SCIREA Journal of Metallurgical Engineering

http://www.scirea.org/journal/Metallurgical

October 29, 2016

Volume 1, Issue1, October 2016

Sulfuric acid leaching of sulfide slag of Sarcheshmeh copper reverberatory furnace

Hossein Aghajani[a,*], Jalil Vahdati Khaki[b], Masoud Goudarzi[c], Naser Hosseini[a]

[a] Materials Engineering Department, University of Tabriz, Tabriz, Iran.

[b] Department of Metallurgy and Materials Engineering, Ferdowsi University of Mashhad, Mashhad, Iran.

[c] School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran, Iran.

[*] Corresponding author E-mail address: h_aghajani@tabrizu.ac.ir

Abstract

Reverberatory furnace slag is a material that is created from metal smelting processes and it is usually assumed as a waste material in these processes. In this research, hydrometallurgical extraction of copper from Sarcheshmeh reverberatory furnace slag has been investigated. Firstly, studies were carried out to determine the chemical composition of the slag by X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) analysis. Slag was crushed and sieved by different meshes. Then, sulfuric acid leaching was performed on the slag with +60, +80, +100, +120 and -120 mesh numbers at 27, 40, 65, 80 and 100℃ leaching temperatures, respectively. Leaching solvent concentrations was set as 1.02, 2.04, 3.06, 4.08 and 5.1 mole.liter^{-1} for 15, 30, 45, 60, 90, 105and 120 minute leaching time and 100, 200, 300 and 400 rpm stirring speed. In order to determine the copper percentage in the leaching solution, Atomic Absorption Spectroscopy (AAS) has been utilized. Also, the leaching mechanism was studied utilizing different kinetic models. Finally, In order to increase the efficiency of the leaching process, the effect of mechanically activation, Ag^{+} addition (as a catalyst ion) and a roasting process before leaching have been studied. Results showed that the best efficiency was coordinated with -120 mesh particle size, 4.08 mole/liter acid concentration, 80℃, 100 rpm stirring speed. Also, mechanism studies show that the chemical reaction at the interface was the controlling factor and the activation energy for the dissolution reaction was 4.95 kj/mol.

Keywords: hydrometallurgy; sulfuric acid; reverberatory slag; leaching; kinetics.

1.Introduction

Continuous usage of high grade ore causes a decrease in mineral resources and results in the usage of the low grade materials for extraction of metals. One of the low grade materials that could be used for copper extraction is the reverberatory furnace slag that is widely used for copper extraction these days. In general, the main components of the reverberatory slag are Fe_3O_4 and SiO_2 with amounts of 25% to 50% for each of them. Nearly all of the copper slags contain considerable amounts of Cu (0.5-3.7%). Depending on used mineral, copper slag can also contain Co, Ni, Zn, As and Pb too. In different types of slags, the mineralogical phases of copper are chalcopyrite, chalcocite and covellite [1-4]. Mineralogical composition of copper slag depends on the type of ores, the type of furnaces and the cooling methods. Slow cooling rates may result in crystallization of slag components and forming different mineral phases. By increasing the cooling rates, the slag may become amorphous and more homogeneous in metal distribution [5, 6].

Hydrometallurgical processes for recovery of non-ferrous metals from slags have been attracted attention recently and leaching process is the most appropriate and economical method. It involves the use of aqueous chemistry for the recovery of metals from ores, recycled or residual materials. The objective of this method is removing copper from slag and introducing it into the aqueous phase [7-9]. In order to increase the efficiency of leaching process, there are lots of techniques such as adding H_2O_2, pressure leaching, mechanically activation and roasting. Basir et al., [10] showed that in the leaching of brass smelting slag with hydrochloric acid, the addition of H_2O_2 causes an increase in extraction of the metal. Vafaeian et al., [11] reported that the optimized mechanically activation has an enormous effect on extraction of copper from sulfide concentrates. Altundogan et al., [12] reported that the high temperature roasting of slag before leaching causes an increase in extraction of copper.

In recent years, various solvents such as chlorate [13], ferric chloride [14], hydrochloric acid [15], hydrogen peroxide [16], and sulfuric acid [17] have been used for leaching of copper from slags. Sulfuric acid leaching is the most conventional method for extraction of copper because of its economic advantages. Several factors affect the solubility of different elements in this acid. As an example, low concentrated sulfuric acid leaches the copper carbonates and the copper oxides and it has a little effect on copper silicates. The sulfuric acid with low concentration causes fewer amounts of Fe and other impurities dissolution in more leaching times. But, sulfuric acid leaching could not recover the sulfide slag copper in high efficiencies, due to sulfur layer formation on the slag particles during the leaching process [8, 17].

In the present study, after analyzing the chemical and the mineralogical composition of the revebrabretory sulfide slag, the effects of different parameters (i.e. temperature, concentration, time, and the stirring speed) on leaching efficiency have been studied. Also, kinetic study to determine the leaching process controlling factors has been done. Finally, the effects of adding a catalyst, mechanical activation and roasting before leaching have been investigated.

2.Experimental procedure

The slag sample used in this investigation is the slag of the reverberatory copper furnace of Sarcheshmeh copper complex (Kerman-Iran). The chemical composition which is determined by X-ray fluorescence method (XRF) is given in Table 1. Also, X-ray diffraction (XRD) method was used for analyzing the mineralogical and the phase composition of the slag. Atomic absorption spectroscopy was used in order to determine the element content of the leaching solution. Sulfuric acid (Merck, Germany) was selected as the leaching solvent.

