

Recovery of metal values from copper smelter slags by roasting with pyrite

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ABSTRACT

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Sulphation roasting of primary and secondary copper slags has been carried out to facilitate the dissolution of copper, nickel, cobalt, zinc and iron. The process comprised preroasting of the ground slag followed by roasting with pyrite and then leaching with water. The effects of the roasting and leaching conditions on the recovery of the metal values were explored.

While a significant amount of copper solubilization was achieved by direct roasting of sulphidic primary slags, roasting with added pyrite increased the recovery. This technique also enabled the copper to be recovered from a secondary smelting slag. Under optimum conditions, more than 95% of copper could be recovered by only a limited recovery of cobalt, nickel and zinc could be achieved by roasting the preroasted slag with pyrite at 550°C for 1 h with a 0.25 pyrite/slag ratio. Around 2% of the iron in the slags was extracted into the leach solutions. An increase in the roasted temperature resulted in reduced iron contamination but the recovery of copper was also reduced. However, aeration seemed to be an appropriate way to reduce the iron contamination of the leach solutions.

INTRODUCTION

The rapid depletion of high grade ores and increasing demand for base metals has prompted intensive investigations into metal recovery from low-grade ores and metallurgical waste materials. Slags discarded in copper plants contain significant amounts of copper and other valuable metals.

Copper recovery is generally achieved by pyrometallurgical routes. For example, re-cycling converter slags with high copper content to the reverberatory furnace, or using a separate slag refining furnace. However, in this process some copper is invariably left behind in the residual slags. It is well recognized that the addition of converter slag to the reverberatory furnace

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makes the operation complicated and increases the slag volume, resulting in an increase in the overall copper loss.

A great deal of effort is being made to investigate the possibility of copper recovery from slags by wet chemical methods. The hydrometallurgical methods employed have included cyanidation [1], atmospheric or pressure acid leaching [2,3], ferric chloride or ferric sulphate leaching [4–6], ammonia–ammonium carbonate leaching [6] and ammonium sulphate or sulphuric acid roasting [7].

It is well known that the roasting of copper sulphide concentrates produces a calcine suitable for hydrometallurgical processing [8,9] and it was therefore decided to assess the possibility of a roasting water leaching system for recovering copper and other valuable metals from the primary smelter slags in which some of the copper is present in the sulphide form. Subsequently, an attempt was made to recover the copper from a secondary smelting slag by roasting the material together with the pyritic waste from a copper ore beneficiation plant. Using this technique it may be possible to leach valuable metals from the calcines and simultaneously to produce H_2SO_4 from the gaseous product.

This paper describes the results from the sulphation roasting of primary and secondary slags with and without the addition of pyrite, followed by water leaching of the calcines.

EXPERIMENTAL METHOD

Materials

Most of the tests were performed on slags obtained from the primary copper plant at Ergani, Turkey, and the IMI James Bridge secondary metal plant at Walsall, England. After optimization of the experimental conditions a number of tests were also carried out on the slag from the Rokana primary copper converter in Zambia. The pyrite used in the study was obtained from the Ergani ore-benefication plant.

The slag samples were crushed and ground in the laboratory and the pyrite was obtained as fine particles. The $-63\ \mu\text{m}$ fraction of pyrite and various fractions of the slags were used in the experiments. The chemical compositions and the phases identified in the slags by X-ray diffraction are given in Table 1 and 2, respectively. The slags, namely two samples from the converter at Ergani, one sample from the Ergani reverberatory furnace, and one from the James Bridge reverberatory furnace, were labelled as slags 1 to 4, respectively.

Procedure

For the sulphation roasting study, 5 g of slag or slag–pyrite mixture in a silica dish were placed in a muffle furnace which was preheated to the re-

TABLE 1

Chemical analyses of slags and pyrite

Constituent	Amount				
	Slag 1	Slag 2	Slag 3	Slag 4	Pyrite
Cu (%)	4.10	10.10	1.70	3.40	2570
Co (mg/kg)	3950	3390	1830	—	2430
Ni (mg/kg)	660	405	435	4780	240
Zn (mg/kg)	980	1150	1370	9.70	250
Fe (%)	52.10	43.50	40.40	21.90	41.30
CaO (%)	0.40	0.70	4.60	2.70	3.45
MgO (%)	2.40	2.80	4.30	3.70	0.90
Al ₂ O ₃ (%)	0.65	0.40	2.40	8.50	4.20
SiO ₂ (%)	19.60	21.85	31.00	31.20	1.25
S (%)	3.60	5.40	2.50	—	43.35

