include leaching with sulfuric acid at atmospheric pressure (1); leaching with H_2SO_4 under oxygen pressure (2); pyrolysis with $(NH_4)_2SO_4$ and H_2SO_4 at high temperature followed by leaching in water (3, 4); pyrolysis of the mixture of converter slag and pyrite, and then dissolving of the sample in H_2SO_4 solution (5); pyrolysis of the converter slag by using reducing agents such as bituminous coal and fuel oil followed by leaching with Fe^{3+} in H_2SO_4 solution (6); recovery of copper and zinc by chlorination roasting (7); leaching with

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cyanide solution to recover copper (8); and recovery of copper and cobalt from converter slag with sulfurization from solution (9). Selected specific studies are described below. The leaching kinetics of covellite (CuS) was investigated in sulfuric acid solution containing chloride. It was determined that 85% of the copper from covellite was leached into 0.5 M H_2SO_4 and 0.5 M NaCl solution at 90°C when O_2 gas was bubbled through the solution for about 6 hours (10). Studies on bioleaching of copper sulfur ores for 360 days were carried out at pH 2 (11). Leaching of calcopyrite in acidic solution was done with various oxidants, and ozone was found to be the best oxidant (12).

In this study converter slag and concantrates were sulfurized under autoclave conditions and the samples obtained were roasted. The copper and cobalt passed into solution as sulfate compounds. In a previous study all of the copper but only 57% of the cobalt were leached after roasting the sulfurized sample (9). The cobalt yield could reach 80% when the sulfurization process was carried out in solution with a closed system.

Sulfurization can be carried out with H_2S pressure under dry conditions for solid–gas reactions. However, when sulfurized samples are roasted and dissolved in water, the amount of cobalt recovered increases. Therefore, this study searched for the best solid–gas sulfurization conditions to maximize cobalt and copper recovery.

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EXPERIMENTAL

This research used enriched ore from flotation and converter slag produced at the Ergani Copper Co. of Etibank (southeast of Anatolia, Turkey). Two samples of the enriched ore and one converter slag were tested.

Analyses showed that the first enriched ore (Sample A) contained 19.6% Cu, 0.26% Co, 30.0% Fe, and 34.0% S; the second enriched ore (Sample B) contained 13.2% Cu, 0.25% Co, 34.0% Fe, and 35.0% S; and the converter slag (Sample C) contained 2.4% Cu, 0.38% Co, 50.30% Fe, and 2.92% S. Samples were roasted in porcelain cruicibles in a Heraus model oven. Analyses of copper, cobalt, and iron were carried out using a Unicam 929 Atomic Absorption Spectrometer, and sulfur was analyzed gravimetrically. The samples were ground to 100 mesh Tyler and dried at 110°C for 24 hours. The study consisted of three steps.

1. Sulfurizing the samples under autoclave conditions. The sulfurization process was carried out with solid–gas interaction in a 1-L Teflon reactor which was placed in a 1.3-L autoclave.
2. Roasting the samples obtained by sulfurization in the autoclave was done in an oven.
3. Leaching with water was used to dissolve the samples obtained from sulfurization.

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Direct Roasting

The experiments compared the values of copper and cobalt leached into solution after direct roasting of samples and after roasting of sulfurized samples. Five grams each of Samples A and Samples B were roasted at 600°C and leached to determine the values of cobalt and copper recovered. Experimental results are given in Table 1.

The maximum values of copper and cobalt leached into solutions without sulfurization were about 70 and 76%, respectively. Although the samples were of the calcopyrite structure and had 34% S, copper and cobalt did not dissolve with high yield. This suggests that the samples may be in a form other than sulfide. To convert copper and cobalt to their sulfides the samples were reacted with the gas in a closed system. A $H_2SO_4 + FeS + H_2O$ mixture was used to produce a $H_2S + H_2O$ gas mixture for the sulfurization process. The various parameters investigated are given below.