Table. 1. Chemical composition of the reverberatory slag.

component	Cu	Fe	S	Zn	Ti	Mg	CaO	SiO_2	Al_2O_3	Bal.
Wt-%	0.66	38.3	1.3	2.4	0.77	0.16	8.4	39	6.1	2.91

The leaching process cannot completely extract copper from the slag because of the low porosity of the slag. Hence, the slag was crushed, sieved and then leached in the sulfuric acid. In order to study the effect of different parameters on the extraction of copper, particle size (+60, + 80, +100, +120 and -120 mesh number), temperature (27 (room temperature), 40, 65, 80 and 100℃), acid concentration (1.02, 2.04, 3.06, 4.08 and 5.1 mole.liter^{-1}), time (15, 30, 45, 60, 90, 105 and 120 minutes) and stirring speed (100, 200, 300 and 400 rpm) were investigated. The extraction efficiency of the leaching process (R) was used to evaluate of the process. R value is defined as follows:

$$R = \frac{C}{C^0} \times 100 \quad (1)$$

Where C^0 is the Cu content in the slag and C is the leached Cu that is determined from the atomic absorption spectroscopy analysis. At the end, in order to increase the extraction process efficiency, some other actions like adding Ag^+ ion, using mechanical activation before leaching and roasting in the presence of ferric sulfate, sodium chloride and sodium carbonate, have been studied. Ag^+ ion was added by dissolution of $AgNO_3$ to achieve 5, 10, 15 and 20 ppm concentrations, mechanical activation was performed utilizing a ball mill for 60, 120 and 180 minutes, Al_2O_3 balls with 1/20 ball to powder ratio were used and the roasting process was carried out at 750℃ for 1 hour in the presence of ferric sulfate, sodium chloride and sodium carbonate.

3. Results and discussion

3.1. Mineralogical and phase analysis of the slag

A XRD analysis of the slag is shown in Fig. 1. Related XRD pattern shows that the main phases are chalcopyrite ($CuFeS_2$), cayalite (Fe_2SiO_4), magnetite (Fe_3O_4) and calcium silicate ($Ca(SiO_4)_2$). By the data revealed from the pattern it is obvious that the major copper in the slag is presented as chalcopyrite, or it can be said that the copper is presented in the sulfide phase.

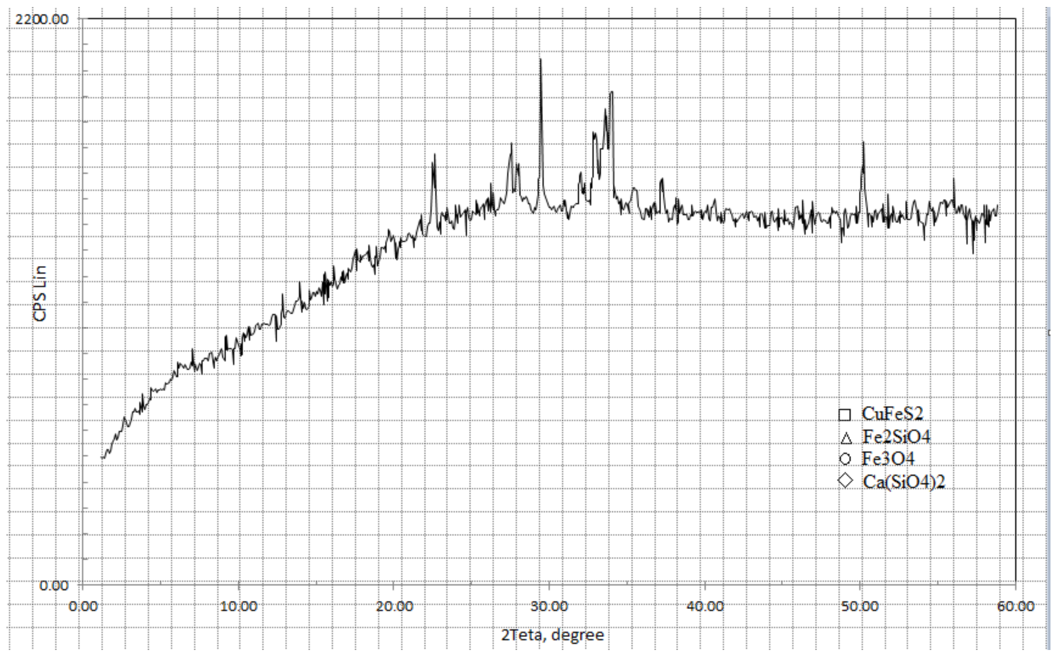

Fig. 1. XRD pattern of Sarcheshmeh reverberatory furnace slag.

3.2. Effects of different parameters on acid sulfuric leaching of the slag

3.2.1. Particle size

Effect of particle size on the copper extraction is shown in Fig. 2. As it can be observed, by decreasing the particle size, the amount of copper dissolution increases. In general, the smaller particle size causes increase in contact surface of the copper with leaching solution. A particle which is floated in the leaching solution can be divided into three regions: 1) surface region of the particle that completely is in contact with the solvent and dissolves in the solution, 2) region near to the surface of the particle that is not utterly in contact with the solvent and can't completely dissolve in the solvent and 3) the core region of the slag particle that solvent cannot penetrate and reach to this region, so the minerals don't dissolve in the solvent. When the particle becomes finer, the dimensions of the second and the third regions will decrease. As the result, the leaching of Cu containing minerals increases.

