

RECOVERY OF METALS FROM COPPER CONVERTER SLAG BY LEACHING WITH $K_2Cr_2O_7$ - H_2SO_4

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Abstract — In this study, the effects of some parameters on the extraction of metals from copper converter slag by using a sulphuric acid/potassium dichromate lixiviant were investigated. The leaching kinetic of copper from converter slag was also investigated. The results indicated that increasing the time and temperature have positive effects on the extraction of metals. The best results were obtained by the leaching of converter slag (-200 mesh, 10 g/L of slag/solution ratio) with a lixiviant containing 0.25 M H_2SO_4 and 0.1 M $K_2Cr_2O_7$ for 120 minutes at 70 °C. Under these conditions, 99.66% Cu extraction yield was achieved. The kinetic evaluations showed that the extraction of Cu from the converter slag is well represented by the shrinking core model controlled by diffusion through the slag matrix. The activation energy of the leach process was calculated as 33.66 kJ/mol for the temperature range of 25 to 70 °C (298 to 343 K). Also, reaction order with respect to dichromate was determined as first order in the concentration range of 0.025 to 0.1 M at 25 °C (298 K).

Résumé — Dans cette étude, on a étudié l'effet de certains paramètres sur l'extraction de métaux à partir des scories de convertisseur de cuivre en utilisant une solution de lixiviation d'acide sulfurique et de bichromate de potassium. On a également étudié la cinétique de lixiviation du cuivre à partir des scories de convertisseur. Les résultats ont indiqué que l'augmentation de la durée et de la température avait des effets positifs sur l'extraction des métaux. On a obtenu les meilleurs résultats par la lixiviation des scories de convertisseur (maille de -200, rapport de 10 g/L de scories/solution) avec une solution de lixiviation contenant 0.25 M H_2SO_4 et 0.1 M $K_2Cr_2O_7$ pendant 120 minutes à 70 °C. Sous ces conditions, on a obtenu un rendement d'extraction de 99.66% de Cu. L'évaluation de la cinétique a montré que l'extraction de cuivre à partir des scories de convertisseur était bien représentée par le modèle du noyau rétrécissant contrôlé par diffusion à travers la matrice de scories. On a calculé l'énergie d'activation du procédé de lessivage à 33.66 kJ/mol dans la gamme de température de 25 à 70 °C (298 à 343 K). Également, on a déterminé l'ordre de réaction par rapport au bichromate comme étant de premier ordre dans la gamme de concentration de 0.025 à 0.1M à 25 °C (298 K).

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 recover most of the copper, returning the converter slag to the smelter furnace is applied as a common practice. In this case in addition to the operational problems encountered, the volume and viscosity of the smelter slag are unnecessarily increased and thus, the high copper loss occurred. As a result of these problems, the converter slag needs to be discarded from time to time. It has been shown that treating the converter slag separately from the main pyrometallurgical cycle has the advantages of low copper loss and high smelter capacity [1,2]. Alternatively, in the 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 pretreatments. Among the leaching materials searched, sulphuric acid [3], cyanide [4,5], ammonia [6], ammonia-ammonium carbonate mixture [7] and ferric chloride [8] can be mentioned. In order to provide an enhanced solubilization, slags have been subjected to sulphation-roasting techniques by using various materials. As sulphation agents, sulphuric acid [9,10], ammonium sulphate [9], ferrous sulphate [11], ferric sulphate [12] and pyrite [13,14] have been used in roast-leach studies. The other pretreatment technique prior to leaching is the reduction-roasting process with carbonaceous materials. It has been shown that various coals and furnace oil could be used as reducing agents prior to ferric chloride leaching for the recovery of metals from the copper converter slag [15]. In this context, reduction with coal prior to acetic acid pressure leaching has also

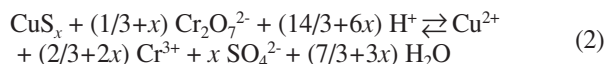
been studied [16]. On the other hand, these recovery methods could not find any application facility on the industrial scale.

