



# A study on the sulphuric acid leaching of copper converter slag in the presence of dichromate

H.S. Altundogan<sup>a,\*</sup>, M. Boyrazli<sup>b</sup>, F. Tumen<sup>a</sup>

<sup>a</sup> Department of Chemical Engineering, Firat University, 23279 Elazig, Turkey

<sup>b</sup> Department of Metallurgical and Materials Engineering, Firat University, 23279 Elazig, Turkey

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## Abstract

In this study, extraction characteristics of Cu, Co, Zn and Fe from copper converter slag by oxidative leaching with potassium dichromate–sulphuric acid lixiviant were investigated. The experimental results indicated that the presence of dichromate has a large influence on the extraction of metals. Cu recovery seems to be feasible by leaching with a lixiviant containing potassium dichromate and sulphuric acid because of high Cu extractions and low Fe concentrations in pregnant liquor. Also, copper extraction yields increased by increasing the dichromate concentration while Co, Zn and Fe extractions considerably decreased.

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## 1. Introduction

The converter slag generated during the pyrometallurgical copper production generally contains significant amounts of some valuable metals such as copper, cobalt, nickel and zinc. In order to lessen the copper lost, returning the converter slag to the smelter furnace is applied as a common practice. In this case, beside the operational problems encountered, the volume and viscosity of smelter slag are unnecessarily increased and thus the high copper loss is occurred. Because of these problems, it is needed to discard converter slag from time to time.

In last few decades, there has been growing interest in hydrometallurgical processes to recover the valuable metals from copper smelting slags. In these studies, efforts are mainly focussed on the leaching processes with or without some pre-treatments. Recently, dichromate compounds have been considered as oxidizing agents for dissolving the sulphide minerals in some studies. For this purpose, oxidation of pyrite (Antonijevic et al., 1993) and chalcopyrite (Antonijevic et al., 1994) by using potassium dichromate and sulphuric acid has been

studied. Similarly, it has been shown that sodium dichromate could be used as an oxidant to remove some copper sulphide minerals from molybdenite concentrates (Ruiz and Padilla, 1998).

The aim of this study is to investigate sulphuric acid leaching of copper converter slag in the presence of dichromate which is an efficient oxidant. In this regard, the effects of the concentration of sulphuric acid and dichromate on the recovery of metals were examined. Besides the extraction efficiencies of copper, cobalt and zinc, the leaching behaviour of iron was traced.

## 2. Experimental

Converter slag sample used in this study was obtained from Ergani Copper Plant, Maden, Elazig, Turkey. The slag sample was crushed in a jaw crusher and ground in a ball mill and then sieved. The fraction of  $-74\ \mu\text{m}$  (200 mesh) was used in all experiments. Particle size distribution analyses indicated that the mean particle diameter of  $-200$  mesh converter slag sample is  $25.3\ \mu\text{m}$ . The chemical analyses of this material was: 0.45% Co, 4.36% Cu, 52.18% Fe, 1.92% S and 0.64% Zn. Fayalite ( $\text{Fe}_2\text{SiO}_4$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) phases were identified as major components while chalcocite ( $\text{Cu}_2\text{S}$ ) was determined as a minor component by X-ray analysis.

\* Corresponding author. Tel.: +90-424-2370000; fax: +90-424-2415526.

E-mail address: [saltundogan@firat.edu.tr](mailto:saltundogan@firat.edu.tr) (H.S. Altundogan).

Batch leaching runs were carried out by shaking 250 ml glass conical flasks containing pre-determined amount of converter slag sample and 100 ml of solutions having a various concentrations of  $K_2Cr_2O_7$  and  $H_2SO_4$ . The flasks were shaken at  $400\text{ min}^{-1}$  by using a shaker (Stuart Scientific SF1) equipped with a temperature controlled water bath. At the end of the pre-determined shaking period, mixtures were filtered. The supernatants were analyzed by atomic absorption spectrophotometry for Cu, Co, Fe and Zn.

In order to determine the most suitable lixiviant composition, the slags were leached with solutions containing 0–0.3 M  $K_2Cr_2O_7$  and 0.1–1.0 M  $H_2SO_4$  keeping other parameters constant i.e., 10 g/l of solid/liquid ratio, 298 K (25 °C) temperature and 120 min contact time. The experiments were regularly performed in duplicate and the mean values were considered.

