

Separation of Copper, Cobalt and Iron in Solution Obtained from Copper Ore

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The aim of this study is to recover copper, cobalt and iron from roasted copper ore which contains copper, cobalt and iron in soluble forms. The solution was evaporated and enriched by copper and the separation process was applied. Basically, copper was separated from the solution by the process of electrolysis, using Pt electrodes at 50-60°C. During the electrolysis process, a constant 2.69 V voltage was applied between electrodes. The remaining solution of electrolysis process was evaporated and a mixture of CoSO_4 , FeSO_4 and H_2SO_4 was remained. In order to separate cobalt and iron ions from the mixture, 96 % of ethyl alcohol solution was used and pure cobalt was left in a solid form of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$.

Key Words: Separation, Purification, Ethyl alcohol, Iron, Cobalt, Copper.

INTRODUCTION

Cobalt is a very strategic and critical metal used in many diverse industrial applications. Processed cobalt is used in medical implants, oil desulphurization and ceramics in the computer industry, each requires high purity (99.8 %) of cathode cobalt¹. Various forms of cobalt including briquettes, cathode (electrolytic cobalt), fines, granules (shot), ingot, powder and rondelles, have been produced and marketed². Cobalt is typically associated with heavy metals such as nickel, zinc and copper which are usually extracted as small quantities. Cobalt is a by-product of non-ferrous metal production from sulfide ores³.

Cobalt is recovered mainly by hydrometallurgical processes. Ores, concentrates, wastes and by-products containing cobalt and copper are subjected to acidic or ammonia leaching^{4,5}. Selection of the leaching and the leaching conditions (such as temperature, air/oxygen pressure, stirring rate) depends on the source and composition of the raw material. In industrial practice, autoclaves are used for metal extraction maximization⁶. Leaching is usually conducted at temperatures 80-95°C and air (oxygen)

pressure around 10-15 atm. These conditions provide 95-100 % of cobalt recovery from various ores (sulphide, arsenic oxide)⁷.

In some cases, especially in ferro-manganese ores leaching, an additional reluctant can be required for cobalt dissolution^{8,9}. Alloys contain significant amount of cobalt as an intermediate product and non-ferrous scraps (with 60 % of cobalt concentration), are magnetic scraps.

A review of the literature shows that a limited number of papers about the recovery of cobalt from alloys are available leached Cu-Co-Fe alloy which was produced from copper slag by using arc furnace reduction method in sulfuric acid¹⁰. The leaching behaviour in sulfuric acid of a metallic alloy matte containing copper, nickel, cobalt, iron, sulfur and carbon has already been investigated¹¹. There are various studies about the anodic dissolution of cobalt alloys slag in sulfuric acid where alloys were prepared from copper converter. Wlodyka¹² investigated electrochemical dissolution of a Co-Ni-Fe-Cu alloy.

A limited data has been reported to describe the leaching behaviour of cobalt alloys in ammonia solutions, although these leachants show some advantages in the leaching of poly metallic materials¹³. The leaching of cobalt is rarely specific as a known fact and separation of co-extracted metals from the leach solution is an important feature for all recovery schemes. Ammonia solutions give the possibility of iron removal during the dissolution step, since the iron is leached into solution in most cases. It is subsequently oxidized by air and gets precipitated as various forms of Fe (III) oxides and/or hydroxides¹⁴. Other metals such as copper, cobalt, nickel are transferred into solution as a soluble ammine complex. However in some industrial processes the lost of cobalt was observed with a recovery level which is less than 50 %. They are attributed to adsorption of cobalt ions on hematite¹⁵ or cobalt co precipitation with iron¹⁶⁻¹⁸.

The separation of copper, cobalt and iron ions from the solution as an easy and economical process is the main purpose of this paper.

EXPERIMENTAL

In this study, a solution of copper, cobalt and iron ions was recovered from the pyrites first by using roasting processes and then by flotation process to enrich the content of the solution. The final product contained 51.40 g/L of Cu²⁺, 5.67 g /L Co²⁺ and 1.64 g/L Fe³⁺ ions.

The experiments were undertaken in a laboratory equipped with instruments for hydrometallurgical operations, including roasting and flotation processes.