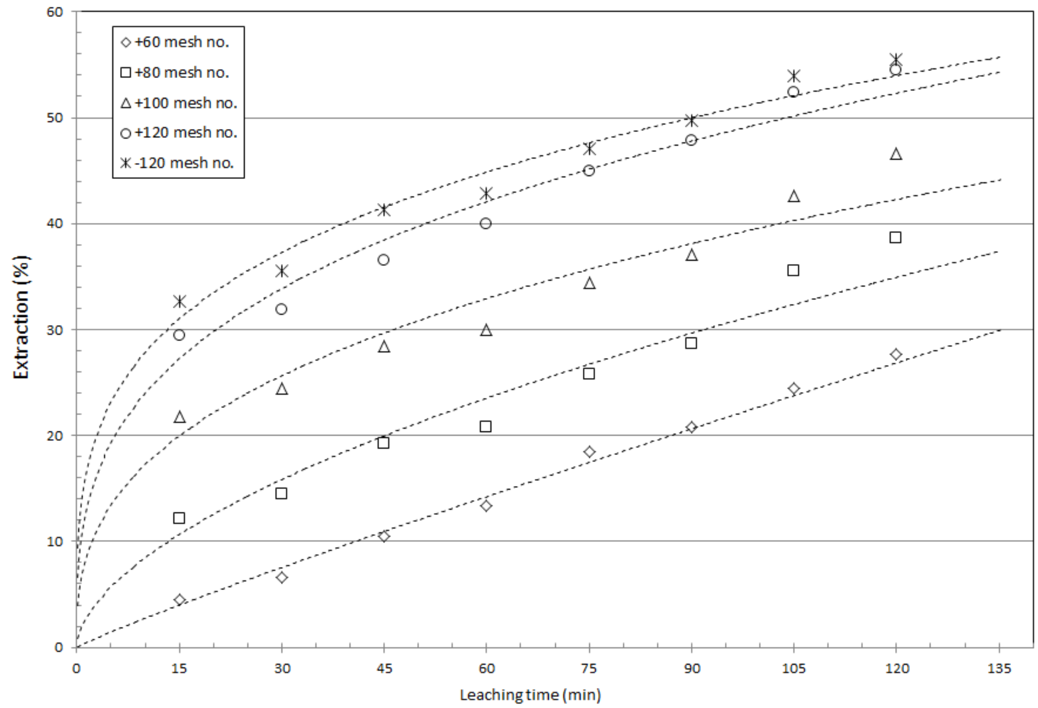

Fig. 2. Copper extraction as a function of particle size.

3.2.2. Sulfuric acid concentration

Copper extraction as a function of the concentration of the solvent is shown in the Fig. 3. This curve indicates that by increasing the concentration of the solvent, copper extraction increases. In low solvent concentrations, the iron minerals as alkali sulfates cover the particle and prevent it from being solved. So, 4.08 mole/lit concentration were selected as the optimum concentration for leaching.

3.2.3. Temperature

Copper extraction as a function of temperature is shown in Fig.4. As the temperature increases, the dissolution of the slag in solvent increases too. With increasing the temperature from 27 to 65 ℃, leaching extraction increases rapidly. In this range, temperature increase has a great effect on the dissolution of the slag. Increasing of temperature from 80 to 100℃ has not a significant effect in the leaching process. Note that, at 100℃, the solution begins to evaporate and the leaching operation becomes difficult. Therefore, 80℃ is considered as the optimum leaching temperature.

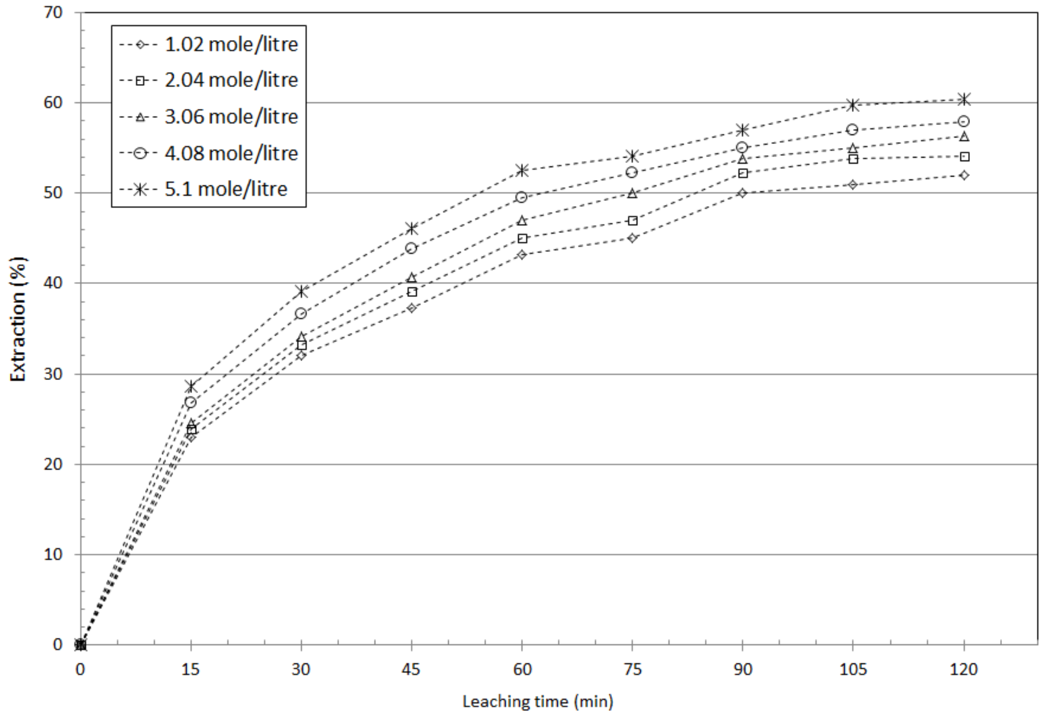

Fig. 3. Copper extraction variations as a function of the solvent concentration.