TABLE 2

Phases identified in slags and pyrite. (Fayalite: Fe₂SiO₄, Magnesian-Fayalite: (Fe,Mg)₂SiO₄, Pyrite: FeS₂, Magnetite: Fe₃O₄, Chalcopyrite: CuFeS₂, Cuprite: Cu₂O, Copper: Cu)

Slag 1	Slag 2	Slag 3	Slag 4	Pyrite
Fayalite	Fayalite	Fayalite	Magnesian-fayalite	Pyrite
Magnetite	Magnetite		Cuprite	
Chalcopyrite	Chalcopyrite		Copper	
	Copper			

quired temperature. After roasting, the sample was removed from the furnace, cooled and placed in a conical flask. The required amount of water was added and the flask was shaken mechanically. For studying the effect of temperature on leaching, the flasks were shaken in a thermostatically controlled water bath; the one exception was the test carried out at boiling point, when the flask content was stirred magnetically under reflux. The pulp was filtered through a Buchner funnel using a Whatman No. 42 filter paper, the leachates were acidified to prevent precipitation, and the solutions were analyzed.

The experimental variables, such as roasting temperature; pyrite/slag ratio; durations of preroasting of slag and roasting with pyrite; and the leaching conditions, were optimized to maximize the recovery of the copper, cobalt, nickel and zinc values with minimum iron contamination. Most of the experiments were carried out in duplicate, and the results generally agreed within $\pm 3\%$.

Methods of Analysis

The slag samples were analyzed by atomic absorption spectrophotometer utilizing the lithium metaborate fusion–nitric acid dissolution route [10], and also by X-ray fluorescence. The pyrite was analyzed by the same atomic absorption spectrophotometric method after roasting at 750°C to remove the sulphur. The sulphur contents of the samples were determined by barium sulphate gravimetric method [11].

The leachates were analyzed for the metal values by atomic absorption spectrophotometry after appropriate dilutions. The amount of metal values extracted was calculated from the metal values in the leach solutions and the compositions of the slag or slag–pyrite mixtures. The slag samples and their roasting products were subjected to X-ray diffraction analysis in order to identify various phases present or formed during roasting.

RESULTS AND DISCUSSION

Initial experiments showed that copper could be leached from the roasted primary converter and reverberatory slags, whereas pyrite addition was necessary for the secondary reverberatory slag. Since certain metals are present in their sulphide form in the slag or the pyrite, sulphation may occur, resulting in the production of sulphates which are readily soluble in water. The sulphation mechanism for the components of slag and pyrite may be explained by the following chemical reactions [12].



If the metal had formed several sulphides and oxides, additional equations would have to be considered for the formation of MeS_2 , Me_2O_3 , and $\text{Me}_2(\text{SO}_4)_3$, etc. Basic sulphates such as $\text{MeO} \cdot \text{MeSO}_4$ may also exist [12].

Initially, the primary slags and the secondary slag with added pyrite (with 0.10 pyrite/slag ratio) were roasted at different temperatures (400–750°C) for 2 h and the calcines obtained were leached with water at a pulp density of 10% for 15 min at room temperature. The effect of increasing the roasting temperature on the extraction of metals is shown in Fig. 1. The rate of extraction of copper increased up to 550°C and thereafter decreased. At this temperature a substantial amount of copper could be extracted while iron solubilization was low. It can be seen that iron contamination can be reduced to values less than 1% by increasing the roasting temperature, but unfortunately,

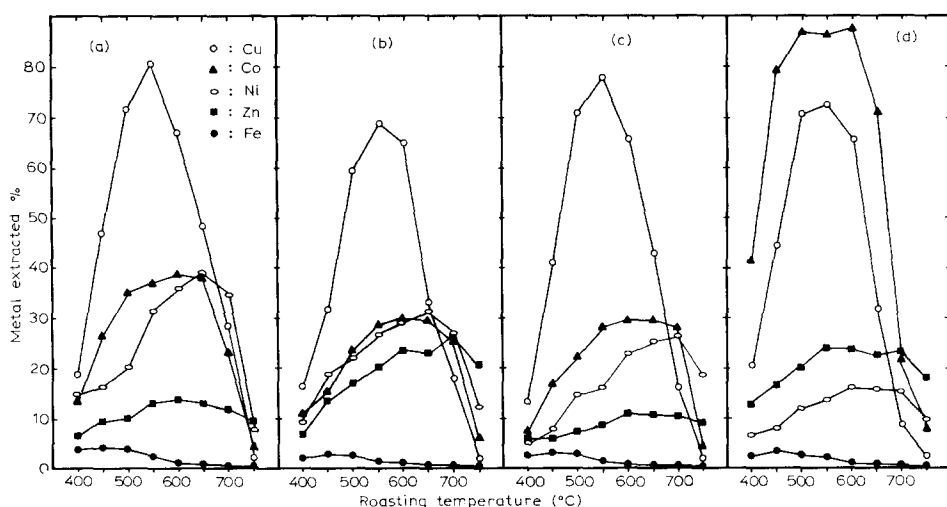
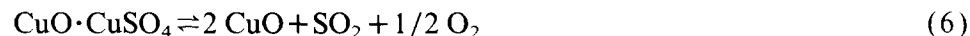