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Roasting and Sulfurization of Enriched Ore

Determination of Appropriate Temperature for Sulfurization

In this study, 150 g samples containing 13.2% Cu were sulfurized in a 1-L Teflon reactor which was placed in a 1.3-L autoclave (a closed system) at 110, 115, 120, or 130°C with the mixture of $H_2S + H_2O$ obtained from 25 mL of 96% H_2SO_4 + 25 mL H_2O + 15 g FeS. The sulfurization time was 1 hour, and the sulfurized samples were then roasted at 600°C. The resulting copper and cobalt leaching values are given in Table 2.

When Table 2 is examined it can be seen that Cu and Co readily dissolved from sulfurized samples at 130°C and then roasted at 600°C. The roasting time should be 3 hours.

TABLE 1
Percentages of Cu and Co Solubilized upon Roasting of Samples A and B at 600°C

Roasting time (h)	Leaching from Sample A		Leaching from Sample B	
	% Cu	% Co	% Cu	% Co
1	7.6	18.0	7.5	17.8
2	20.0	30.0	20.0	29.1
3	30.4	50.0	30.4	48.7
4	51.3	65.0	51.3	69.8
5	67.0	70.0	70.9	76.7
6	67.0	60.0	73.2	57.2
7	41.8	58.0	42.8	56.6

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TABLE 2
Percentages of Cu and Co Dissolved upon Roasting at 600°C of Sulfurized Samples at Various Temperature

Roasting time (h)	Leaching from sample sulfurized at 110°C		Leaching from sample sulfurized at 120°C	
	% Cu	% Co	% Cu	% Co
1	3.2	18.8	19.0	11.8
2	18.0	44.5	26.5	19.6
3	25.3	65.7	49.2	33.9
4	32.6	79.4	54.5	36.7
5	57.9	82.5	84.1	69.4
6	67.9	81.3	89.3	75.1
7	59.6	79.2	82.3	75.1
	Leaching from sample sulfurized at 120°C		Leaching from sample sulfurized at 130°C	
	% Cu	% Co	% Cu	% Co
1	4.1	22.5	49.9	60.0
2	16.0	22.8	79.5	80.0
3	94.6	86.9	100.0	95.0
4	80.2	79.6	91.4	95.0
5	87.4	75.0	83.1	100.0
6	73.4	77.1	81.2	99.0
7	72.8	76.9	68.3	100.0

Determination of H_2S Used in Sulfurization Process

In this study, 100, 150, 200, 250, or 300 g from Samples A and B were sulfurized for 1 hour with a mixture of $H_2S + H_2O$ obtained from 25 mL of 96% H_2SO_4 + 25 mL H_2O + 15 g FeS. The sulfurized samples were roasted at 600°C. The dissolved copper and cobalt values are given in Tables 3 and 4.

When the ore's copper content increases, the H_2S should also be increased. For a 100–150 g sample, 6 g H_2S is sufficient.

Determination of Quantity of H_2O for Sulfurization

In this study three different sulfurization processes were tested with Sample B. For this purpose, 100 g samples were treated with either 6 g H_2S + 10 g H_2O, 6 g H_2S + 15 g H_2O, or 6 g H_2S + 25 g H_2O in a closed system at 130°C for 1 hour. The sulfurized samples roasted at 600°C and their leached values are given in Table 5, which shows that the copper and cobalt recovered

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TABLE 3
Percentages of Cu and Co Dissolved after Roasting 600°C: Results from Sulfurization of Sample A

Roasting time (h)	Leaching from treated 100 g sample		Leaching from treated 150 g sample	
	% Cu	% Co	% Cu	% Co
1	8.5	18.0	41.8	59.2
2	46.9	50.9	63.4	84.0
3	92.2	81.6	93.5	93.2
4	99.9	94.9	95.7	95.1
5	90.9	96.9	68.6	100.0
6	84.2	92.2	55.5	99.6
7	76.0	92.2	59.4	100.0
	Leaching from treated 200 g sample		Leaching from treated 250 g sample	
	% Cu	% Co	% Cu	% Co
1	52.2	68.5	41.3	33.7
2	62.7	94.6	47.3	65.5
3	87.9	96.4	88.8	87.8
4	71.3	94.8	69.3	93.7
5	59.6	93.0	50.8	96.1
6	51.8	93.0	47.6	93.3
7	54.5	91.7	45.5	91.8

are maximum for samples sulfurized with the 25 g H_2O + 6 g H_2S mixture and roasted for 4 hours.