Copper can exist in the form of metal, sulphide and oxide or their various combinations in the converter slag. While copper in oxide form can readily be dissolved in leaching agents, copper in metal and/or sulphide form necessitates oxidative conditions. Pressure provided by using an oxygen containing gas is a convenient route of creating oxidative leach conditions. It is well known that the pressure leaching process using oxygen gas provides a reduced extraction of iron which is considered as a contaminant. In the acidic leaching processes applied under oxygen pressure, Fe^{3+} ion is precipitated by hydrolyzing to its insoluble compounds such as hematite, goethite and jarosite [17]. Some researchers have reported that the mechanisms of these processes are very complex [18,19]. It has been reported that 90% of copper could be extracted with only 0.8% extraction of iron from the converter slag by using pressure leaching [20]. Recently in some studies, dichromate compounds have been considered as oxidizing agents for dissolving the sulphide minerals. For this purpose, oxidation of pyrite [21] and chalcopyrite [22] 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 molibdenite concentrates [23].

The oxidative action of dichromate ion in acidic solutions is based on its reduction according to [24].



The overall oxidation reaction for copper metal and/or sulphidic copper compounds can be generalized as



where x is a stoichiometric coefficient and its value depends on the oxidation degree of copper (for example, $x=0$, $1/2$ and 1 represent metallic copper, chalcocite and covellite, respectively).

In our earlier study, the effects of sulphuric acid and potassium dichromate concentrations on the extraction of metals from copper converter slag were investigated [25]. The results of this study showed that the presence of dichromate has a large influence on the extraction of metals. It was determined that the copper extraction yields increased with dichromate concentration, while cobalt, zinc and iron extractions decreased considerably probably due to some precipitation phenomena and surface passivation effect caused by dichromate ions [25].

The aim of the present study is to investigate the effects of the parameters such as temperature, time and slag/solution ratio on the recovery of metals. Additionally, some kinetic evaluations based on copper extraction were also made for the leaching process.

EXPERIMENTAL

The converter slag sample used in this study was obtained from Ergani Copper Plant, Maden, Elazığ-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.

The potassium dichromate and sulphuric acid used in the study were both reagent grade chemicals ($\text{K}_2\text{Cr}_2\text{O}_7$, Riedel-De Haan, 12255 and H_2SO_4 , Riedel-De Haan, 7102). All other chemicals used were of analytical reagent grade.

The slag samples were analyzed with an atomic absorption spectrometer (Perkin-Elmer, 370) by using the LiBO_2 fusion- HNO_3 dissolution route [26] for copper, cobalt, iron and zinc. The sulphur, aluminum and silica contents of converter slag were determined by gravimetric methods used for sulphur and silica-based materials [27,28]. The converter slag sample was subjected to X-ray diffraction analysis by using a Shimadzu XRD-6000 diffractometer to identify its mineralogical compositions. The mean particle diameter of the slag sample was determined by a Malvern Inst MasterSizer X particle size analyzer.

Batch leaching experiments were carried out by shaking 250 mL glass conical flasks containing a predetermined amount of converter slag sample and 100 mL of solutions having various concentrations of $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 . The suspensions were shaken (400 min^{-1}) by using a flask shaker (Stuart Scientific SF1) equipped with a temperature controlled water bath. At the end of the predetermined shaking period, mixtures were filtered. The supernatants were analyzed by an atomic absorption spectrophotometry for Cu, Co, Fe and Zn. Metal extractions were calculated from their individual concentrations in leach solutions and from slag composition.

In our recent study [25], the most suitable lixiviant composition was determined as 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ and 0.25 M H_2SO_4 keeping other parameters constant, i.e., 10 g/L of solid/liquid ratio, 25 °C temperature and 120 minutes of contact time. In the present study, the effects of various parameters such as temperature (25 to 70 °C), leaching time (5 to 240 minutes) and solid/liquid ratio (5 to 400 g/L) on the extraction of metals were studied by using the most suitable lixiviant composition.

To make some kinetic analyses, the effect of temperature (25 to 70 °C) and initial dichromate concentration (0.025 to 0.1 M), depending on time, were studied at fixed conditions of 0.25 M H_2SO_4 and 10 g/L slag/solution ratio.

The experiments were performed regularly in duplicate and the mean values were considered. A group of experiments were repeated a number of times to ascertain the reproducibility of the results and the results were found to vary within $\pm 5 \%$.

RESULTS AND DISCUSSION

The chemical composition of the converter slag sample is given in Table I. Fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4) phases were identified as major components by X-ray analysis. Also, chalcocite (Cu_2S) was determined as a minor component. It was concluded that the converter slag had significant copper, cobalt and zinc contents as well as a high amount of iron.