Fig. 1. The effect of roasting temperature on extraction of metals: Particle size: $-63\ \mu\text{m}$; roasting time: 120 min; leaching time: 15 min; leaching temperature: ambient; pulp density: 10% solid. a, b. Ergani primary converter slags (slag 1 and 2). c. Ergani primary reverberatory slag (slag 3). d. James Bridge secondary reverberatory slag (slag 4) + pyrite (pyrite/slag ratio, 0.10).

the rate of copper extraction is then significantly reduced. On the other hand, the amount of cobalt extracted from primary slags was relatively low. High extraction was obtained from the secondary slag-pyrite mixture but, in this case, the cobalt originated from the pyrite. The nickel and zinc recoveries were also relatively low, being significantly reduced as the temperature was increased above 700°C .

It is apparent that the results were highly temperature-dependent, the extraction values reaching an optimum at about 550°C . The decreased metal recoveries at higher temperatures can be attributed to the decomposition of metal sulphates, that is, to the shift of the equilibrium in eqs. (3) and (4) to the left. A chalcopyrite roasting study [13], indicated that decomposition could take place through the basic copper sulphate. Thus, the following reactions may occur:



Copper oxysulphate and its further decomposition product, copper oxide, have limited solubility in water [13]. There is also the possibility that ferrite may be formed (7):



Other metals may also undergo similar processes. The decomposition temperatures of iron, copper, cobalt, nickel and zinc sulphates have been quoted

as 480, 650, 735, 848 and 600°C, respectively [14]. XRD studies have confirmed that CuSO_4 was formed in the primary converter slag, and the secondary slag-pyrite mixture, on heating to 500–600°C. In addition, a spinel-type compound (CuFe_2O_4) was identified in the samples heated above 700°C.

In addition, although leach solutions obtained from calcines were weakly acidic, pH values of solutions were increased by increasing the roasting temperature. For example, the pH for the leachate of the calcine obtained from the James Bridge slag-pyrite mixture was 2.6 at 450°C; while values were more than 5.0 in the case of roasting at 600°C. This may also explain the decomposition of, or weak tendency for, formation of sulphates at higher temperatures, so that such sulphates produce acid in aqueous solutions. Additionally, the lower values of extracted iron of calcines roasted at higher temperatures may be attributed to the hydrolysis of iron(III) ions which precipitate above pH 3.2 [15]. Thus, in the later experiments it was decided to roast the mixtures at 550°C, which seemed to be an optimum.

The rate of copper extraction seems to be dependent on the sulphur content of the slag. For this reason a series of experiments were carried out with selected slags (1 and 4) varying the amount of pyrite added. The results given in Fig. 2 shows that the recovery of copper increased by increasing the amount of pyrite added up to a pyrite/slag ratio of 0.25; thereafter, no appreciable increase in the copper recovery was found. For example, 88% of the copper could be extracted from the mixture of primary slag and pyrite (pyrite/slag ratio: 0.25) whereas the extraction value was about 80% for the original primary slag. The same values for the secondary slag were 78% and 0%, respec-

