

COBALT AND COPPER RECOVERY FROM THE ANCIENT FLOTATION TAILINGS BY SELECTIVE SULFATION ROAST - LEACHING PROCESS

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Abstract

The ancient flotation tailings from Lefke, Cyprus, have a potential for non-ferrous metals such as cobalt and copper from more than 9.5 million tons of reserves containing 0.38% Cu, 0.032% Co, and 22.6% Fe. Recovery of cobalt and copper from these tailings can provide great benefits from economic and environmental perspectives. While the ancient tailings were kept long time in storage in dumps, the characteristics of the material has become different from the common Co and Cu bearing ores. In order to extract these valuable metals, a process involving combination of roasting and leaching was applied in this study. Since this process responded to recovery to some extent, an innovative technique of using Na_2SO_4 as a promoter during roasting was proposed. Utilizing of Na_2SO_4 did not provide only higher metal extractions, but also resulted in high selectivity. In the scope of the study, following the determination of the mineralogy and chemical composition of the tailings, certain processes such as direct leaching and sulfation roasting with/without additives before leaching were applied. Since low metal extractions were obtained from direct leaching, a selective sulfation process was applied on the tailings before leaching in order to produce a pregnant solution containing higher amounts of Co and Cu metals by reducing the iron concentration. When sulfation roasting was performed without any additive, the desired selectivity could not be provided, since the sample was considerably oxidized under the atmospheric conditions in the past. Therefore, the usage of Na_2SO_4 as an additive with the amount of 25% at a roasting temperature of 700°C was tested. Consequently, Na_2SO_4 improved the sulfation and resulted in higher cobalt (90.1%) and copper (71.2%) recovery during leaching. Beside this, an improvement with a selective sulfation was obtained by combined effect of Na_2SO_4 addition and temperature, and the iron extraction decreased from 26.1% to 3.9%.

Keywords: Flotation tailings; Cobalt; Copper; Roasting; Selective sulfation; Sodium sulfate

1. Introduction

The rapid depletion of high-grade ores and increasing demand for base metals, such as copper and cobalt, to become secondary raw materials, instead of being discarded as tailings in mineral processing and metallurgical plants, as well as to be seen as important sources for the metal industry. From the economic and environmental perspectives, the application of alternative processes for metal recovery and recycling of secondary raw materials could provide great benefits [1-4]. Physicochemical enrichment methods such as gravity, magnetic separation and flotation are the most important alternatives in the recovery of such secondary sources. However, it is possible to meet some disadvantageous by the application of these methods. That is, changes in the structural and mineralogical properties of such residues lead to changes in the flotation properties of these materials. Therefore,

investigating the surface properties of such secondary sources in detail is an important issue. [5-7]

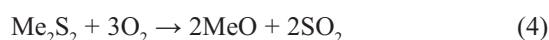
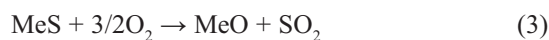
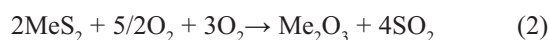
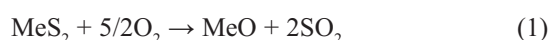
Roasting + hydrometallurgy followed by mineral processing are one of the most applicable processes for the extraction of copper and cobalt from sulfides-bearing ores. After obtaining a sulfide concentrate containing a sufficient grade of cobalt and copper by flotation, a thermal process (roasting) is applied to the concentrate to transform most of the cobalt and copper sulfide to a soluble sulfate, while iron originated from other sulfides is converted to an oxide form, such as Fe_2O_3 and Fe_3O_4 . Thus, the iron remains practically insoluble and can be discarded as tailings from the liquor containing the copper and cobalt metals [8, 9]. As well known, higher Fe concentration in the solution influences the recovery of copper and cobalt from solution negatively in the following process [10, 11]. Solvent extraction and electrolysis are the routes to produce cobalt and copper selectively from pregnant solution obtained from the leaching of

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roasted materials. As a result, the success of production directly depends on the selective sulfation roasting [12].

Roasting is a solid gas reaction that occurs in three main steps. In the first step, metal sulfides are oxidized to metal oxide (Eq. 1-4). In the second step, sulfur dioxide is oxidized to sulfur trioxide (Eq. 5). In addition, this reaction is supported by copper and iron acting as catalysts. Finally, the metal oxides react with sulfur trioxide to form sulfates and basic sulfates (Eq. 6 and 7). Thus, direct sulfation of metal sulfides is also possible, where the O_2 and SO_2 pressure is important for all reactions [8]. Me in equations denotes mainly Cu, Co, and Fe, but also Ni, Ca, and Mg.