### 3. Results and discussion

Effects of  $H_2SO_4$  and  $K_2Cr_2O_7$  concentrations on the extraction of metals from converter slag are shown in Fig. 1. It is seen that the extraction yields of all metals increase with increasing  $H_2SO_4$  concentration. But, Cu extraction yields are generally low for leaching media without  $K_2Cr_2O_7$ . For example, Cu, Co, Fe and Zn extraction yields for 1.0 M  $H_2SO_4$  concentration are 20.5%, 66.6%, 62.1% and 65.7%, respectively, at the conditions of 120 min of contact time, 10 g/l of slag/solution ratio and 298 K of temperature. Under the same conditions and in the presence of 0.3 M  $K_2Cr_2O_7$ , the extraction yields of these metals were found to be as 81.15%, 12.0%, 3.15% and 10.27%, respectively. Low extractions of Cu in the leaching media  $H_2SO_4$  alone can be attributed to its mineralogical form in converter slag. It can be said that most of the Cu in slag is in sulphide form. Also, similarities in extraction trends of Co, Zn and Fe may show that these metals are mostly present in fayalite and magnetite matrices. On the other hand, concentrations of Fe, considered as a contaminant for leaching processes, are rather high in the absence of dichromate. For example, Fe concentrations in leachates obtained by using 1.0 M  $H_2SO_4$  solution with and without dichromate (0.3 M  $K_2Cr_2O_7$ ) were found to be 0.165 and 3.43 g/l, respectively. It can be concluded that  $H_2SO_4$  leaching procedure without dichromate for recovery of Cu from converter slag seems to be inappropriate. The presence of dichromate has a positive effect on the rate of copper dissolution. On the other hand, it is clear that the presence of dichromate has important adverse effects on the extractions of Fe, Co and Zn. Also, a further increase in the  $H_2SO_4$  concentration above the 0.25 M does not influence Cu extraction yields significantly.

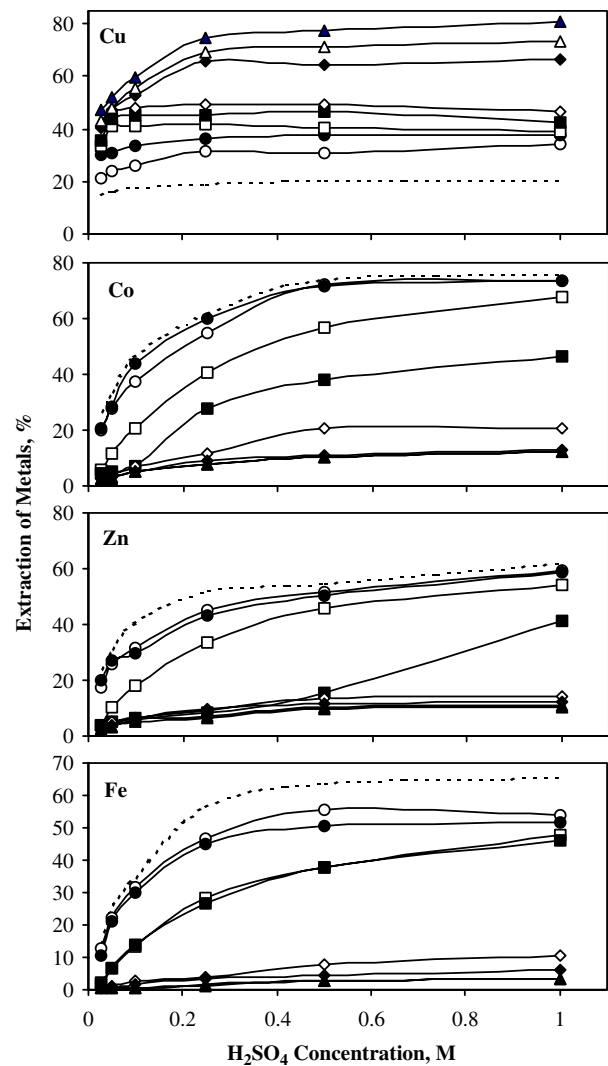


Fig. 1. Effects of  $H_2SO_4$  and  $K_2Cr_2O_7$  concentration on the extraction of metals from converter slag (slag/solution ratio: 10 g/l; leaching time: 120 min; temperature: 298 K;  $K_2Cr_2O_7$  concentration: (○) 0.0025 M, (●) 0.005 M, (□) 0.01 M, (■) 0.025 M, (◇) 0.05 M, (◆) 0.1 M, (△) 0.2 M, (▲) 0.3 M; dashed lines show that the results of leaching with sulphuric acid alone).