Table I – Chemical composition of the converter slag sample

Constituents	%, w/w
Al	1.54
Co	0.45
Cu	4.36
Fe	52.18
S	1.92
Si	8.72
Zn	0.64
L.O.I. (100-1000 °C)	*-5.39

*Loss on ignition (negative value indicates that iron (II) compounds convert to ferric oxide)

Particle size distribution analyses indicated that the mean particle diameter of -200 mesh converter slag sample used in the study was 25.3 μm .

Effect of Leaching Temperature

The effect of temperature on the extraction of metals from converter slag is shown in Figure 1. As seen, metal extraction yields increase with temperature. The copper could be completely extracted from slag at 70 °C. Also, extraction yields of the other metals increased depending on temperature. In our earlier study [25] in which the effect of dichromate concentration on the extraction of metals from converter slag with H_2SO_4 was investigated, the decrease in the extraction of metals (i.e., Fe, Co and Zn) in oxide-silicate matrices with an increase of dichromate concentration was explained as a probable passivation caused by adsorption of chromate ions on mineral surfaces. In the present study,

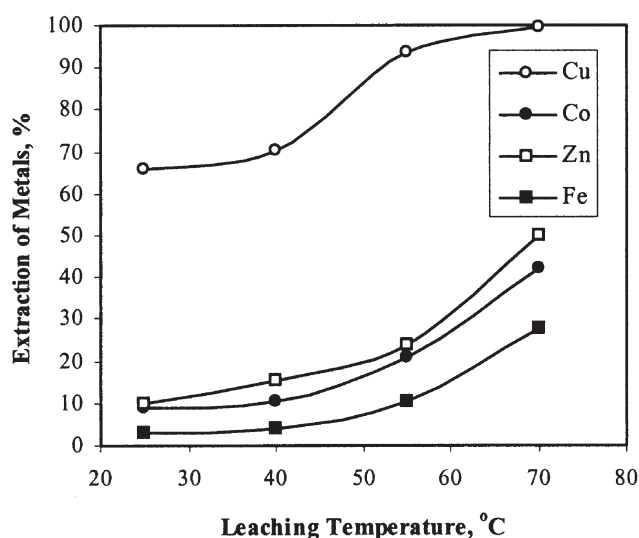


Fig. 1. Effect of temperature on the extraction of metals from converter slag (slag/solution ratio: 10g /L; $K_2Cr_2O_7$ Conc.: 0.1 M; H_2SO_4 Conc.: 0.25 M; Leaching time: 120 minutes).

increased Co, Zn and Fe extraction yields obtained at an elevated leaching temperature may be attributed to decreasing the adsorbed amounts of dichromate ions which are responsible for passivation effects. As a result, it can be noted that the amount of extracted iron, an important impurity, increased significantly by increasing the temperature. While the iron concentration was 0.167 g/L at 298 K, this value was found to be 1.44 g/L at 70 °C. However, the extraction yield of cobalt (about 42%) which is a valuable metal is not at a satisfactory level at this leaching temperature.

Effect of Leaching Time

Figure 2 shows the effect of leaching time on the extraction of metals from converter slag. As seen from this figure, amounts of extracted metals increase with an increase in the contact time. At the end of the contact period of 120 minutes, Cu, Co, Fe and Zn extraction yields reached the values of 99.66, 42.09, 27.59 and 49.86%, respectively.

Effect of Solid/Liquid Ratio

In the practical application of leaching processes, the solid/liquid ratio is desired to be as high as possible in order to obtain concentrated pregnant liquors. For that reason, the effect of the slag/solution ratio on the extraction of metals was investigated. Results of this study are shown in Figure 3. As expected, extraction yields of all metals decrease with an increase in the slag/solution ratio. However, although the extraction yield of Cu is lower, higher slag/solution ratios can be preferred to obtain concentrated pregnant solutions. For a comparison, while the Cu extraction yields are 99.7 and 76.4% for 10 and 100 g/L slag/solution ratios, respectively;