During these processes, a number of reactions occur simultaneously, and they frequently influence one another. To explain the sequence of various reactions and products formed, a thermal analysis technique is often employed [13-18]. On the other hand, the thermodynamics of roasting can be expressed by predominance area diagrams or Kellogg

diagrams [19]. These diagrams indicate the most stable species as a function of the partial pressures of SO_2 and O_2 at a given roasting temperature. The stable phases formed during oxidative roasting depend on the specific conditions of the roaster such as the gas composition (O_2 , SO_2 , and SO_3) and temperature. Thermodynamically, the formation of copper, cobalt, and ferrous sulfates is likely to occur at lower temperatures, whereas their oxides are more stable at higher temperatures and at the lower partial pressure of SO_2 and O_2 . The SO_2 level, which is favorable for the sulfation reactions, depends on the sulfur content of the feed material. Related findings in literature have shown that PSO_2 should be higher than 1% v/v to favor the formation of sulfates during the roasting of base metal sulfides [8, 20].

Figure 1 shows the predominance area diagrams in Me-S-O (Me = Fe, Cu, Co) system at 680 °C to predict the prevailing phase equilibria in the roasting process [21]. The marked area shows the region in which the non-ferrous metal sulfates are stable, while the iron sulfate is not. As a result, the roasting conditions should fall within this area in order to achieve the selective sulfation roasting.

Although the majority of research present in the literature [17, 22, 23] is about the chemistry and thermodynamics of the sulfation roasting process using synthetic mixtures as well as natural chalcopryrite concentrates, studies about the thermodynamic and kinetic behavior of low-grade and complex secondary metal sources are very limited. Thus, Ozer et al. (2017) stated that it was not possible to obtain a selective sulfation without any additive between copper and iron in the roasting of tailings that had been stored for a long time and oxidized under atmospheric conditions, at any temperature due to their heterogeneous structure and mineralogical-chemical compositions [24].

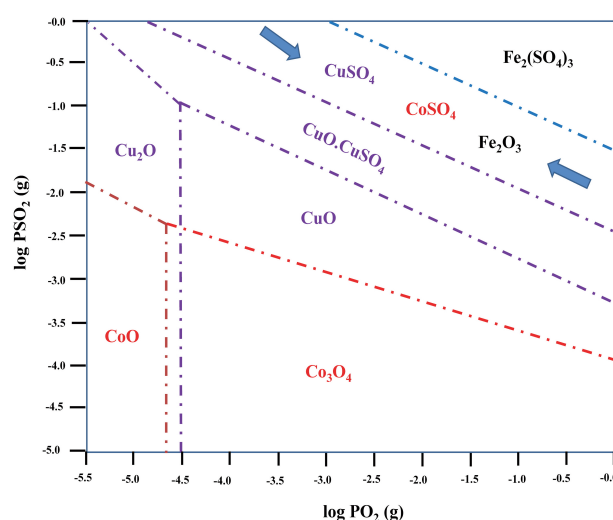


Figure 1. The predominance area diagram in Me-S-O (Me = Fe, Cu, Co) system at 680 °C adapted from [21]

In order to improve the sulfation conditions and obtain higher selectivity, a number of promoters such as Fe_2O_3 , Fe powder, Na_2S , Na_2SO_4 , FeSO_4 , H_2S , H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, FeS_2 , KOH , NaOH , K_2SO_4 , Na_2CO_3 , NH_4Cl , KCl , and others can be used during roasting [23, 25-29]. Especially the effects of alkali sulfates have been studied as additives in the selective sulfation processes of materials containing nonferrous metals such as copper, cobalt, and nickel. It is well known that the amount of SO_3 is a critical factor in the formation of sulfates during roasting. In addition, this type of sulfate compound can act as a reservoir of SO_3 and increase the SO_3 partial pressure in the roaster [28]. Some researchers suggested that Na_2SO_4 can also enhance the degree of sulfation of non-ferrous metals by means of the catalytic effect of Na_2SO_4 during the sulfation of complex sulfide ore as per the following cyclic reaction [10, 30, 31].



It was explained that the catalytic action was due to the formation of sodium pyro-sulfate, which makes the reactant surface porous. This porous surface enhances the diffusion of SO_3 gas [30]. Lu et al. stated that improving the reduction kinetics and the catalytic reaction activity of sodium sulfate depends on its dosage and reduction temperature [32]. While a higher temperature enhances the catalytic activity, increasing the dosage of sodium sulfate accelerates the surface reaction rate and facilitates the formation of a Fe-S solid solution. This solid solution improves the mass transfer and diffusion.

With reference to the information given in the literature, application of the sulfation roasting method was thought as a rational option to extract Cu and Co from ancient flotation tailings in this study. Since these tailings were exposed to atmospheric conditions in the past 100 years, the sulfide characteristics of the material has transformed into oxides, which resulted in a complex mineralogy. It is well known that while the effects of alkali sulfates were investigated as additives on the selective sulfation processes for many minerals in the literature, application of this technique on ancient tailings having a complex mineralogy (oxides, sulfides, etc.) puts this study in a distinctive place. In addition, by means of this study, a solution to overcome the environmental issues regarding to ancient tailings was suggested, while recovering valuable metals from idle materials can be achieved at the same time.

