

Technical Note

Metal recovery from copper converter slag by roasting with ferric sulphate

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Abstract

A study of the recovery of copper, cobalt, nickel and zinc from copper converter slag by roasting with ferric sulphate is reported. Roasting of converter slag with ferric sulphate, followed by leaching with water, was carried out in order to bring the metal values into solution. For 500°C roasting temperature, 120 min roasting time and $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}/\text{slag} = 1$ ratio, recoveries of copper, cobalt, nickel and zinc were about 93%; 38%; 13% and 59%, respectively. Higher extraction yields could be achieved with a higher ratio of $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}/\text{slag}$ for copper and zinc, whereas cobalt and nickel could not be extracted in acceptable yields. Using H_2SO_4 in the leaching process markedly improves the metal recoveries.

1. Introduction

It is well known that even in the most efficient pyrometallurgical method for the extraction of copper, the slag obtained from the converters always contains a considerable amount of copper. An alternative approach to the slag cleaning methods is to process the slag through hydrometallurgical routes. Metal recovery studies have been focused mainly on leaching processes using ferric chloride with or without prior reduction [1,2], sulphuric acid with or without pressure [3–5], ferric sulphate [6], ammonia [6,7] and cyanide [8,9]. Copper recovery through slag flotation has also been investigated [10]. Various combined sulphatizing processes, such as roasting with or

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without pyrite and leaching [11,12], roasting with ammonium sulphate and sulphuric acid and leaching [13,14], have been studied. In a patent work [15], the recovery of the metal values from reverberatory slag by roasting with ferrous sulphate was reported.

When iron sulphate is heated to temperatures exceeding 480°C, it decomposes yielding SO₃ and/or a mixture of SO₂ and O₂ [16,17]. In this study, an attempt has been made to recover metal values from converter slag by roasting with ferric sulphate, the gaseous product of decomposition, which may cause sulphation of metal constituents. For this purpose, copper converter slag was subjected to roasting with ferric sulphate under different conditions and calcines obtained were leached with water and sulphuric acid solutions.

2. Experimental

The copper converter slag used in this study was obtained from the Etibank Ergani Copper Works at Maden, Turkey. The slag sample was crushed in jaw and roll crushers and ground in a ball mill and then sieved. The fraction of under 74 µm size was used in experiments. Fe₂(SO₄)₃ · xH₂O was used as sulphatizing agent. The chemical analysis of Fe₂(SO₄)₃ · xH₂O showed that it contained about 79% Fe₂(SO₄)₃.

An appropriate amount of ferric sulphate was blended with 5 g of slag. The mixtures were placed in a porcelain dish and roasted in a muffle furnace preheated to the required temperature. Leaching was carried out in the cooled dishes containing calcines by magnetic stirring of the solution. In the runs undertaken to examine the effect of roasting conditions, water leaching was carried out under standardized conditions at 25°C, in a pulp density of 20% solids and for a stirring time of 30 min. For the leaching with H₂SO₄, different conditions were applied.

The experiments were performed in duplicate and the mean values were considered. In order to ascertain the reproducibility of results, a group of experiments were repeated a number of times and the results were found to vary within ±5%.

The slag samples were analyzed with atomic absorption spectrophotometer by using the lithium metaborate fusion–nitric acid dissolution route [18]. The sulphur content of converter slag was determined by barium sulphate gravimetric method [19]. A representative sample of slag was subjected to X-ray diffraction analysis to find its composition. Extracts were analyzed by atomic absorption spectrophotometry for Cu, Co, Ni and Zn. Iron in the extracts was estimated by complexometric titration [19].

3. Results and discussion

The chemical composition of copper converter slag is given in Table 1. Fayalite (Fe₂SiO₄), magnetite (Fe₃O₄) and covellite (CuS) phases were identified in the slag sample by X-ray analysis.