The compositions of the solutions and the samples recovered from sulphurized copper ore in water were obtained by using an atomic absorption spectrometer (Unicam 929 AAS). The initial solution consisted of

copper, cobalt and iron ions. Further analyses were also necessary to check the potential existence of As, Sb, Se, Te, Pb, Zn, Bi and Cd contents in the solution. The final solution didn't contain the elements such as As, Sb, Se, Te, Pb, Zn, Bi and Cd. A series of analyses were done to obtain As, Sb and Se, by using Jobin Yvon 24 ICP-AES and Te, Pb, Zn, Bi, Cd by Unicam 929 AAS. The standard solutions used in the analyses were as 1-10 ppm. A laboratory model tunnel furnace (Carbolite) was used for the roasting processes. The chemicals were analytical grade (Merck) and the solutions were prepared by using the deionized water.

RESULTS AND DISCUSSION

Separation of the copper ions from the initial solution: To obtain the solutions saturated with copper ions, the samples containing the copper, cobalt and iron ions were heated. The processed solution was then used in all roasting processes. To separate the copper from the processed solution, the electrolysis technique was used. In the first experiment, it was found that 250 mL of the solution contains 12.85 g Cu^{2+} , 1.42 g Co^{2+} , 0.41 g Fe^{3+} with a measured pH of 2.78. In the electrolysis process, Pt electrodes at 50-60°C were used. The constant applied voltage was 2.69 V DC. The electrical current between electrodes was 0.12A in the beginning but because of the reactions in the solution, this value did not remain constant. The electrolysis process continued till the copper content of the solution was completely eluted. The applied voltage was increased to 3.50 V in the last 15 min and the solution changed into a pink colour whereas the pH value decreased to 0.43. The electrode with the copper collection was analyzed and it was found that there is no cobalt and iron ions left¹⁹⁻²². The solution was subjected to electrolysis and then evaporated. The final product of the evaporation was a mixture of CoSO_4 , FeSO_4 and H_2SO_4 .

Separation of cobalt and iron ions in the mixture after the removal of copper

Roasting of the samples under various conditions and ethyl alcohol extraction: For a detailed examination of the separation process, a copper rich solution was used. 250 mL of the solution contains 12.85 g Cu^{2+} , 1.42 g Co^{2+} and 0.41 g Fe^{3+} . The pH of the solution is 1.55 measured. The electrolysis process was conducted using Pt electrode under 2.69 V potential voltages as described in the previous electrolysis process. The applied voltage was increased to 3.50 V in the last 15 min and then the electrolysis process was ended. After this process the colour of the solution changed to the pink which was blue in the beginning. Copper ions were then removed from the solution and the cobalt and iron ions were left in the solution. The pH value of this solution was measured as 0.53. The solution then evaporated and resulted with a CoSO_4 , FeSO_4 and H_2SO_4

mixture. 2.00 g of the sample was taken from the mixture and roasted for 2 h at 200, 250 and 300°C, respectively. Final roasted samples were mixed with 100 mL of ethyl alcohol and left for 1 h and then filtered. The cobalt and iron ions dissolved in the ethyl alcohol are shown in Table-1.

TABLE-1
EXTRACTION OF SAMPLE OBTAINED FROM CoSO_4 , FeSO_4 AND H_2SO_4 MIXTURE BY ROASTING AT DIFFERENT TEMPERATURE WITH ETHYL ALCOHOL EXTRACTION

Extraction (%)	Roasting temperature (°C)					
	200		250		300	
	Fe	Co	Fe	Co	Fe	Co
Passed to the Solution	86.78	-	74.65	0.76	68.92	0.84
Remained at the solid phase	13.22	100	25.35	99.24	31.80	99.16

The values shown in Table-1 were found not to be satisfactory, experimentation continued in order to see the results of the roasting process at 200 and 225°C, for 2, 3, 4, 5 and 6 h, with an assumption that the process run at 200°C will be more efficient. The samples then were roasted and 0.15 mL of 96 % H_2SO_4 was added and left for 2 h in 50 mL of ethyl alcohol. The analysis results of the samples to obtain Fe and Co amounts are shown in Table-2.

TABLE-2
EXTRACTION OF SAMPLES OBTAINED FROM MIXTURE BY ROASTING AT TWO DIFFERENT TEMPERATURES AFTER ETHYL ALCOHOL EXTRACTION

Roasting period (h)	Temperature (200°C)		Temperature (225°C)	
	Extraction (%)		Extraction (%)	
	Fe	Co	Fe	Co
2	91.28	-	94.80	-
3	92.86	-	95.65	-
4	93.17	-	95.52	0.05
5	84.01	-	92.56	0.18

In order to separate the iron ions from the solid form, cobalt sulfate which did not dissolve in ethyl alcohol at both 200 and 225°C, same procedure was applied for a second time. 0.25 mL of 96 % H_2SO_4 was added to the samples, roasted and left for 2 h in 50 mL of ethyl alcohol. The results of first and second experiments are shown in Table-3.