2. Experimental

2.1 Materials

In this study, the ancient flotation tailings from Lefke, Cyprus, were used to recover copper and cobalt. The tailings from mining and mineral processing activities were produced between the years of 1913–1974 and have been stored for a long time under atmospheric conditions in a total of 12 ponds. The color and composition of the tailings are similar in each pond. They are mostly fine-grained material and dark in color, highly acidic in nature with pH below 3.0, and they contain significant amounts of iron, copper, and sulfur, as well as other heavy metals.

For characterization studies, the tailing samples were taken from each pond by coring. To calculate the reserve amount and chemical composition of the materials in the ponds, analyses were performed on the core samples taken from each pond. The amount and composition of the tailings are given in Table 1. It was found that nearly 9.5 million tons of tailings exist in the 12 ponds, with varying chemical contents.

During the experimental studies, the test samples were obtained by blending and homogenizing according to their ratio in each pond and a final representative sample was produced having common characteristics of the different ponds. Blended samples with a maximum particle size of 500 μm were ground to less than 100 μm by a laboratory scale pulverizator (ring mill) and were used in the characterization and experimental studies. The particle size measurements were performed using the Malvern Particle Sizer 2000, which was based on the laser diffraction method. The particle size distribution curve of the ground sample is given in Figure 2.

Also, chemical analysis was performed using the Perkin Elmer-OPTIMA8300 Inductively Coupled Plasma (ICP) method to determine the composition of the representative samples, and the results are presented in Table 2.

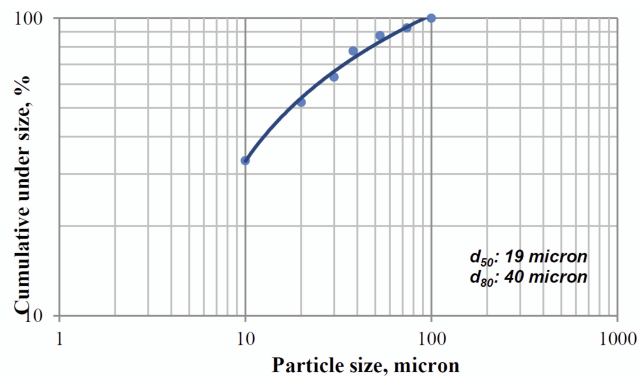
As seen from Table 2, the sample contains 0.38% Cu, 0.032% Co, and 22.6% Fe. Besides the chemical composition, the mineral form of the existing elements is an essential factor for any beneficiation process. Therefore, mineralogy studies have been conducted by Outotec (2009) in order to determine the mineralogical composition and the results are outlined in Table 3.

The mineralogical analysis of the tailings reflects the typical character of materials with oxides (goethite), sulfides (pyrite, chalcopyrite), silicates-quartz, sulfate minerals (iron sulfate, gypsum, and alunite). Sulfates are basically the result of slow oxidation of sulfides during a long pressure time to oxygen and water in the ponds. In this way, metal sulfides change their structures to sulfates. Especially pyrite is transformed to iron sulfates (14.3% of tailing). The presence of sulfides and sulfates in the ancient flotation tailings is also given in Figure 3.



Table 1. Chemical analysis results for each of the ponds

Pond	Material amount, tons	Amount%	Cu	Co	Au	Zn
			%	ppm	ppm	ppm
10	176,846.45	2	0.24	63	0.03	175
11A	307,352.63	4	0.27	150	0.16	232
11B	44,010.17	1	0.17	110	0.15	317
11C	988 353.50	11	0.58	457	0.69	751
12	1 022 837.90	11	0.44	364	0.68	1020
13	749 109.45	8	0.78	446	1.03	750
14	394 503.48	5	0.2	205	0.48	271
15	2 749 165.88	29	0.2	301	0.7	431
16	523 152.32	6	0.19	117	0.27	215
17	676 361.20	7	0.5	270	0.67	357
19	321 846.45	4	0.2	82	0.19	388
21	1 588 602.42	17	0.46	213	0.43	478

**Figure 2.** Particle size distribution curve of the representative sample**Table 2.** Chemical analysis results of blended samples

Element	Cu	Co	Fe	Zn	SiO ₂
Composition %	0.38	0.032	22.6	0.051	24.0

Table 3. Mineral composition of tailings; *All mineralogy work was done by Outotec Research Oy [33]

Mineral composition, %		Distribution of iron, %	
Pyrite	23.8	Pyrite	48.9
Chalcopyrite	1.2	Chalcopyrite	1.6
Galena	0	Fe-sulfate	20.8
Gypsum	8.1	Goethite	28.7
Calcite	1.2	Distribution of calcium, %	
Alunite	7.1	Gypsum	63.4
Fe-sulfate	14.3	Calcite	16.9
Goethite	10.3	Silicates	19.8
Silicates	13	Distribution of sulfur %	
Quartz	16.1	Pyrite	69
Others	4.9	Chalcopyrite	2.2
Total	100	Galena	0
		Gypsum	8.2
		Alunite	6
		Fe-sulfate	14.7

2.2 Methods

In the experimental studies, in order to determine the dissolution behavior of the tailings without any oxidation process, leaching tests were conducted at various sulfuric acid concentrations (0; 10; 20; 40; 80; 160 g/L) and a 1/5 solid liquid ratio (w/w) for 1 hour with 400 rpm mixing rate. In the all experiments, Merck quality with 95-97 % extra purity H_2SO_4 was used. After leaching, the mixture was filtered through a Buchner funnel using a filter paper and the solutions were analyzed using an Atomic Adsorption Spectrometer (AAS). The metal extractions were calculated based on the amount of Cu, Co, and Fe in the solution. The tests were repeated three times to obtain reproducible results with 0.5% accuracy.