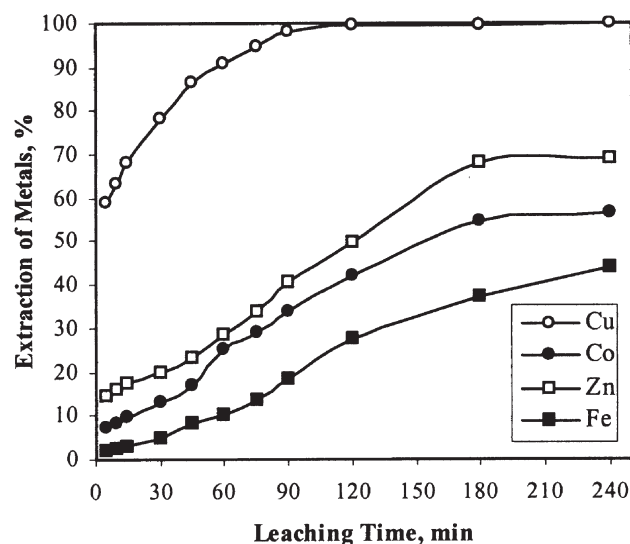


Fig. 2. Effect of leaching time on the extraction of metals from converter slag (slag/solution ratio: 10g/L; $K_2Cr_2O_7$ Conc.: 0.1 M; H_2SO_4 Conc.: 0.25 M; Temp.: 70 °C).

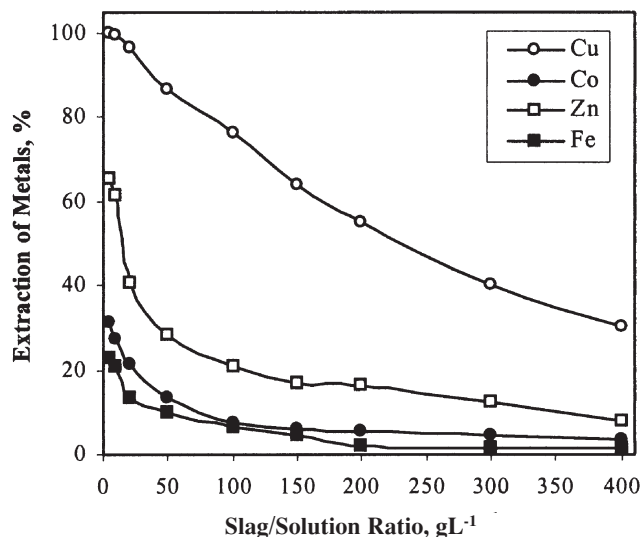


Fig. 3. Effect of slag/solution ratio on the extraction of metals from converter slag ($K_2Cr_2O_7$ Conc.: 0.1 M; H_2SO_4 Conc.: 0.25 M; Leaching time: 120 minutes; Temp.: 70 °C).

Cu concentrations of leach solutions increase about eight times (from 0.43 to 3.33 g/L) for corresponding slag/solution values. The copper loss in the case of high slag/solution ratio, however, could be reduced by applying a countercurrent leaching system in practice.

Further, the amount of iron per unit amount of copper passed into pregnant solution is another important issue. This ratio (kg Fe/kg Cu) was found to significantly decrease with increasing slag/solution values. For example, while the Fe/Cu ratio is about 3.2 for 10 g/L pulp density, this value is about 1 for that of 100 g/L.

Leaching Kinetics

Cu leaching from converter slags by using lixiviant containing $K_2Cr_2O_7$ and H_2SO_4 is a complex heterogeneous process. In addition to revealing the effect of leaching parameters, it will also be useful to have kinetic information. Kinetic analyses were made based on the data of the effect of temperature and $K_2Cr_2O_7$ concentration on the Cu extraction depending on the leaching time. The effects of temperature and $K_2Cr_2O_7$ concentration on the Cu extraction rate are shown in Figures 4 and 5, respectively.

The Cu extraction yields obtained depending on time and temperature (Figure 4) were applied to various heterogeneous kinetic models [29]. The experimental data were well fitted to the relationship between time and conversion for the shrinking core model which assumes the diffusion through the ash (slag matrix) is a rate limiting step (Equation 3).

$$1-3(1-X)^{2/3} + 2(1-X) = kt \quad (3)$$

where X is the extraction of Cu, t is time (min) and k is the apparent rate constant (min^{-1}). From Equation 3, the