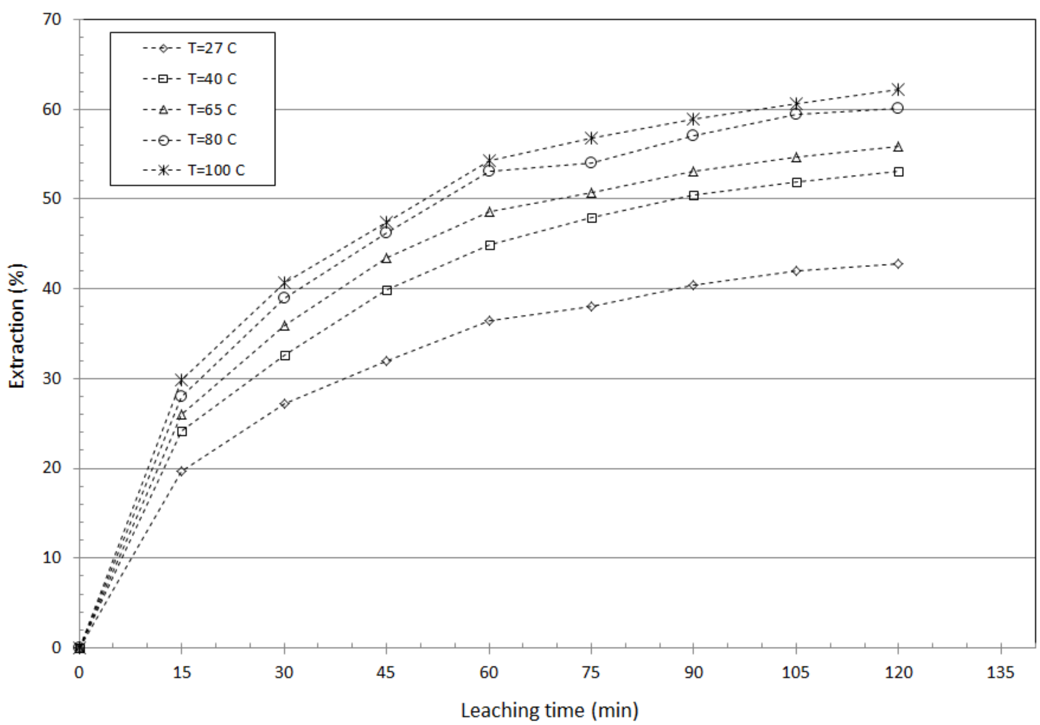

Fig. 4. Copper extraction variations as a function of temperature.

3.2.4. Stirring speed

Fig. 5 illustrates the copper extraction in four stirring speeds of 0, 100, 200 and 400 rpm. It can be seen that with increasing the stirrer speed from 0 to 100, the extraction increases. However, with increasing the stirrer speed from 200 to 400, little changes occurred in the extraction process. According to these results, the stirring speed of 200 rpm is considered as the optimum stirring value. In this case, it can be said that the stirring operation prevents the formation of a thick passive layer on the surface of particles and increases the extraction of copper.

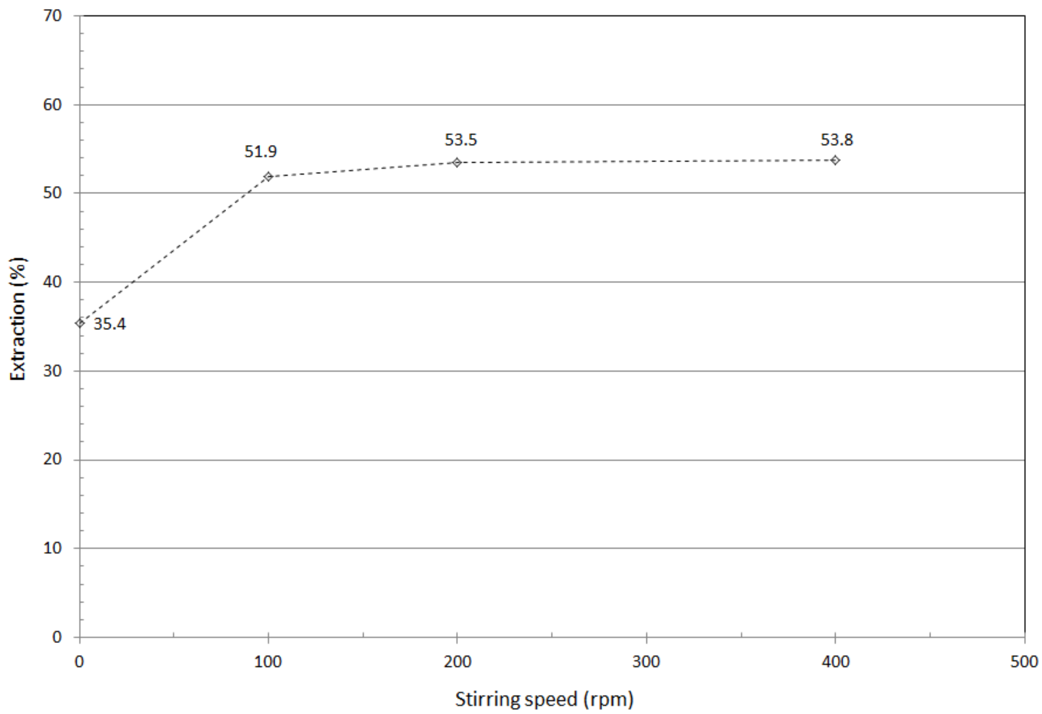

Fig. 5. Copper extraction in the four stirrer speed of 0, 100, 200 and 400 rpm.

3.3. Kinetics of leaching

For selecting the kinetics behavior of the leaching of this slag, the shrinking core model (SCM) has been utilized with respect to R-time curves at different temperatures (Fig. 4). So, the controlling step of the dissolution process could be one of these three following steps:

- Diffusion through solution boundary layer

- Chemical reaction at the interface

- Diffusion through the solid product layer

If the diffusion through solution boundary is the controlling step of leaching, there would be a linear relationship between R and t as follows:

$$R=Kt \qquad (1)$$

Where K is the apparent rate constant of mass transfer in liquid phase.