In the second part of the study, sulfation roasting experiments were carried out to increase the cobalt and copper extractions by converting the existing sulfides to sulfates. The experiments were performed at different temperatures (500, 600, 650, and 700°C) for a roasting time of 1 hour. The roasting furnace with a constant air inlet was used for the experiments, while the temperature reached up to 1200°C with ± 1 sensitivity.

All the roasting experiments were performed with approximately 10 g of representative sample under atmospheric conditions. First, the test sample was put in a silica plate (crucible), and then placed into furnace once it had reached the required temperature. After roasting, the samples were removed from the furnace, cooled, and placed into beakers. The leaching test was performed using 10 g/L sulfuric acid at 1:5 solid liquid ratio (w/w) for 30 min. After the leaching process, pregnant solution obtained from the filtration step was analyzed and the metal extractions were calculated based on the amount of Cu, Co, and Fe in the solution.

After determining the optimum conditions, finally the effect of sodium sulfate (Na_2SO_4) addition on selective sulfation during the roasting was investigated. Na_2SO_4 used in the experiments is a Merck quality with >99% assay. The samples were prepared by adding various amounts of Na_2SO_4 (0%, 2.5%, 5% 10%, 15%, 20%, and 25%) and were roasted in the roasting furnace at different temperatures (500, 600, and 700°C). In these experiments, the roasting time was 1 hour and the leaching tests were performed on the roasted materials under the same conditions as applied in the previous experiments. The results of the tests were evaluated in terms of metal extractions. In the last group of experiments, the effect of roasting time was also investigated under the optimum conditions (roasting temperature (700°C) and additive amount (25%)).

3. Results and Discussion

The results of mineralogical and chemical analysis on the test samples showed that the target metals were in the form of sulfides and sulfates with 0.38% Cu, 0.032% Co, and 22.6% Fe contents, respectively. The experimental studies were performed in two groups: direct leaching and sulfation roasting before leaching.

3.1 Direct leaching tests

The direct leaching tests were performed with/without H_2SO_4 . The water leaching tests resulted in 54.8% Cu, 39.4 Co, and 6% Fe extractions, which showed that some parts of the sample were easily soluble in water due to the presence of sulfates. In addition, the leaching experiments were also carried out to investigate the effect of the H_2SO_4 concentration, which provided a more acidic medium, on the dissolution of copper and cobalt. The results of the leaching experiments conducted at different concentrations of H_2SO_4 (10, 20, 40, 80, and 160 g/L) and 1:5 solid liquid ratio (w/w) for 1 hour are given in Figure 4.

As seen from the leaching experiment results, although H_2SO_4 was used as a solvent, the cobalt and copper extractions had linear trends even with increasing H_2SO_4 concentrations. This was because only the water-soluble copper and cobalt sulfates dissolved, while the dissolution of metals in the sulfide structure was not possible even at higher acid concentrations. While the increase of H_2SO_4 concentration did not provide any increase in the extractions of copper and cobalt, the iron extraction increased from 6% to 20%. This might be related to the presence of iron sulfates in higher amounts than the other metal sulfates.

As it is well known, metal sulfates easily dissolve even in water environment. However, higher acid concentration is needed in order to dissolve the materials resulting from the partial oxidation of metal sulfides. Therefore, oxidation of sulfide ores during or before the leaching process is a mandatory step that should be applied [34].

3.2 Leaching following roasting

Roasting is an oxidation method before leaching which provides the oxidation of sulfide minerals at a certain temperature and leads to an improved dissolution rate of the metals even in dilute medium [10]. For this purpose, roasting and leaching experiments were performed to recover copper and cobalt. Leaching experiments were conducted on material obtained from the roasting process at various temperatures (400, 500, 600, and 700°C) during 1 hour. The leaching tests were performed under the