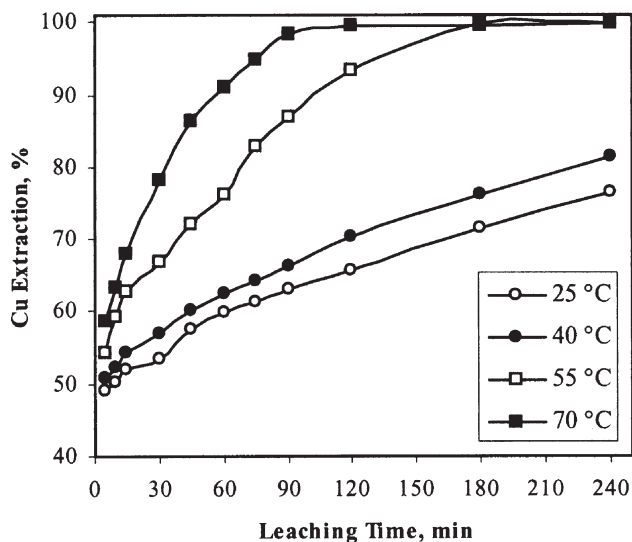


Fig. 4. Effect of temperature on the extraction rate of Cu from copper converter slag (slag/solution ratio: 10 g/L; $K_2Cr_2O_7$ Conc.: 0.1 M; H_2SO_4 Conc.: 0.25 M).

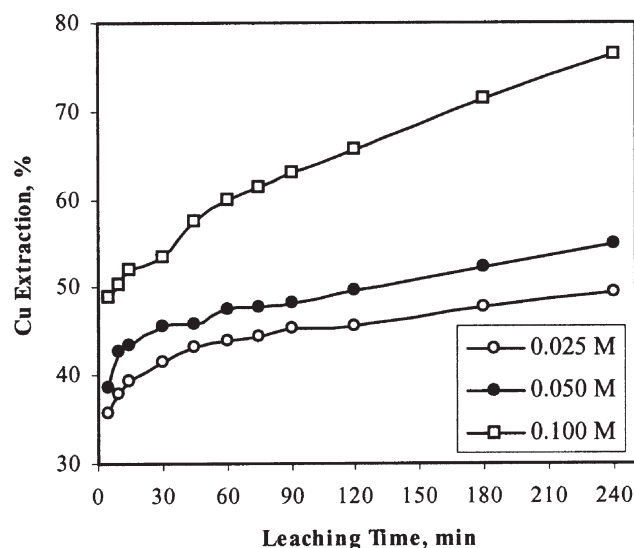


Fig. 5. Effect of $K_2Cr_2O_7$ concentration on the extraction rate of Cu from copper converter slag (slag/solution ratio: 10 g/L; 0.1 M; H_2SO_4 Conc.: 0.25 M; Temp.: 25 °C).

variation of $1-3(1-X)^{2/3} + 2(1-X)$ with time were plotted as shown in Figure 6. The apparent rate constant, k , was obtained from the slopes of the lines in the figure. Calculated apparent rate constants and correlation coefficients (R^2) for various temperatures are given in Table II. The Arrhenius equation was used to calculate activation energy of leach process by plotting $\ln k$ versus $1/T$ (Figure 7). The activation energy for Cu extraction from the copper converter slag was calculated as 33.66 kJ/mol. This value may be considered as high for a process controlled by diffusion. However, for a mechanism governed by diffusion

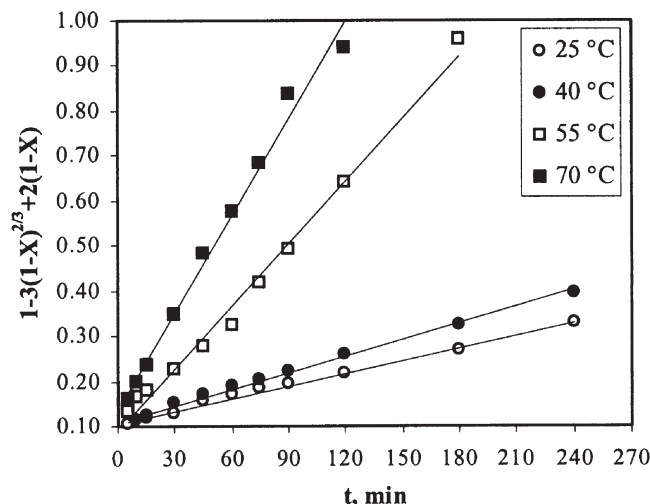


Fig. 6. A plot of $1-3(1-X)^{2/3}+2(1-X)$ versus time for various temperatures during Cu extraction from converter slag by potassium dichromate leaching (slag/solution ratio: 10 g/L; $K_2Cr_2O_7$ Conc.: 0.1 M; H_2SO_4 Conc.: 0.25 M).