The results showed that the maximum extraction rate was obtained at 200°C and for 4 h of roasting process.

TABLE-3
EXTRACTION OF SAMPLE OBTAINED FROM MIXTURE BY
ROASTING AT TWO DIFFERENT TEMPERATURE AND DIFFERENT
TIMES WITH ETHYL ALCOHOL

Extraction (%)	Roasting temperature (200°C)							
	Roasting period (h)							
	2		3		4		5	
	Fe	Co	Fe	Co	Fe	Co	Fe	Co
Passed to the solution	98.08	-	98.90	-	99.12	-	98.03	0.50
Remained at the solid phase	1.92	100	1.06	100	0.82	100	1.96	99.50
Extraction (%)	Roasting temperature (225°C)							
	Roasting period (h)							
	2		3		4		5	
	Fe	Co	Fe	Co	Fe	Co	Fe	Co
Passed to the solution	96.68	-	97.69	-	97.03	0.05	94.76	0.19
Remained at the solid phase	3.32	100	2.31	100	2.97	99.95	5.24	99.80

In the next experiment, 0.25, 0.50, 1.0, 1.50 and 2.0 mL of 96 % of H₂SO₄ were added to the 3.00 g of each dissolved solutions and roasted at 200°C for 4 h. The same dissolved solution was also roasted directly without H₂SO₄ addition at 200°C and for 4 h. After the roasting process finished, all the solutions were mixed with 50 mL of ethyl alcohol and left for 2 h (Table-4).

TABLE -4
VALUES FOUND FROM THE EXTRACTION OF SAMPLES WITH
ETHYL ALCOHOL OBTAINED BY ROASTING
THE MIXTURE AT 200°C FOR 4 h

Extraction (%)	96 % of H ₂ SO ₄ added to the CoSO ₄ -FeSO ₄ mixture (mL)											
	No acid		0.25		0.50		1.0		1.50		2.0	
	Fe	Co	Fe	Co	Fe	Co	Fe	Co	Fe	Co	Fe	Co
Passed to the solution	61.82	-	83.68	0.54	94.18	0.98	94.86	2.16	95.28	5.78	95.30	6.15
Remained at the solid phase	38.18	100	16.32	99.46	5.82	99.02	5.14	97.84	4.72	94.22	4.69	93.85

The results shown in Table-5 showed that the addition 96 % of H₂SO₄ and roasting of the mixture did not make a significant change in the iron extraction whereas it created a considerable increase in the amount of cobalt extraction. This change in cobalt amount shows that the oxidation state of cobalt from divalent state to trivalent state creates a better dissolving effect in ethyl alcohol.

In conclusion, to reduce the trivalent cobalt, it was decided to add water into the solution. For this purpose, 0.50 and 2.0 mL of 96 % H₂SO₄ were added to 3.00 g of each solution and roasted at 200°C for 3 h 45 min. After the roasting process, 2.0 mL of water was added to each solution and roasted for 0.5 h. The final solutions then were kept in 50 mL of ethyl alcohol for 2 h (Table- 5).

TABLE-5
VALUES FOUND FROM THE EXTRACTION OF SAMPLES WITH
ETHYL ALCOHOL OBTAINED BY ROASTING MIXTURE IN THE
SAME CONDITIONS AS WELL AS ADDITION OF WATER*

Extraction (%)	0.50 mL of H ₂ SO ₄ addition		2.0 mL of H ₂ SO ₄ addition	
	Fe	Co	Fe	Co
Passed to the solution	97.34	0.11	99.42	0.28
Remained at the solid phase	2.66	99.89	0.58	99.72

*Roasting temperature: 200°C.

*Roasting period: 3 h 45 min + 30 min (after the water addition).