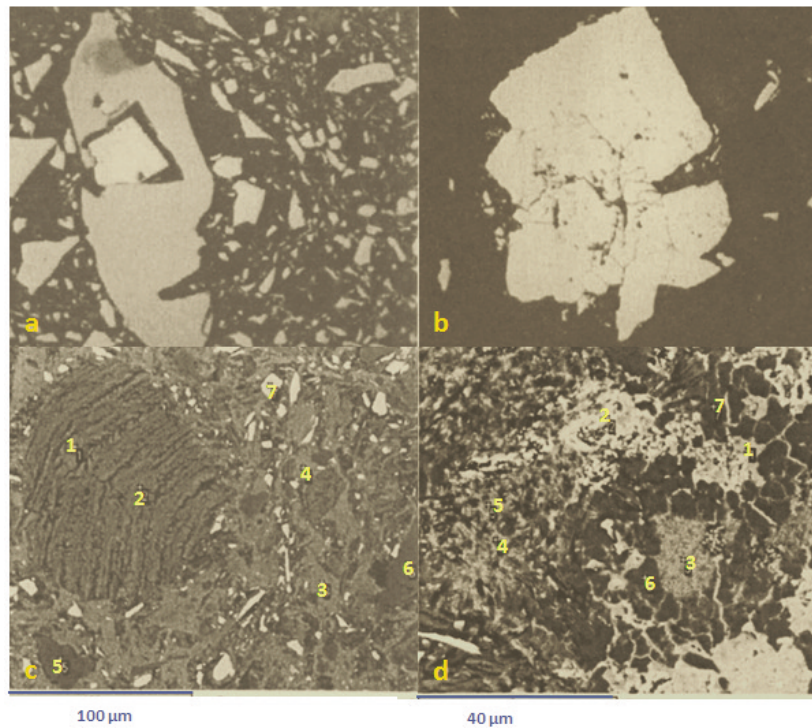


Figure 3. The main sulfides and sulfates occurring in the samples a) pyrite locks chalcopyrite that is rimmed by covellite; b) relatively coarse pyrite grain with fine-grained chalcopyrite inclusions; c) gypsum (1-2), iron sulfate (3-4), agglomerate quartz (5-6), and pyrite (7) grains; d) weathering of sulfides has produced iron oxides with varying Cu contents (1-4), and iron sulfates (5-6) that fill the fractures and envelop quartz (6-7)

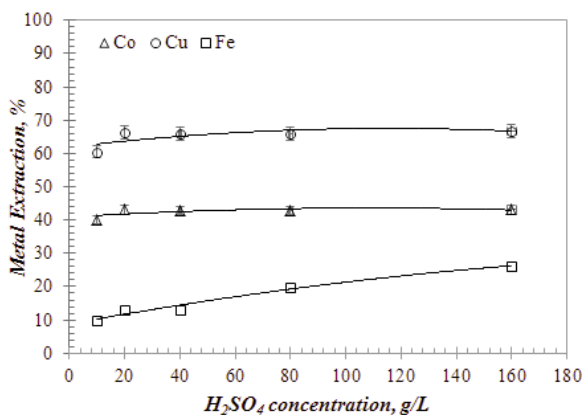


Figure 4. The effect of H₂SO₄ concentration in direct leaching of tailings representative sample

constant conditions previously reported. The changes in extraction for Cu, Co, and Fe are given in Figure 5.

As seen from Figure 5, the effect of the roasting temperature on the metal extraction can be observed in two regions. Copper, cobalt, and iron extractions increase to a maximum, when the roasting temperatures are between 400°C and 500°C. The increase in metal extractions can be related to the sulfation reactions (Eq.10 and 11) of these metals

during the roasting process. On the other hand, the second region contains the roasting temperatures between 500°C and 700°C. Since decomposition of the primary or secondary metal sulfates (Eq.12 and 13) occurs at this temperature range, the copper, cobalt, and iron extractions decrease dramatically.



According to the literature [17, 35], it is possible to provide a selective sulfation between non-ferrous metals such as copper–cobalt and ferrous metals at 650–700°C. Namely, while copper and cobalt are converted to sulfated forms at this temperature, iron remains in the oxide form (Fe₂O₃ and Fe₃O₄). However, in the roasting of these tailings, which had been stored for a long time and oxidized under atmospheric conditions, completely different results were obtained. The cobalt, copper, and iron extractions of the material roasted at 500°C reached the maximum levels of 76.8%, 61.2%, and 26.1%,

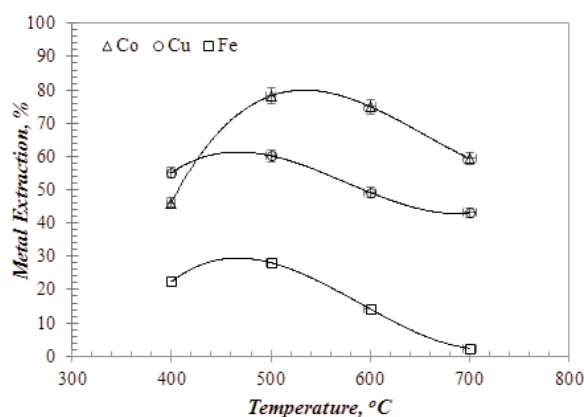


Figure 5. Results of roasting and leaching experiments at different temperatures (Roasting time: 1 hour; 10 g/L sulfuric acid leaching at 1:5 solid/liquids for 30 min)

respectively, while selective sulfation could not be achieved during the roasting. Previous studies showed that these kinds of materials had different roasting behavior due to their mineralogical and chemical structures. It was also concluded that the decomposition of non-ferrous metal sulfates took place at a lower temperature, similar to ferrous sulfates [24].