Roasting and Sulfurization of Converter Slag

The optimum conditions obtained from enriched ore (Samples A and B) were applied to converter slag (Sample C). In a closed system, 100 g of converter slag was exposed separately to the following gas mixtures at 130°C for 1 hour:

C_1: 5.5 g H_2S + 25 g H_2O
C_2: 5.8 g H_2S + 25 g H_2O
C_3: 6.1 g H_2S + 25 g H_2O
C_4: 6.6 g H_2S + 25 g H_2O
C_5: 6.9 g H_2S + 25 g H_2O
C_6: 7.3 g H_2S + 25 g H_2O

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TABLE 4
Percentages of Cu and Co Dissolved after Roasting at 600°C: Results from Sulfurization of Sample B

Roasting time (h)	Passing to solution from treated 100 g sample		Passing to solution from treated 150 g sample	
	% Cu	% Co	% Cu	% Co
1	10.1	20.0	49.9	60.1
2	54.2	52.0	79.5	80.3
3	95.5	81.0	100.0	95.2
4	98.6	96.0	91.4	95.1
5	97.6	91.0	83.1	100.0
6	84.1	90.0	81.2	99.6
7	76.0	90.0	68.3	100.0
	Passing to solution from treated 200 g sample		Passing to solution from treated 250 g sample	
	% Cu	% Co	% Cu	% Co
1	52.4	69.0	29.6	30.0
2	69.9	90.0	55.3	65.0
3	90.3	96.1	94.84	88.1
4	80.5	95.2	75.4	93.7
5	69.6	93.0	66.6	96.1
6	63.8	93.2	54.02	93.3
7	57.5	90.2	52.0	92.2

The amounts of copper and cobalt dissolved after roasting sulfurized samples at 600°C are presented in Table 6. The amounts of copper and cobalt dissolved after 6 hours were 99.2 and 98.8%, respectively. No significant quantity of iron was dissolved under these conditions.

It was found that the amounts of copper and cobalt dissolved after roasting Sample C_3 at 600°C for 6 hours were 99.2 and 98.8%, respectively. No significant quantity of iron passed into solution under these conditions.

RESULTS AND DISCUSSION

In previous studies converter slag and oxidized copper ore were sulfurized while submerged in solution and then the samples were roasted at 600°C. While copper recovery was high, only approximately 60% of the cobalt was recovered (9). When sulfurization was done in a closed system, the recovery of cobalt reached 80% (13). If the sulfurizing press is done with a gas–solid reaction in a closed system, the recovery of cobalt reaches about 100.0%.

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TABLE 5

Percentages of Cu and Co Dissolved after Roasting at 600°C: Results of Sulfurization with Various Amount of Water Vapor

Roasting time (h)	Leaching from sample treated with 10 g H_2O + 6 g H_2S		Leaching from sample treated with 15 g H_2O + 6 g H_2S		Leaching from sample treated with 25 g H_2O + 6 g H_2S	
	% Cu	% Co	% Cu	% Co	% Cu	% Co
1	15.9	29.8	1.0	20.4	8.5	18.0
2	34.0	51.0	18.9	57.0	46.9	50.9
3	56.74	91.4	65.2	83.6	92.24	81.6
4	59.3	100.0	70.5	80.8	99.92	94.9
5	65.2	95.2	82.7	96.7	90.9	96.86
6	59.8	87.7	71.9	92.6	84.2	92.2
7	63.6	86.7	61.8	93	76.0	92.2