If the chemical reaction at the interface controls the reaction rate, relationship between R and t will be expressed as follows:

$$1-(1-R)^{\frac{1}{3}} = Kt \qquad (2)$$

Where, K is the rate of the chemical reaction at the interface.

If the diffusion through the solid product layer is the controlling step of the reaction, relationship between R and t is express as follows:

$$1-(\frac{2}{3}R)-(1-R)^{\frac{2}{3}} = Kt \qquad (3)$$

Where, K is the apparent rate constant of diffusion through the solid product layer.

In all three equations K is calculated from the slope of extrapolated curve that is best fitted on data points at the time of zero. Calculations that was performed on the data given in Fig. 4 showed that K is about 2.1667, 2.7256, 2.8268, 3.2044 and 3.4354 respectively at temperatures of 27, 40, 65, 80 and 100 ^{o}C. In order to analyze the kinetics, the shrinking core models with diffusion through solution boundary, chemical reaction at the interface and diffusion through the solid product layer, Eq. (1), Eq. (2) and Eq. (3) were used, respectively with respect to calculated K. Based on this model and experimental results and values for different kinetic models can be compared at each of the above mentioned temperatures. Fig. 6 shows that experimental data of 27 ^{o}C is approximately near to the values that represent the chemical reaction at the interface. So, Eq. (2) should be used for kinetically study of the experimental results (Fig. 6). The variations of Eq. (2) with time at different temperatures are shown in Fig. 7. The activation energy can be obtained from the following Arrhenius equation:

$$K=A \exp(-E/RT) \qquad (4)$$

The Arrhenius plot constructed with the rate constant value (k), which is calculated from the data given in Fig 7. , is presented in Fig. 8.

So, the calculated activation energy (E_a) for the dissolution of the reverberatory copper slag is 4.95 kJ/mol.

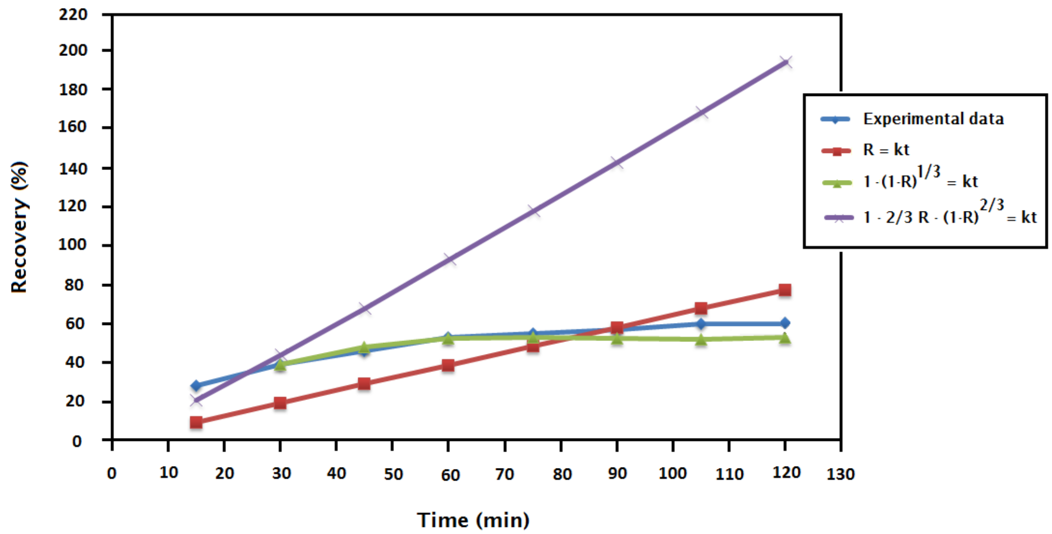

Fig. 6. Selection of kinetic model for the linearization of the results using shrinking core (SCM) method at temperature of 27 °C.

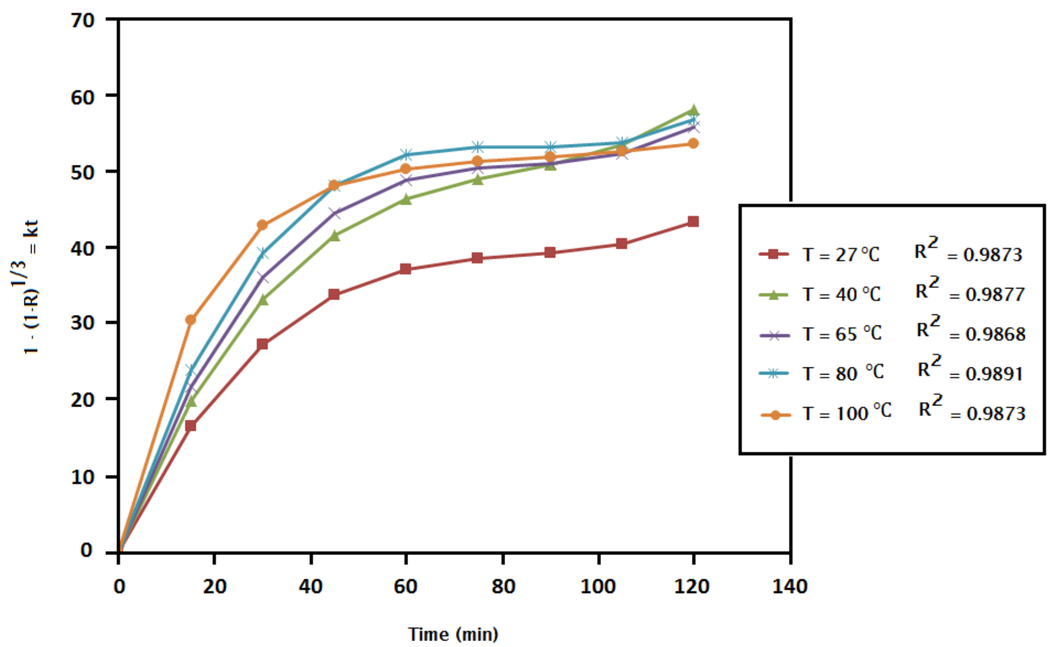

Fig. 7. Plots of 1- $(1\text{-R})^{1/}$3 = kt versus time at different temperatures.