Hence, it is worth noting that, during the recovery of copper and cobalt from that type of material, the most important issue is to prevent iron dissolution during leaching by selective sulfation [10, 11]. In other words, a high Fe concentration in the pregnant solution negatively influences the recovery of copper and cobalt from the solution in the metal extraction technology, such as solvent extraction. To sum up, the conditions for a selective sulfation should be very precisely controlled during the roasting process to eliminate the effect of iron in the leachate solution. Therefore, in order to identify a solution for this issue, roasting experiments were carried out by the addition of Na_2SO_4 to obtain the highest Cu and Co sulfate formations and provide a selective sulfation during roasting. The leaching of the roasted materials obtained with different amounts of sodium sulfate additions (5%, 10%, 15%, 20%, and 25%) during roasting at the temperatures of 500, 600, 650, and 700°C was conducted at the H_2SO_4 concentration of 10 g/L. The results of the experiment are given in Figure 6.

As seen from Figure 6, in which Cu, Co, and Fe extractions were demonstrated as a result of leaching experiments, the positive effect of Na_2SO_4 was observed at roasting temperatures higher than 600°C. However, no change was observed in the metal extractions at the roasting temperature of 500°C. Thus, it can be concluded that the enhancement of the metal extractions started at 600°C and peaked at 700°C. This result can be attributed to the higher

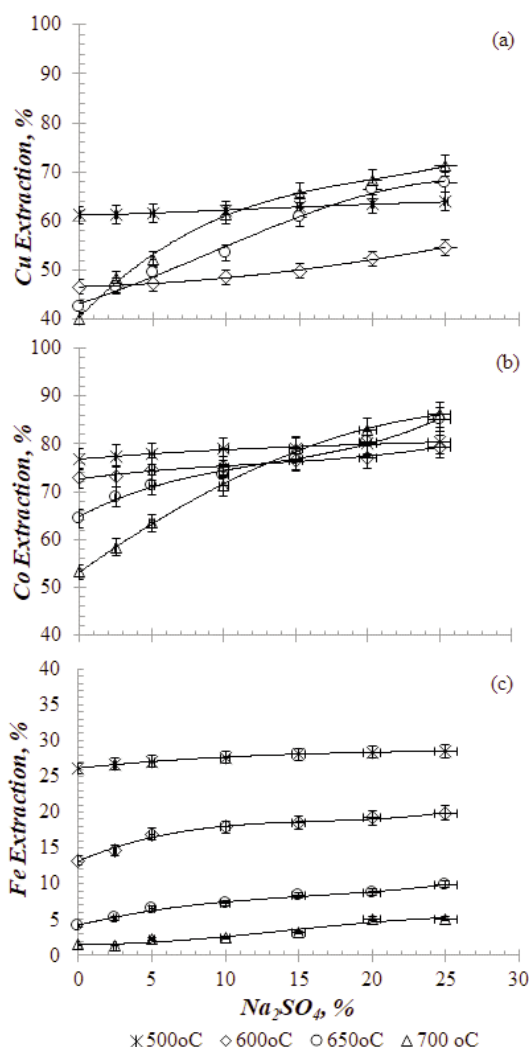


Figure 6. Effect of Na_2SO_4 addition on metal extractions (Roasting time: 1 hour; 10 g/L sulfuric acid leaching at 1:5 solid/liquids for 30 min)

decomposition temperature of Na_2SO_4 . It is known that Na_2SO_4 acts as a reservoir of SO_3 for the sulfation of MeO with the decomposition via the following reactions (Eqs. 14 and 15) [26, 30].



If an assessment is made in terms of the amount of Na_2SO_4 , an increase in metal extraction is obtained with the increase of the amount of additive. The maximum extraction of non-ferrous metals was obtained after roasting at 700°C with 25% Na_2SO_4 addition. Under this condition, 71.2% Cu and 86.2% Co extractions were achieved. On the other hand, the iron extraction was determined as well at 6%. The increase in metal extractions as the effect of roasting up to 700°C was due to the

improvement of sulfation reactions by the addition of Na_2SO_4 , which was explained in the literature by the porosity and catalytic effect on the sulfation reactions [10, 27]. In addition to the sulfation effect of this alkaline salt, the decomposition effect of the higher roasting temperature (700°C) can be also considered as the reason for the selective sulfation (Figure 7).

At the first stage, the metal sulfates, which were at the maximum level at 500°C , decomposed due to increasing the temperature to the value at which Na_2SO_4 started to decompose. Subsequently, re-sulfation started as the effect of SO_3 released from Na_2SO_4 , as shown in Equation 14 and 15. So, it is clear from Figure 7 that the re-sulfation effect of the additive on iron is much smaller than that of Cu and Co metals ($\beta < \alpha$). This, therefore, causes selective sulfation between Cu–Co and Fe during roasting at the temperature of 700°C . As a result of the combination of the high temperature and the effect of Na_2SO_4 , it became possible to obtain a pregnant solution with higher copper–cobalt and lower iron extractions in the leaching experiments after roasting.