The fact that the decreasing Fe, Co and Zn extraction values with the increasing of dichromate concentration necessitates further mechanistic explanations. Firstly, it must be noted that the presence of Co and Zn in iron-based mineral phases i.e., fayalite and magnetite restrict their extractions. The lower extraction values of metals such as Co, Fe and Zn mostly present in silicate and ferrite matrices may show the passivation of slag particle surfaces stemming from the adsorption of chromate species such as  $Cr_2O_7^{2-}$  and/or  $HCrO_4^-$ . Adsorption of these anionic species may inhibit the contacting of  $H_3O^+$  ions with fayalite and magnetite which are major mineral phases in slag. On the other hand, satisfactory extraction rate of copper, in this case, suggest that the

copper minerals are not affected from the passivation may be due to being in separate phases.

Furthermore, reduced values in Fe, Co and Zn extraction yields in the presence of dichromate originated from the other reasons such as formation of insoluble chromate compounds with iron, and/or hydrolysing of iron(III) under the high oxidative conditions present. Olazabal et al. (1997) have reported that the formation of some insoluble iron chromate compounds in the Fe(III)–Cr(VI) system is possible at the mildly acidic conditions. Under the conditions of extremely high potassium dichromate concentration and high acidity for K–Fe(III)–Cr(VI)–H<sub>2</sub>O system, the formation of some insoluble potassium iron chromate compounds such as KFe<sub>3</sub>(CrO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub> (chromate analogue of potassium jarosite) and KFe(CrO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O has been reported (Baron et al., 1996).

It is well known that the amount of soluble Fe is reduced by hydrolysing to its insoluble compounds such as hematite, goethite and jarosite in the acidic leaching processes applied under oxygen pressure. It has been reported that the mechanism of such iron removal processes is very complex (Riveros and Dutrizac, 1997; Rubisov and Papangelakis, 2000). Also, all of these iron precipitation processes are generally carried out under high pressure and elevated temperature above 343 K (70 °C) (Davey and Scott, 1976). Our experimental conditions, such as high acidity medium, atmospheric pressure and low temperature, do not seem to be sufficient for a hydrolysis. Consequently, it can be stated that the decreasing in the extracted iron depending on increasing dichromate concentration may be mainly due to some precipitation phenomena and surface passivation effect causing by dichromate ions.

#### 4. Conclusions

From the results of this study, the following conclusions can be drawn: sulphuric acid leaching of copper converter slag in the presence of dichromate is more advantageous with respect to the leaching with sulphuric acid alone. Significant amount of Cu could be extracted by leaching with a lixiviant containing potassium dichromate and sulphuric acid. Also, iron concentration of leachates could be decreased significantly by using this process comparing with the ordinary H<sub>2</sub>SO<sub>4</sub> leaching. Co and Zn showed similar decreasing trends as Fe exhibits.

Cu extraction from converter slag increased with the concentration of dichromate used in leach process. Also, extraction of Cu increased with H<sub>2</sub>SO<sub>4</sub> concentration. However, an increase in H<sub>2</sub>SO<sub>4</sub> concentration above the 0.25 M did not influence Cu extraction significantly. On the other hand, Co, Zn and Fe extractions decreased with increasing dichromate concentration and increased with H<sub>2</sub>SO<sub>4</sub> concentration.

In conclusion, since copper extraction is high and iron contamination is limited, it can be considered that the sulphuric acid leaching of copper converter slag in the presence of dichromate is a reasonable recovery method. Forthcoming studies related to the leaching kinetics and the effect of various parameters on the metal extraction by using sulphuric acid–dichromate lixiviant are in progress.

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