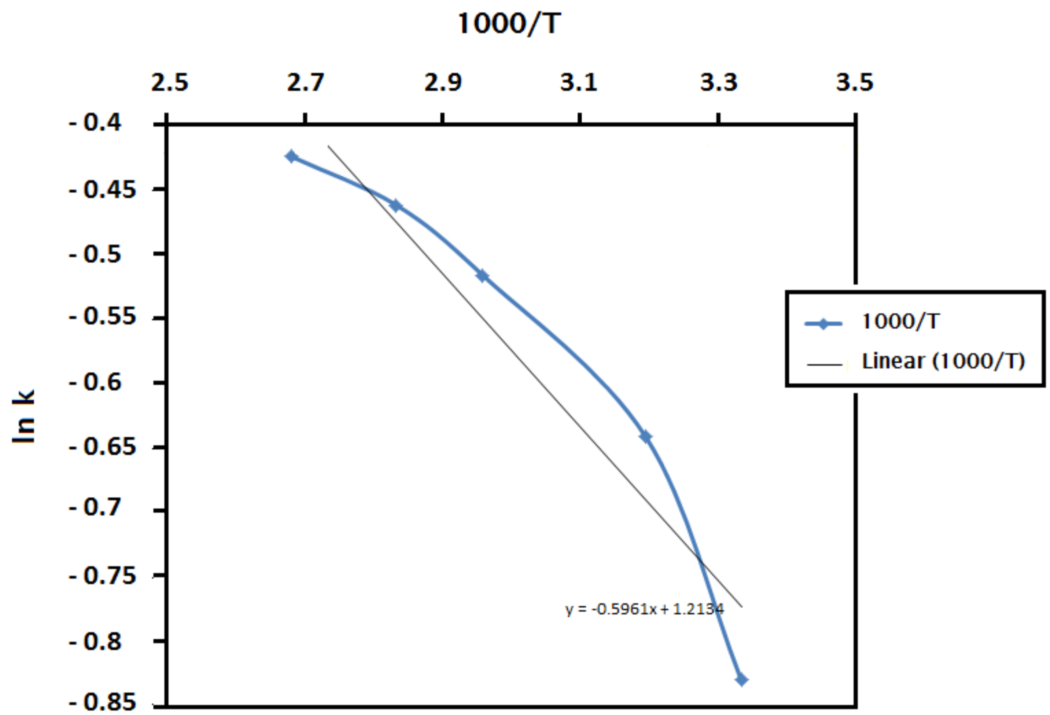

Fig. 8. Arrhenius plot for determination of activation energy of dissolution of slag.

3.4. Effect of mechanical activation on acid sulfuric leaching of the slag

The effects of mechanical activation on the extraction of copper are shown in Fig. 9. It can be seen that with increasing the time of the mechanical work, copper extraction increased. Mechanically activation before leaching is one of the well-known methods that can improve the leaching operation. In general, mechanical activation causes an increase in contact area, reactivity of surface and improvement of the slag’s microstructure. Also, lower reaction temperature, preparation of water soluble compounds, formation of new surface and creation of lattice are some other advantages of applying mechanical activation.

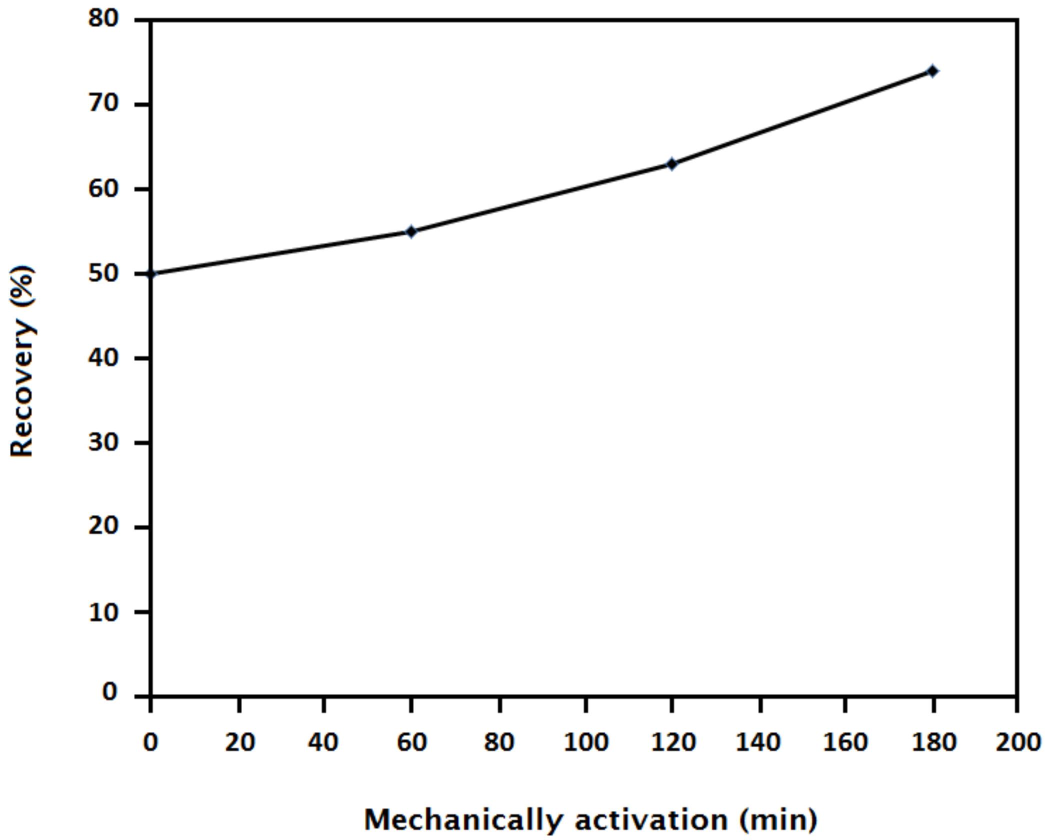

Fig 9. Effect of mechanically activation on the extraction of copper.