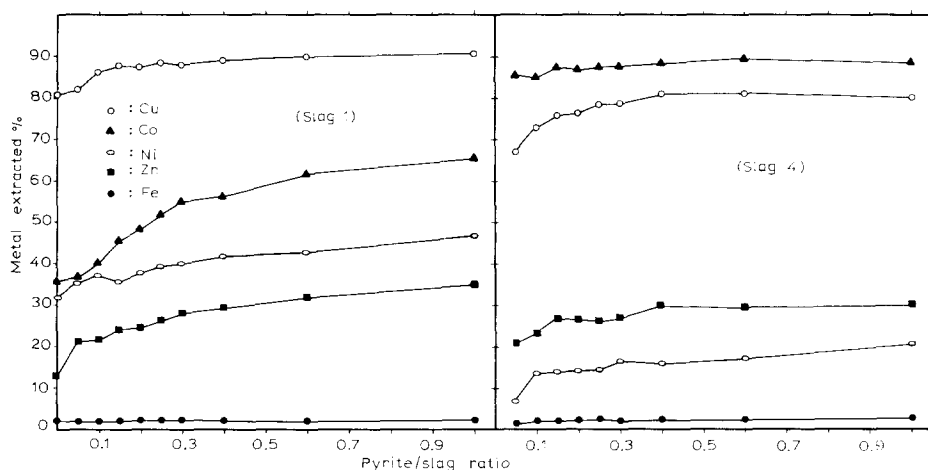


Fig. 2. The effect of pyrite/slag ratio on extraction of metals from slags 1 and 4. (Particle size: $-63\ \mu\text{m}$; roasting at 550°C for 120 min; leaching time: 15 min; leaching temperature: ambient; pulp density: 10% solid.)

tively. On the other hand, most of the cobalt recovered from slag 1 probably originated in the pyrite. The James Bridge slag did not originally contain any cobalt, and about 90% of the cobalt was recovered from the pyrite. The nickel and zinc recoveries were relatively low, and the amount of iron extracted was about 2–3%.

These results show that the primary slags having original sulphur could be sulphated to a significant degree by roasting, but extra sulphur was necessary for further sulphation. The copper in the secondary slag could be efficiently sulphated on roasting together with pyrite. In the sulphation process, the metal oxide matrix of slag probably plays a catalytic role.

The effect of the roasting time on the rate of metal extraction from slags is shown in Fig. 3. The effect of preroasting the slag, when metallic copper is likely to be converted into the oxidic form, was also studied. The rates of metal extraction from the preroasted slags are summarized in Table 3. If the values shown in Table 3 and Fig. 3 are compared, it can be concluded that preroasting considerably improves the extraction rate. For example, over 95% of the copper could be extracted from both the slags roasted with pyrite for 60 min after preroasting for 60 min; while values less than 90% were obtained in the case of roasting for 120 min with pyrite. Preroasting also improved the extraction of cobalt but a significant proportion still remained undissolved from slag 1. This may be attributed to the fact that the cobalt is mostly present in the iron oxide matrix. This also applies to nickel. However, zinc is probably present in the silicate phase because its recovery, like that of iron, and nickel, was not significantly affected by preroasting. Since the results were

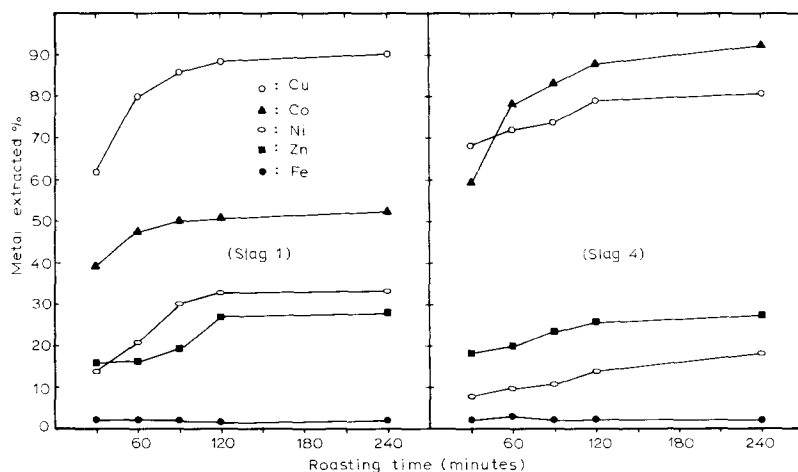


Fig. 3. The effect of roasting time on extraction of metals from slags 1 and 4. (Particle size: $-63 \mu\text{m}$; pyrite/slag ratio: 0.25; roasting temperature: 550°C ; leaching time: 15 min; leaching temperature: ambient; pulp density: 10% solid.)