The effect of roasting temperature on metal extractions and iron contents of extracts are shown in Fig. 1. The considerable amount of dissolved metals from the calcine shows that slag constituents can be sulphated by the SO₃ (or SO₂ + O₂ mixture), which

Table 1
Chemical composition of converter slag

Constituents					
Fe	Cu	Co	Ni	Zn	S
52.0%	2.60%	3600 mg/kg	450 mg/kg	4250 mg/kg	4.90%

are the decomposition products of ferric sulphate. The decrease in the iron content of water extracts with roasting temperature confirms the decomposition of ferric sulphate. As seen from Fig. 1, copper recovery increased with the roasting temperature up to 500–550°C and thereafter decreased with a further increase in temperature. The recoveries of cobalt, nickel and zinc, however, are similarly affected at noticeably higher temperatures. This may be due to the higher decomposition temperatures of copper, cobalt, nickel and zinc sulphates (which are 650; 735; 848 and 600°C [17], respectively). The decrease in recovery at higher temperatures may be due to the escape of SO_3 , whereby there is insufficient retention time for sulphation. In addition, the formation of

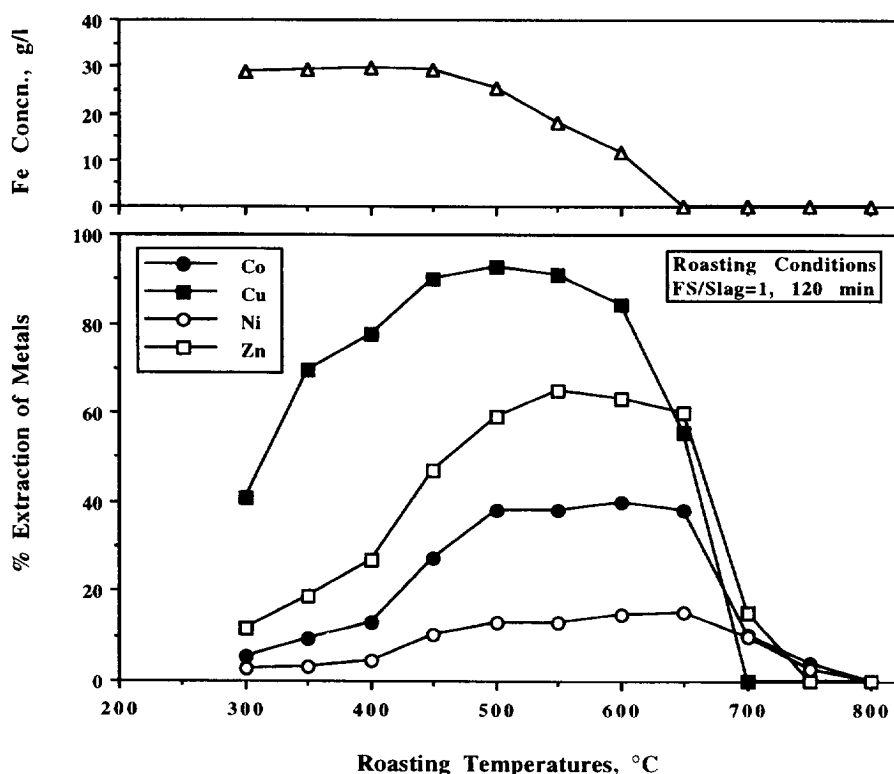


Fig. 1. Effect of roasting temperature on the recovery of metals by leaching the calcine of converter slag–ferric sulphate mixture and iron contents of extracts. Leaching conditions: 20% solid, 30 min, 25°C.