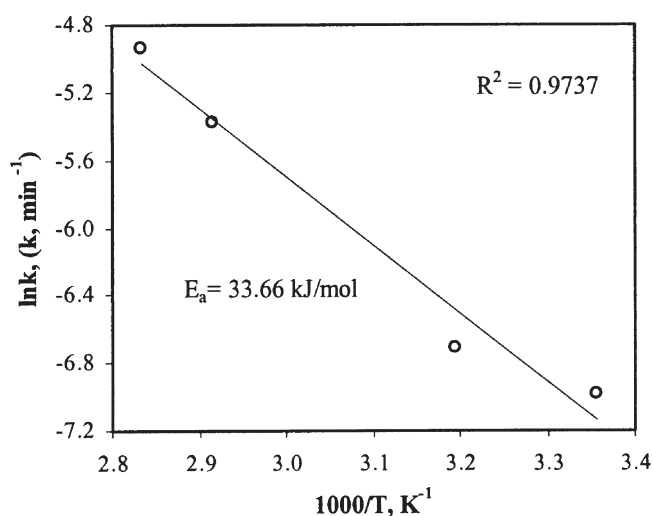


Fig. 7. Arrhenius plot for the Cu extraction from converter slag by potassium dichromate leaching.

control, activation energies reported in the literature for leaching of copper sulphide minerals by various lixiviants are in the range of 33.5 to 67 kJ/mol [23,30,31].

The data obtained from experiments carried out for various dichromate concentrations depending on time (Figure 5) were also applied to this leaching model. Calculated apparent rate constants for various initial dichromate concentrations are given in Table III. Reaction rate order with respect to dichromate concentration can be determined from the slope of the line obtained for $\ln k$ versus $\ln C$ (Figure 8). This figure shows that Cu leaching from converter slag is a first order reaction with respect to the dichromate concentration in the interval of 0.025 to 0.1 M.

Table II – Correlation coefficients and apparent rate constants for extraction of Cu from copper converter slag at various temperatures

Temperature, °C	$k \times 10^3, \text{min}^{-1}$	R^2
25	0.923	0.9948
40	1.220	0.9915
55	4.631	0.9905
70	7.129	0.9952

Table III – Correlation coefficients and apparent rate constants for extraction of Cu from copper converter slag at various initial concentrations of potassium dichromate

$K_2Cr_2O_7$ Conc., M	$k \times 10^4, \text{min}^{-1}$	R^2
0.025	2.091	0.8649
0.050	2.711	0.9267
0.100	9.229	0.9948

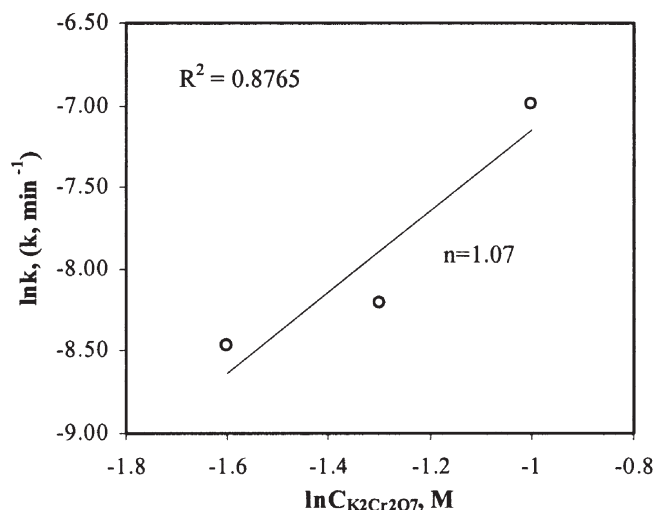


Fig. 8. Plot of Cu leaching rate versus initial $K_2Cr_2O_7$ concentration (slag/solution ratio: 10 g/L; Temp.: 25 °C; H_2SO_4 Conc.: 0.25 M).