TABLE 3

Effect of preroasting on metal extraction from slags 1 and 4. (Preroasting at 550°C; roasting at 550°C; pyrite/slag ratio: 0.25; leaching time: 15 min; leaching temperature: ambient; pulp density: 10% solid)

Preroasting time (min)	Roasting time after adding pyrite (min)	Metals extracted %									
		Slag 1					Slag 4				
		Cu	Co	Ni	Zn	Fe	Cu	Co	Ni	Zn	Fe
30	—	58.4	21.2	19.5	9.9	2.6	—	—	—	—	—
30	30	86.5	52.6	23.9	21.4	2.3	84.1	94.2	13.1	24.6	1.7
30	60	92.5	54.7	30.5	26.9	2.4	90.6	97.2	17.3	27.8	1.6
30	90	94.9	56.3	35.8	28.0	2.9	93.0	96.4	19.2	29.1	1.8
30	210	95.5	58.0	37.1	29.1	2.4	96.3	98.0	20.7	29.1	1.6
60	—	75.9	28.6	25.4	13.6	2.0	—	—	—	—	—
60	30	89.2	55.8	32.2	26.7	2.1	87.4	95.4	17.6	28.3	1.4
60	60	95.8	58.5	35.1	28.8	2.2	96.7	98.6	20.0	29.2	1.7
60	180	97.0	57.9	36.3	28.5	2.7	98.5	98.4	22.2	31.0	1.4
120	—	80.3	36.2	32.5	17.4	1.7	—	—	—	—	—
240	—	78.6	37.3	30.2	19.7	2.0	—	—	—	—	—

TABLE 4

Effect of particle size on metal extraction from slags 1 and 4. (Preroasting for 60 min at 550°C; roasting for 60 min at 550°C; pyrite/slag ratio: 0.25; leaching time: 15 min; leaching temperature: ambient; pulp density, 10% solid)

Fractions (μm)	Metals extracted %									
	Slag 1					Slag 4				
	Cu	Co	Ni	Zn	Fe	Cu	Co	Ni	Zn	Fe
250–180	40.8	21.1	11.9	14.7	1.9	29.8	95.9	8.5	11.9	1.4
180–125	53.2	26.4	19.5	18.5	2.3	40.6	97.5	10.0	14.1	1.7
125–90	69.9	36.4	24.6	19.1	2.3	52.9	96.4	15.9	19.3	1.8
90–63	83.4	42.1	35.0	25.4	2.7	74.1	98.0	17.4	23.6	1.6
–63	95.8	58.5	35.1	28.8	2.2	96.7	98.6	20.0	29.2	1.7

promising, further studies on other variables were carried out by roasting the slag for two, 60-minute periods, firstly on its own and then with pyrite.

The effect of the particle size of the fractions is presented in Table 4. As expected, the recovery generally increased with decreasing particle size. Copper recovery values of 75–80% would be expected for the $-100\ \mu\text{m}$ fraction.

For the studies of leaching parameters, only the extraction values for copper, cobalt and iron were considered in connection with the experiments performed with slag 1. The results are given in Table 5 and Figs. 4 and 5. From

TABLE 5

Effect of leaching temperature on metal extraction from slag 1. (Pyrite/slag ratio: 0.25; particle size: $-63\ \mu\text{m}$; pre-roasting of slag at 550°C for 60 min; roasting of slag-pyrite mixture at 550°C for 60 min; leaching time: 15 min; pulp density: 10% solid)

Temperature ($^\circ\text{C}$)	Metals extracted %		
	Cu	Co	Fe
Room temperature	95.8	58.5	2.2
40	94.7	59.1	3.0
60	96.4	61.8	2.7
80	95.3	60.2	2.9
Boiling point	96.2	63.4	3.1

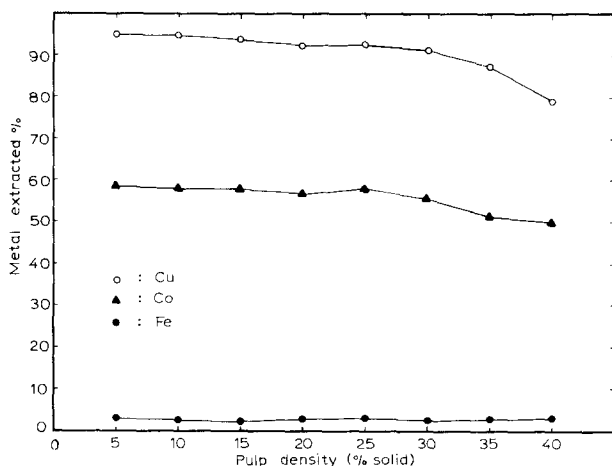


Fig. 4. The effect of pulp density on extraction of metals from slag 1. (Particle size: $-63\ \mu\text{m}$; pyrite/slag ratio: 0.25; pre-roasting of slag: 550°C for 60 min; roasting of slag-pyrite mixture: 550°C for 60 min; leaching time: 15 min; leaching temperature: ambient.)