The changes in metal extractions depending on the temperature in the presence of 25% Na_2SO_4 are also given in Figure 8. As seen from Figure 8, as a result of the combined effect of Na_2SO_4 addition and temperature, a selective sulfation can be achieved, increasing the Cu and Co extraction while decreasing the Fe extraction.

It is well known from the literature that the roasting time is another factor that influences the selectivity in the sulfation roasting. The longer roasting time is, up to a certain point, the more non-ferrous sulfides to sulfate will convert, and this will lead to an increase of the metal extractions in the leaching step [28]. Therefore, the samples were subjected to roasting tests performed

at 700°C with the addition of 25% Na_2SO_4 for various periods of time. According to the results illustrated in Figure 9, it was clear that the selectivity of sulfation improved, while the iron extraction decreased to 3.9%.

Referring to Figure 9, the maximum cobalt and copper extractions were achieved after the roasting time of 2 hours. Longer roasting periods had a negative effect on the extractions, which tended to decline slowly. Also, Fe extraction showed a continuous decreasing trend with the increase of roasting time. Although the roasting time of 3 hours resulted in the minimum iron extraction, 2 hours can be chosen as the optimal roasting time considering the more economical process with the maximum copper and cobalt extractions. This way, 90.7% of Co, 71.8% of Cu, and 3.9% Fe extractions were achieved with a selective sulfation.

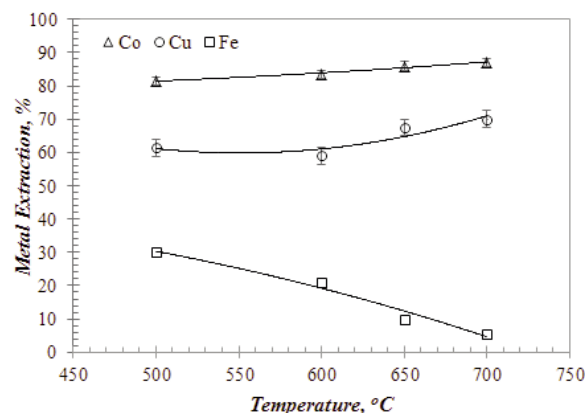


Figure 8. Effect of temperature on metal extractions in the presence of Na_2SO_4 (Roasting time: 1 hour; amount of Na_2SO_4 : 25%; with 10 g/L sulfuric acid leaching at 1:5 solid/liquids for 30 min)

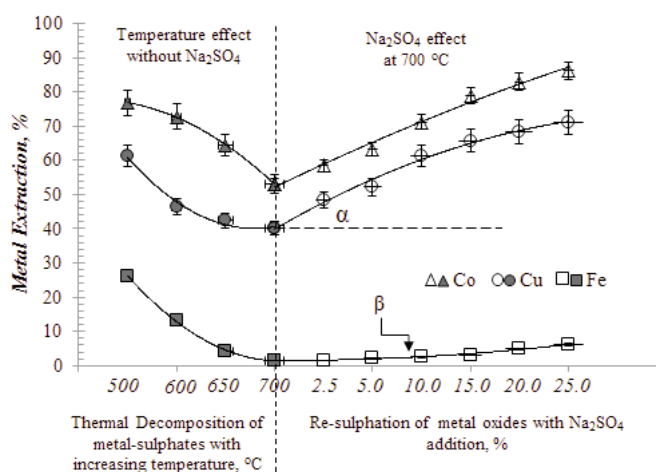


Figure 7. Combined effect of Na_2SO_4 addition and temperature for selective sulfation

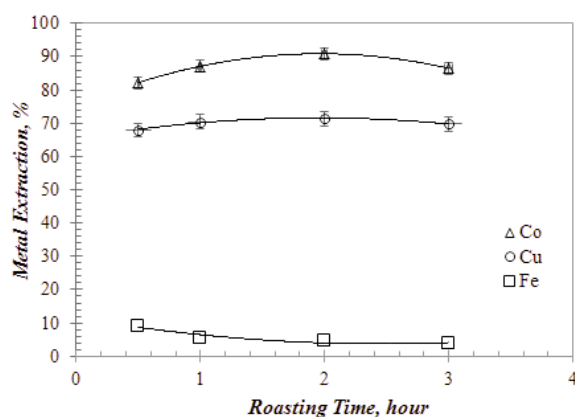


Figure 9. Effect of roasting time on metal extractions in the presence of Na_2SO_4 (Roasting temperature: 700°C ; amount of Na_2SO_4 : 25%; with 10 g/L sulfuric acid leaching at 1:5 solid/liquids for 30 min)

4. Conclusions

The recovery of cobalt and copper by applying direct leaching and selective sulfation-leaching processes to ancient flotation tailings was investigated. The mineralogical and experimental studies showed that the sulfide minerals, especially pyrite, in the tailings, which contain 0.38% Cu, 0.032% Co, and 22.6% Fe, changed their structures to sulfate because of slow oxidation during a long pressure time to oxygen and water in the ponds. The direct leaching with water resulted in only 54.8% of Cu, 39.4% of Co and 6.0% of Fe extractions due to the presence of metal sulfates in the tailing. On the other hand, the fact that the copper and cobalt minerals were not in an oxidized form at an adequate level caused the copper and cobalt extractions to remain at low levels during leaching with sulfuric acid (65.6% Cu and 44.0% Co), while iron extraction went up from 6% to 23%.