3.5. Effect of catalyst on acid sulfuric leaching of slag

In order to study the effects of addition of catalyst on the extraction of copper, Ag^+ ions was added by dissolution of $AgNO_3$ to achieve 5, 10, 15 and 20 ppm concentrations .The effects of additional Ag^+ in the leaching solution on extraction of copper are shown in Fig. 10. The results show that with increasing silver ion in solution, the extraction of copper from slag increases. Addition of silver ions increases the chalcopyrite and other sulfide compounds of copper solubility in sulfuric acid significantly. Presence of Ag^+ catalyst forms a complex porous layer on the surface of the slag particles. This layer prevents particle surface from covering by sulfur due to the reaction of sulfur with sulfuric acid. Hence, leaching of slag in solution will be done more easily.

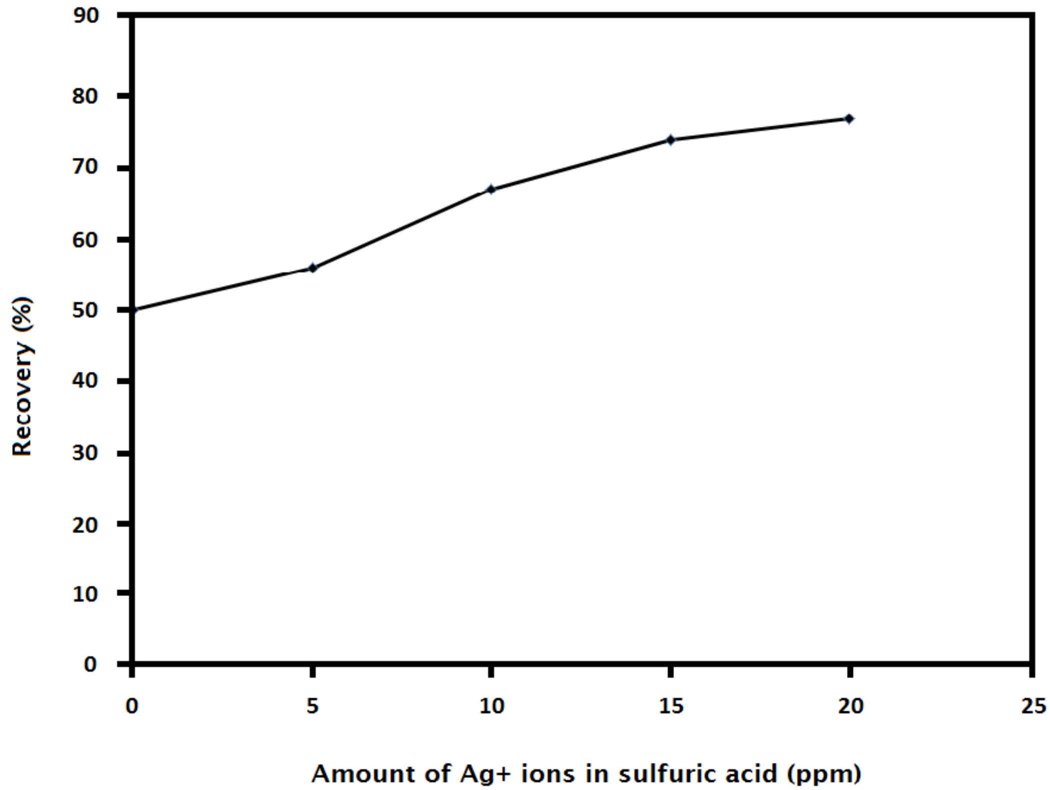

Fig. 10. Effects of Ag^+ additional in the leaching solution on extraction of copper.

3.6. Effect of roasting on acid sulfuric leaching of the slag

Roasting operation before leaching is performed on the slag. This action causes the leaching process done better and extraction of copper from slag improves. By roasting before leaching, insoluble phases in the used acid sulfuric reduces. So, the leaching process will be more economical. By presence of some additives in leaching solution, selective leaching process can be done better. Fig. 11 shows the extraction of copper in the presence of various additives. It can be seen that the presence of various additives causes an improvement of leaching process and the extraction of copper. It is predicted that the following reaction between the additives and copper sulfide phase can be done.

$$Cu_2S(s)+Na_2CO_3(s)\rightarrow CuCO_3(s)+Na_2S(s) \quad (5)$$

$$Cu_2S(s)+FeSO_4(s)\rightarrow CuSO_4(s)+FeS(s) \quad (6)$$

$$Cu_2S(s)+2NaCl(s)\rightarrow CuCl_2(s)+Na_2S(s) \quad (7)$$

As it is seen, in the roasting processes the adding of Na_2O_3, $FeSO_4$ and NaCl generate $CuCO_3$, $CuSO_4$ and $CuCl_2$, respectively. These three phases dissolve more easily than sulfide phase in sulfuric acid. Additionally the roasting operation in the presence of Na_2CO_3 has more influence than the other additive on leaching process and the phases containing copper like $CuCO_3$ dissolved in sulfuric acid more than the other phases.