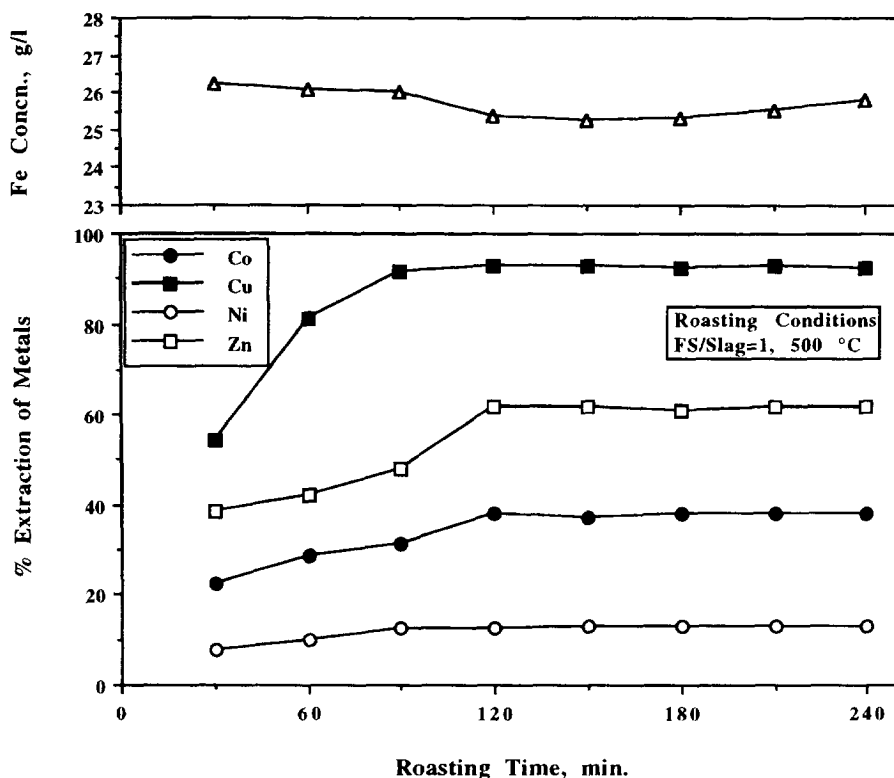
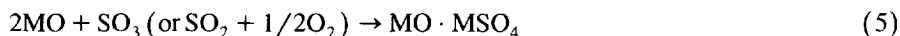
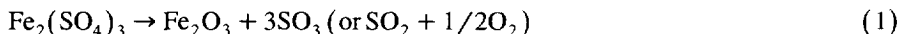


Fig. 2. Effect of roasting time on the recovery of metals by leaching the calcine of converter slag–ferric sulphate mixture and iron contents of extracts. Leaching conditions: 20% solid, 30 min, 25°C.

insoluble compounds such as oxysulphates and/or spinel type compounds (i.e. ferrites) at higher temperatures may be considered as another reason for the decreasing recovery. Decomposition and sulphation reactions can be represented by:



where M = metals.

Since the best results were obtained at 500°C, studies on the effects of roasting time and the amount of sulphating agent were undertaken at this temperature. Fig. 2 shows the effect of the former parameter. Metal extractions attained a maximum within a roasting period of 120 min.

The effect of changing the amount of ferric sulphate used in the roasting with slag is shown in Fig. 3. The copper extraction yield rose to about 95% by increasing the ratio of