CONCLUSIONS

From the results of this study, the following conclusions can be drawn:

1. Extraction yields of all metals increased with increasing temperature and time and decreasing slag/solution ratio. Also, Fe/Cu ratio (kg/kg) in solution, an important parameter for practical application of such processes, decreased by increasing the slag/solution ratio. On the other hand, Cu concentrations in the pregnant liquor were found to be higher for increased slag/solution ratios. Thus, in spite of the lower extraction yields obtained for Cu, increased slag/solution ratios may be preferred.

2. The kinetics of Cu extraction from converter slag by using dichromate can be described by means of the diffusion controlled shrinking core model. Activation energy for this process for the temperature range of 25 to 70 °C (298 to 343 K) was calculated as 33.66 kJ/mol.
3. Cu leaching rates with respect to dichromate concentration, in the range of 0.025 to 0.10 M, was determined as first order.

A proposed flow sheet for metal recovery from converter slag by this process is illustrated in Figure 9. As seen, following the liquid-solid separation after the leaching, solubilized copper, cobalt, nickel and zinc can be separated from the pregnant solution containing dichromate by using a sulfide precipitation. For this reason, sodium sulfide can be used as a precipitation agent. Sulfide precipitation may require a pH adjustment to increase the sulfide formation yield. After the precipitation, the metal sulfide concentrate obtained can be utilized pyrometallurgically. On the other hand, the liquid fraction obtained from the precipitation stage can be used to obtain regenerated lixiviant solution by adding sulfuric acid and dichromate. Also, in this stage, reduced chromium (Cr^{3+}) during the leaching may be reoxidized to dichromate by using some oxidation agents such as MnO_2 or H_2O_2 .

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REFERENCES

1. I.L. Barker, J.S. Jacobi and B.H. Wadia, *Trans. Am. Inst. Min. Engrs.*, 1957, vol. 209, pp. 774-780.
2. R.T. Jones, D.A. Hayman and G.M. Denton, *International Symposium on Challenges of Process Intensification, 35th Annual Conference of Metallurgists*, 24-29 August, 1996, Montreal, pp. 451-466.
3. S. Anand, P. Kanta Rao and P.K. Jena, *Trans. Inst. Min. Metall.*, 1980, vol. 33, pp. 77-81.
4. S. Guy and N.T. Bailey, *Copper Metallurgy, Practice And Theory*, 11 February, 1975, Brussels, *Meet. Inst. Min. Metall.*, 1979, pp. 35-41.
5. I. Kayadeniz and U. Sağdıç, *Chim. Acta Turc.*, 1980, vol. 8, pp. 299-309.
6. I. Kayadeniz and U. Sağdıç, *Chim. Acta Turc.*, 1977, vol. 5, pp. 183-188.
7. T.R. Shelley, *Trans. Inst. Min. Metal*, 1975, vol. 4(C), pp. 1-4.
8. S. Anand, P. Kanta Rao and P.K. Jena, *Hydrometallurgy*, 1980, vol. 5, pp. 355-365.
9. L.B. Sukla, S.C. Panda and P.K. Jena, *Hydrometallurgy*, 1986, vol. 16, pp. 153-165.
10. C. Hamamcı and B. Ziyadanoğulları, *Sep. Sci. Technol.*, 1991, vol. 26(8), pp. 1147-1154.
11. K.O. Lindbland, *Recovery of Metal Values from Copper Reverberatory Slag*, 1977, U.S. Pat. No. 4043804 (C1.75-47; C 22 B 15/00).
12. H.S. Altundoğan and F. Tümen, *Hydrometallurgy*, 1997, vol. 44, pp. 261-267.
13. F. Tümen and N.T. Bailey, *Hydrometallurgy*, 1990, vol. 25, pp. 317-328.
14. I. Kayadeniz and U. Sağdıç, *Chim. Acta Turc.*, 1981, vol. 9, pp. 341-352.
15. S. Anand, R.P. Das and P.K. Jena, *Hydrometallurgy*, 1981, vol. 7, pp. 243-252.
16. M.G. Bodas and S.B. Mathur, *Ind. Eng. Chem. Res.*, 1997, vol. 36, pp. 5419-5424.
17. P.T. Davey and T.R. Scott, *Hydrometallurgy*, 1976, vol. 2, pp. 25-35.
18. P.A. Riveros and J.E. Dutrizac, *Hydrometallurgy*, 1997, vol. 46, pp. 85-104.
19. D.H. Rubisov and V.G. Papangelakis, *Hydrometallurgy*, 2000, 58, 13-26.
20. S. Anand, K. Sarveswara and P.K. Jena, *Hydrometallurgy*, 1983, vol. 10, pp. 305-312.
21. M.M. Antonijevic, M. Dimitrijevic and Z. Jankovic, *Hydrometallurgy*, 1993, vol. 32, pp. 61-72.