The comparison of Table-5 and Table-6 indicate an important result. The samples resulted from roasting process with the 0.50 mL and 2.0 mL of 96 % H₂SO₄ water addition and the samples resulted from roasting process without water addition were both extracted in ethyl alcohol and the result showed that there was a significant difference in the cobalt amounts dissolved in the solution. It was also observed that the amount of iron dissolved in the solution was increased. Thus, it was concluded that it will be possible to dissolve full amount of iron ions in the solution and to keep the cobalt ions in the solid phase. By taking this conclusion into consideration, 2.0 mL of 96 % H₂SO₄ was added into 3.00 g of three different samples and roasted at 200°C, for 3 h 45 min. Following the roasting process, 2.0, 2.50 and 3.0 mL of water were added consequently and roasted for 0.5 h 50 mL of ethyl alcohol was then added to the final solutions from roasting process and the solutions left for 2 h. The results are shown in Table-6.

TABLE-6
VALUES FOUND FROM THE EXTRACTION OF SAMPLES WITH
ETHYL ALCOHOL OBTAINED BY ADDITION OF WATER
DIFFERENT RATES

Extraction (%)	2.0 mL H ₂ O		2.50 mL H ₂ O		3.0 mL H ₂ O	
	Fe	Co	Fe	Co	Fe	Co
Passed to the solution	99.90	0.20	99.99	-	100	-
Remained at the solid phase	0.10	99.80	0.01	100	-	100

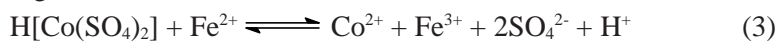
Roasting temperature 200°C.

Roasting period: 3 h 45 min + 30 min (after the water addition).

The reactions occurred during the roasting process with the addition of H₂SO₄ at 200°C are given below:



The new reactions with the addition of water to the produced mixture above are given below:



The reactions above showed that all the cobalt ions in the mixture formed as CoSO₄ and the iron ions as H[Fe(SO₄)₂]. With the addition of ethyl alcohol, the iron ions were dissolved and the cobalt remains as a solid. The analysis of solid phase showed that cobalt was in CoSO₄·7H₂O form.

Then the extraction of mixture with ethyl alcohol after the roasting process for the various durations was undertaken. For this purpose, 2 mL of 96 % H₂SO₄ was added into 3 g of six different samples and roasted at 200°C, for 3 h 45 min. Following the roasting process, 2 mL of water was added and roasted for 0.5 h. Then 50 mL of ethyl alcohol was added to the final solutions of roasting process and the solutions left for 1, 2, 2.5, 3, 3.5 and 4 h consequently. The results are shown in Table-7.

The experiment results showed that the equilibrium occurred in 2 h at room temperature (25°C). The experiments were then continued with 3 g of four different samples at various temperatures and under the same conditions of the previous experiment. The samples were mixed for 1 h at 35, 45, 55 and 60°C temperatures and then extracted. The results are shown in Table-8.

TABLE-7
EXPERIMENTAL RESULTS FOR THE MIXTURE EXTRACTED WITH
THE ETHYL ALCOHOL FOR THE VARIOUS DURATIONS (25°C)

Extraction (%)	Duration for Extraction (h)											
	1.0		2.0		2.5		3.0		3.5		4.0	
	Fe	Co	Fe	Co	Fe	Co	Fe	Co	Fe	Co	Fe	Co
Passed to the solution	97.18	-	99.90	-	99.99	-	99.99	-	99.99	0.08	99.99	0.12
Remained at the solid phase	2.82	100	0.01	100	0.01	100	0.01	100	0.01	99.92	0.01	99.88

TABLE-8
EXPERIMENTAL RESULTS FOR THE MIXTURE EXTRACTED AT
VARIOUS TEMPERATURES WITH 2 mL OF WATER ADDITION*

Extraction (%)	Temperature for the Extraction Process (°C)							
	35		45		55		60	
	Fe	Co	Fe	Co	Fe	Co	Fe	Co
Passed to the solution	99.28	-	99.79	-	99.91	-	99.98	-
Remained at the solid phase	0.72	100	0.21	100	0.09	100	0.02	100

*2 mL of water was added at roasting process.

The experiment showed that the equilibrium occurred in a short time and a higher amount of iron was dissolved in the solution at high temperature. Since the iron was not completely dissolved in the solution, it was concluded that by increasing the amount of added water, it will be possible to dissolve full amount of iron ions. Considering 3 mL of water was added to the solution and the experiment was repeated. The results are shown in Table-9.

The experiments then were continued with 3.00 g of four different samples under the same conditions of the previous experiment except with no acid addition. The solutions were mixed with ethyl alcohol at 35, 45, 55 and 60°C for 1 h and 2.0 and 3.0 mL of water were added consequently. The results are shown in Table-10.