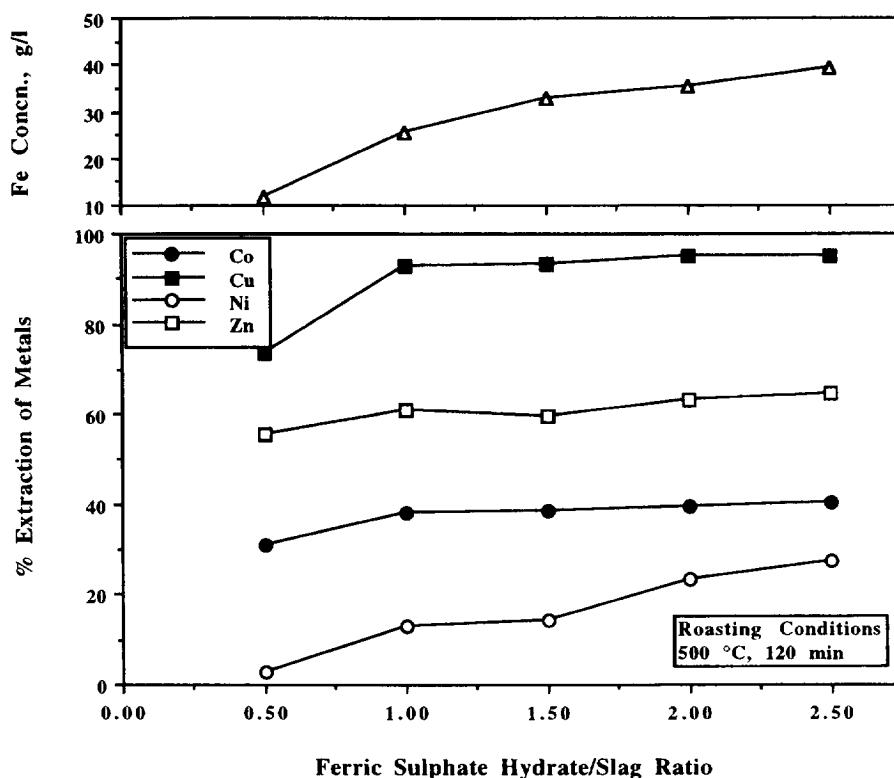


Fig. 3. Effect of ferric sulphate on the recovery of metals by leaching the calcine of slag-ferric sulphate mixture and iron contents of extracts. Leaching conditions: 20% solid, 30 min, 25°C.

$\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ /slag to 2.5, whereas cobalt, nickel and zinc recoveries obtained were limited to about 40%; 27% and 65%, respectively.

Considering that roasting the slag with ferric sulphate may cause structure change, such as the formation of oxysulphates, a series of H_2SO_4 leaching experiments were performed. For this purpose, the calcine obtained by roasting the slag with ferric sulphate at 650°C was subjected to leaching with sulphuric acid in varying amounts. As seen from Table 2, the extraction yields of metals may increase under severe leaching conditions. The limited values of cobalt and nickel recoveries found in these runs show that the cobalt and nickel are mostly in magnetite and fayalite matrices. Copper and zinc can be extracted almost completely, whereas the yields of cobalt and nickel are 69% and 57%.

4. Conclusions

It was found that roasting the converter slag with ferric sulphate caused the sulphation of slag constituents. Results obtained from roasting the slag with $\text{Fe}_2(\text{SO}_4)_3 \cdot$

Table 2

Extraction of metals and iron content of extracts found under different conditions

H ₂ SO ₄	Leaching time	Metal extraction (%)				Fe concentration
(g/kg calcine)	(h)	Co	Cu	Ni	Zn	(g/l)
Leaching temperature 25°C						
0	1	38.20	55.80	15.35	60.06	0.18
500	1	41.50	76.61	21.16	63.04	0.74
500	2	43.97	88.46	29.50	72.40	1.01
500	4	48.25	93.04	33.42	80.19	1.27
1000	1	44.88	83.65	26.05	66.45	1.40
1000	2	50.35	90.30	29.85	81.00	1.92
1000	4	56.80	95.80	37.22	87.25	2.75
Leaching temperature 75°C						
0	1	38.43	68.09	20.13	60.90	0.56
500	1	43.19	93.67	27.43	65.04	1.54
500	2	52.55	95.90	33.00	79.77	2.37
500	4	64.07	98.31	43.14	83.60	3.30
1000	1	56.90	95.61	41.29	81.62	5.04
1000	2	67.17	95.78	53.70	90.10	5.74
1000	4	69.09	98.31	57.33	92.64	6.70

Roasting conditions: 650°C for 120 min.; ferric sulphate/slag ratio: 1.0. All leaching experiments were performed at a pulp density of 20% solid.

xH₂O and leaching the calcine with water showed that 93% of copper could be recovered. However, cobalt and nickel could not be extracted in acceptable yields through this route. Using sulphuric acid solutions in the leaching of calcine could markedly improve the cobalt and nickel recoveries. It seems to be necessary to break the oxide and silicate phases for a further increase in the yields.

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