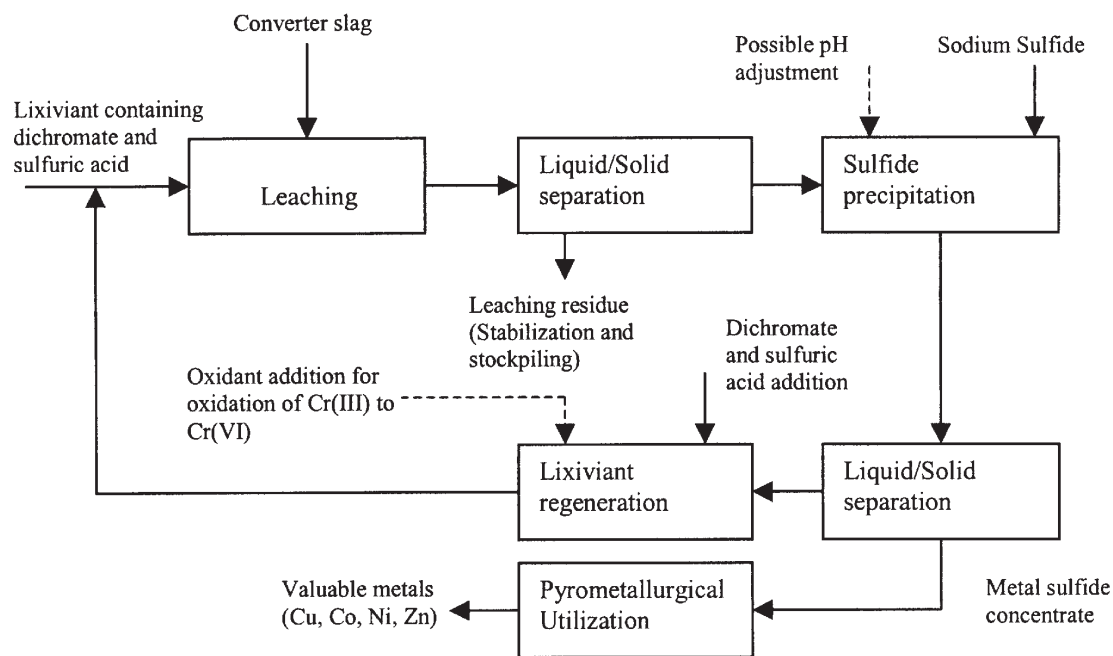


Fig. 9. Proposed flow sheet for metal recovery from converter slag by $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ leaching.

22. M.M. Antonijevic, Z. Jankovic and M. Dimitrijevic, *Hydrometallurgy*, 1994, vol. 35, pp. 187-201.
23. M.C. Ruiz and R. Padilla, *Hydrometallurgy*, 1998, vol. 48, pp. 313-325.
24. E. Jackson, *Hydrometallurgical Extraction and Reclamation*, 1986, Ellis Harwood Limited, London.
25. H.S. Altundoğan, M. Boyrazlı and F. Tümen, *Minerals Engineering*, 2004, vol. 17, pp. 465-467.
26. N.T. Bailey and S.I. Woods, *Anal. Chim. Acta.*, 1974, vol. 69, pp. 19-25.
27. J.S. Fritz and G.H. Shenk, *Quantitative Analytical Chemistry*, 3rd Ed., 1974, Allyn and Bacon Incorporated, Boston.
28. A.I. Vogel, *Vogel's Textbook of Quantitative Chemical Analyses*, 1989, 5th edition, revised by G.H. Jefferey *et al.*, Longman, London.
29. O. Levensiple, *Chemical Reaction Engineering*, 1974, John Wiley and Sons, New York.
30. M. Bonan, J.M. Demarthe, H. Renon and F. Baratin, *Met. Trans. B*, 1981, vol. 12B, pp. 269-274.
31. R.Z. Vracar, I.S. Parezanovic and K.P. Cerovic, *Hydrometallurgy*, 2000, vol. 58, pp. 261-267.