Table 5 it can be seen that no advantage is gained by increasing the leaching temperature. Recoveries did not differ very much up to a pulp density of 25%, and thereafter the extraction efficiency decreased (Fig. 4). About 90% of the copper and 55% of the cobalt were recovered in less than 5 min (Fig. 5). About 3% of the total iron was extracted. It is therefore clearly demonstrated that leaching under these mild conditions results in good recovery of the copper with relatively low amounts of iron in the leachates. Increased leaching temperature and extended leaching time did not significantly influence the recovery of metals, which confirms the fact that the solid state reactions are the controlling step of the total process investigated.

Since a precipitate formed in some leachates which were unacidified, ex-

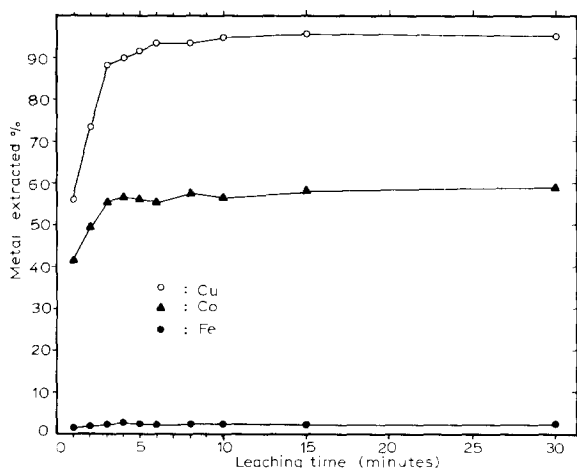


Fig. 5. The effect of leaching time on extraction of metals from slag 1. (Particle size: $-63\ \mu\text{m}$; pyrite/slag ratio: 0.25; preroasting of slag: 550°C for 60 min; roasting of slag-pyrite mixture: 550°C for 60 min; leaching temperature: ambient; pulp density: 10% solid.)

periments were also carried out in order to remove the iron by air entrainment. More than half of the iron content of leachates could be precipitated in this way without significant copper and cobalt loss. This may be explained by oxidation and hydrolysis of the iron, the pH of the leachates being in the range 3.8–4.0.

The optimum conditions described above were applied to other slags, and also to the Rokana primary converter slag, which contained 2.60% cobalt. The copper recoveries were found to be satisfactory, and a limited amount of the cobalt could also be extracted. For the Rokana slag, the copper and cobalt recoveries were 88.5% and 43.6%, respectively.

The results of this study have shown that the roasting of copper slags with pyrite, followed by water leaching of the calcines obtained, is a good method for copper recovery, but only a proportion of the cobalt, nickel and zinc is extracted. Additionally, the cobalt in the pyrite seems to be extracted efficiently.

CONCLUSION

It has been shown that primary smelter slags containing sulphur can be roasted to produce calcines from which some of the metal values can be extracted. Pyrite addition increases the recovery of copper from these slags and also makes it possible to extract copper from secondary slags.

The roasting temperature proved to be the most important parameter, but above certain temperatures recovery of the metals decreased. Preliminary oxidizing roasting was found to be beneficial. Because they are probably present

in the iron oxide and/or silicate matrix, only a proportion of the cobalt, nickel and zinc could be extracted; copper extraction, however, was nearly complete. The oxidic matrix of slags may be an important factor in the sulphation process, acting as a catalyst. Leaching of the product with water results in a high copper recovery. The iron solubilization is relatively low, and iron can be further removed by aeration.

Suitable conditions for roasting appear to be: a preroasting of the slag for 60 min at 550°C; roasting of preroasted slag-pyrite mixture (pyrite/slag ratio=0.25) for 60 min at 550°C; and leaching with water for about 15 min at a pulp density of 10% at room temperature. By using these conditions more than 95% of the copper could be recovered from both the Ergani primary converter slag and the James Bridge secondary smelter slag. More than 98% of the cobalt in the pyrite added to the James Bridge slag was extracted. The extraction values for cobalt, nickel and zinc were from the Ergani converter slag 58, 35 and 29%, respectively. Iron contamination was around 2% but aeration could be used to reduce this value to half.

In conclusion, if the pyritic waste of a copper ore beneficiation plant is roasted with primary or secondary slags, copper, cobalt contained in pyrite can be efficiently extracted from the calcines.

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