As can be seen in Table-11, the roasting process with no acid addition at 55°C temperature with ethyl alcohol extraction resulted in the dissolving of all iron ions, with the cobalt remaining at the solid phase.

TABLE-9
EXPERIMENTAL RESULTS FOR THE MIXTURE EXTRACTED AT
VARIOUS TEMPERATURES WITH 2 mL OF WATER ADDITION*

Extraction (%)	Temperature for the Extraction Process (°C)							
	35		45		55		60	
	Fe	Co	Fe	Co	Fe	Co	Fe	Co
Passed to the solution	99.34	-	100	-	100	-	100	-
Remained at the solid phase	0.66	100	-	100	-	100	-	100

*3 mL of water was added at roasting process.

TABLE-10
EXPERIMENTAL RESULTS FOR THE MIXTURE EXTRACTED AT
VARIOUS TEMPERATURES

Extraction (%)	2 mL water addition							
	Temperature for the extraction process (°C)							
	35		45		55		60	
	Fe	Co	Fe	Co	Fe	Co	Fe	Co
Passed to solution	96.42	-	97.17	-	99.12	-	99.57	0.87
Remained at the solid phase	3.57	100	2.83	100	0.88	100	0.43	99.13
Extraction (%)	3 mL of water addition (no acid addition)							
	Temperature for the extraction process (°C)							
	35		45		55		60	
	Fe	Co	Fe	Co	Fe	Co	Fe	Co
Passed to solution	96.56	-	97.65	-	100	-	100	-
Remained at the solid phase	3.44	100	2.35	100	-	100	-	100

The next experiment was held for the extraction of the final mixture (Table-10) with ethyl alcohol at 55°C and for various durations. The results are shown in Table-11.

As can be seen in Table-11, extraction process was completed in 1 h. Same experiment was repeated for 3.00 g of mixture with 2.0 mL of ethyl alcohol at 55°C for 1 h and 98.60 % of iron was dissolved in ethyl alcohol, whereas all cobalt ions remained in solid phase. To separate all the iron ions from the cobalt, 3.00 g of mixture was processed with *ca.* 25 mL of 96

% ethyl alcohol and final product did not contain any ions, whereas the cobalt remained in solid form.

The hydrometallurgical method that invested in present studies, it was aimed to recover copper, cobalt iron from copper ore. The copper was separated from the mixture by electrolytic method. By evaporation the pink colour mixture the sample contain CoSO_4 , FeSO_4 and H_2SO_4 were obtained. This sample was roasted, so there was enough H_2SO_4 , therefore more H_2SO_4 was not added to the reaction mixture. By extracting the sample obtained after roasting with ethyl alcohol, the $\text{H}[\text{Fe}(\text{SO}_4)_2]$ and the H_2SO_4 left after roasting were extracted into ethyl alcohol phase, on the other hand cobalt was left in the solid phase as in the form of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ as it can be seen from the values in the Table-11.

TABLE-11
EXPERIMENTAL RESULTS FOR THE MIXTURE EXTRACTED
AT VARIOUS DURATIONS*

Extraction (%)	Extraction duration (min)							
	15		30		45		60	
	Fe	Co	Fe	Co	Fe	Co	Fe	Co
Passed to the solution	85.26	-	96.99	-	99.56	-	100	-
Remained at the solid phase	14.74	100	3.01	100	0.44	100	-	100

*3 mL of water was added at roasting process.

*Averages calculated for data obtained from three independent extraction experiments.

Conclusions

The goal of this study was the recovery of copper, cobalt and iron ions from the copper ore in a simple and economic process. By electrolysis, the copper was separated from the solution with a high purity level. With the evaporation of the roasted solution, a mixture of CoSO_4 , FeSO_4 and H_2SO_4 was transferred into a mixture of CoSO_4 , $\text{H}(\text{Fe}(\text{SO}_4)_2)$ and H_2SO_4 . The extraction of the final mixture by using 96 % of ethyl alcohol at 55°C for 1 h showed that iron and H_2SO_4 dissolved within ethyl alcohol, whereas cobalt remained as a solid in $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ form. The evaporation of ethyl alcohol resulted in $\text{Fe}_2(\text{SO}_4)_3$ and H_2SO_4 mixture. The iron in the mixture was in Fe^{3+} .

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