To provide the maximum Co and Cu extractions with minimum Fe extraction in the pregnant solution, a sulfation roasting process was carried out before leaching. However, it was not possible to obtain a desired leach solution with low iron concentration. Selective sulfation could not be achieved in the roasting of this kind of tailing due to the origin of the material. Na_2SO_4 was then chosen as an additive to improve the selective sulfation in the last section and was indicated as a promoter which led to an increase in the Co and Cu concentration in the pregnant solution after the roasting+leaching process, as well as decreasing the iron concentration. Extractions of 71.8% of Cu, 90.7% of Co, and 3.9% of Fe were obtained from roasting with 25% Na_2SO_4 at the temperature of 700°C during 2 hours of roasting. Evaluating all the results, it can be stated that two main factors created the selective sulfation at the temperature of 700°C . One of them was the

temperature effect, which caused a decrease in the metal extraction by increasing the temperature to this point. The second was an additive effect, which led to the re-sulfation of metal oxides with Na_2SO_4 . Thus, extractions of 90.7% of Co, 71.8% of Cu, and 3.9% Fe were achieved.

Based on the results achieved in this study, the significant role of Na_2SO_4 was proposed for the extraction of Cu and Co with a high selectivity against Fe. To reveal the structural transformations, detailed experimental study was conducted related to the thermal decompositions. It was found that the enhancement of the metal extractions started at 600°C and peaked at 700°C , since the decomposition temperature of Na_2SO_4 was relatively high. At this temperature, Na_2SO_4 acted as a SO_3 reservoir for a reaction with Cu and Co minerals leaving Fe in the oxide form. Consequently, in the recovery of non-ferrous metals from the oxidized tailings, Na_2SO_4 can be used as a promoter additive in the roasting process to provide a selective sulfation.

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DOBIJANJE KOBALTA I BAKRA IZ VRLO STARE FLOTACIJSKE JALOVINE POSTUPKOM SELEKTIVNOG ŽARENJA-LUŽENJA U SULFATNOJ SREDINI

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Apstrakt

Vrlo stara flotacijska jalovina iz Lefke na Kipru ima potencijal da postane resurs za dobijanje obojenih metala kao što su kobalt i bakar zbog toga što postoji više od 9,5 miliona tona rezervi koje sadrže 0,38% Cu, 0,032% Co, kao i 22,6% Fe. Dobijanje kobalta i bakra iz ove jalovine može mnogo doprineti na ekonomskom planu, kao i iz ugla zaštite životne sredine. Zbog toga što se ova stara jalovina dugo vremena čuvala na deponijama, karakteristike ove jalovine su postale drugačije od onih koje imaju rude koje sadrže kobalt i bakar. Da bi se ovi vredni metali izdvojili, tokom ovog istraživanja je primenjen postupak koji uključuje prženje i luženje. Zbog činjenice da je ovaj postupak dao delimične rezultate, uvedena je nova tehnika gde je Na₂SO₄ korišćen kao aktivator tokom postupka prženja. Korišćenje Na₂SO₄ nije dovelo do samo do veće ekstrakcije metala, već je prouzrokovalo i veću selektivnost. U okviru ovog istraživanja, nakon utvrđivanja mineralnog i hemijskog sastava jalovine, primenjeni su određeni postupci, kao što su direktno luženje i sulfatizacija prženja sa ili bez aditiva, pre nego što je primenjen postupak luženja. Pošto su dobijene male količine metala prilikom direktnog luženja, na jalovinu je primenjen postupak selektivne sulfatizacije pre postupka luženja da bi se dobio rastvor bogat kobaltom i bakrom sa manjom koncentracijom gvožđa. Kada je sproveden postupak sulfatizacionog prženja bez aditiva nije postignuta željena selektivnost zbog toga što je uzorak oksidirao pod atmosferskim uticajem u prošlosti. Zbog toga je korišćen Na₂SO₄ kao aditiv gde je činio 25% ukupne količine prilikom prženja na temperaturi od 700°C. Kao posledica toga, Na₂SO₄ je poboljšao sulfatizaciju i dobila se veća količina kobalta (90.1%) i bakra (71.2%) tokom postupka luženja. Pored toga, postignuta je i bolja selektivna sulfatizacija zbog korišćenja Na₂SO₄ kao aditiva i temperature, a ekstrakcija gvožđa je smanjena sa 26,1% na 3,9%.

Ključne reči: Flotacijska jalovina; Kobalt; Bakar; Prženje; Selektivna sulfatizacija; Natrijum sulfat