It is possible for a portion of the copper and cobalt to be in forms other than as sulfides. This hypothesis is supported by the low values of copper and cobalt dissolved from different ores by roasting alone (14). From studies with converter slag and reverber slag of the recovery of various copper ores and from the pyrometallurgical recovery of copper it was observed that either the yield did not reach to the expected level or a large amount of iron and other foreign substances passed into the solution. These foreign ions caused great difficulty in the separation of cobalt and copper, and therefore increased the cost greatly. With the application of this method, dissolution of foreign matter, mainly iron, decreased, and the method reduced the disadvantages of other hydrometallurgical methods used to separate copper and cobalt. No matter what the structure of the ore, during recovery of copper and cobalt all elements are converted into metal sulfides. The conversion of sulfides into sulfates required a temperature of 600°C. At this temperature iron sulfate was converted into iron oxides which are not soluble in water, and so less iron passed into solution.

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TABLE 6
Percentages of Cu and Co Dissolved after Sulfurization by H_2S with Various Amounts of Converter Slag and Roasting at 600°C

Roasting time (h)	Percent leached by roasting of sample C_1			Percent leached by roasting of sample C_2		
	% Cu	% Co	% Fe	% Cu	% Co	% Fe
1	15.6	28.5	3.1	16.2	28.6	2.1
2	32.7	40.1	0.9	34.9	43.02	0.8
3	52.5	56.7	8×10^{-3}	56.7	59.1	1×10^{-3}
4	69.7	69.5	—	70.1	72.5	—
5	77.5	79.8	—	82.6	89.6	—
6	82.9	87.6	—	96.7	95.8	—
7	81.7	82.8	—	91.5	93.8	—
	Percent leached by roasting of sample C_3			Percent leached by roasting of sample C_4		
	% Cu	% Co	% Fe	% Cu	% Co	% Fe
1	19.8	30.6	2.3	18.7	29.0	1.9
2	39.6	49.9	0.7	39.2	49.7	0.9
3	59.8	67.6	1×10^{-3}	59.4	65.2	2×10^{-3}
4	74.5	82.6	—	73.6	81.7	—
5	89.9	91.8	—	89.2	89.8	—
6	99.2	98.8	—	98.7	98.4	—
7	97.6	96.5	—	96.2	96.0	—
	Percent leached by roasting of sample C_5			Percent leached by roasting of sample C_6		
	% Cu	% Co	% Fe	% Cu	% Co	% Fe
1	15.7	29.2	2.5	17.6	22.7	1.3
2	29.5	36.8	0.6	3•.6	39.6	0.2
3	52.8	59.7	2.2×10^{-3}	47.7	52.8	1.2×10^{-3}
4	71.6	77.9	—	68.9	77.9	—
5	82.5	87.6	—	82.7	86.2	—
6	95.8	96.8	—	95.4	94.3	—
7	93.1	92.2	—	94.3	93.8	—

An advantage of this method is that no waste materials other than SO_2 are produced. The waste obtained during roasting contained 40–50% Fe and 20–30%% SiO_2. If the amounts of gold and silver in the residue are of economic value, these elements could be recovered since a suitable hydrometallurgical method is available (9). The residues of this process could be used in cement factories as raw materials.

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In this study of the sulfurization of 100–150 g concentrates, the gas formed from a 25 g H_2O + 6 g H_2S mixture was used at 130°C for 1 hour. Under these conditions the amounts of cobalt and copper leached into the solution reached their maximum levels after being roasted at 600°C. The optimum conditions for sulfurization of converter slag by various concentrations of H_2S are similar to those of concentrates. The high yield of copper and cobalt dissolved after roasting samples is better when the sulfurization process is carried out in a solid–gas phase rather than in solution.

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Received by editor January 1996
First revision received August 1996
Second revision received October 1999
Third revision received November 1999

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