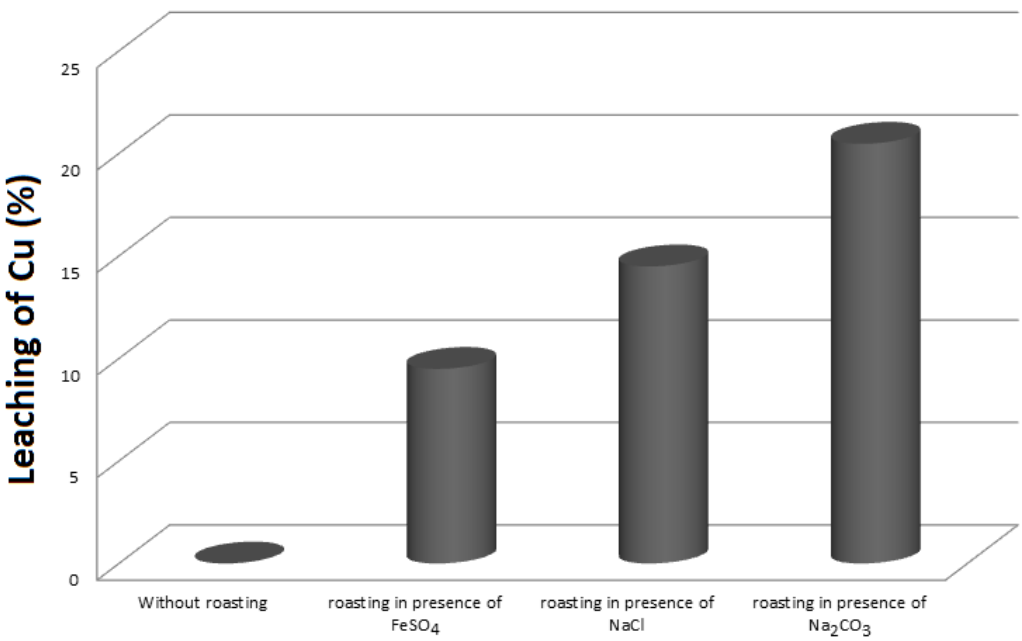

Fig. 11. extraction of copper in the presence of various additives.

Conclusion

- Decreasing the particle size, increases the amount of dissolved copper and the optimal particle sizes were found the particles which were -120 mesh.

- With increasing the solvent concentrations, the extraction of copper increased and 4.08 ml/lit selected as optimal temperature of the leaching process.

- As the temperature increases, the dissolution of the slag in the solvent increased and 80℃ selected as the optimal temperature of the leaching process.

- The stirring speed as fast as 200 rpm to optimal mixing are considered.

- The kinetic characterization has shown that Chemical reaction at the interface is controlling factor for leaching of reverberatory slag in optimal condition. According to kinetic study, activation energy of chemical reaction at the interface is 4.95kJ/mol.

- The Presence of Ag^+ catalyst lead to a formation of a complex porous layer on the surface of the slag particles and with increasing silver ion in solution, the extraction of copper from the slag increased.

Refrence

[1] Bipra Gorai, R.K. Jana, Premchand, Characteristics and utilization of copper slag-/a review, Resources, Conservation and Recycling 39 (2003) 299-313.

[2] O. Herreros, R. Quiroz, E. Manzano, C. Bou, J. Vinals, Copper extraction from reverberatory and flash furnace slags by chlorine leaching, Hydrometallurgy 49 (1998) 87–10.

[3] Huiting Shen and E. Forssberg, An overview of recovery of metals from slags, Waste Management, 23 (2003) 933–949.

[4] Philip K. Gbor, Valentina Mokri and Charles Q. Jia, Characterization of smelter slags, Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering, 35(2) (2000) 147-167.

[5] N. Tshiongo, R K.K. Mbaya , K Maweja, L.C. Tshabalala, Effect of Cooling Rate on base Metals Recovery from Copper Matte Smelting Slags, World Academy of Science, Engineering and Technology 46 (2010).

[6] N Tshiongo, R K K Mbaya, and K Maweja, Leaching kinetics of Cu, Co, Zn, Pb and Fe from copper smelting slags cooled in different ways after tapping, 6th Southern African Base Metals Conference 2011.

[7] Gordon M. Ritcey, Solvent Extraction in Hydrometallurgy: Present and Future, TSINGHUA SCIENCE AND TECHNOLOGY, 11 (2006) 137-152.

[8] H.S. Altundogan, M. Boyrazli, F. Tumen, A study on the sulfuric acid leaching of copper converter slag in the presence of dichromate, Minerals Engineering 17 (2004) 465–467.

[9] Ewa Rudnik, Lidia Burzyn ´ska, Wanda Gumowska, Hydrometallurgical recovery of copper and cobalt from reduction-roasted copper converter slag, Minerals Engineering 22 (2009) 88–95.

[10] S.M. Abdel Basir, Mahmoud A. Rabah, Hydrometallurgical recovery of metal values from brass melting slag, Hydrometallurgy 53(1999) 31–44.

[11] S. Vafaeian , M. Ahmadian , B. Rezaei, Sulfuric acid leaching of mechanically activated

copper sulfide concentrate, Minerals Engineering 24 (2011) 1713–1716.

[12] H. S. Altundogan, F. Tumen, metal recovery from copper converter slag by roasting with ferric sulfate, Hyrometallurgy 44 (1997) 261-267.

[13] Zhang Yang, Man Rui-lin, Ni Wang-dong, Wang Hui, Selective leaching of base metals from copper smelter slag, Hydrometallurgy 103 (2010) 25–29.

[14] S. Anand, P. Kanta Rao and P.K. Jena, recovery of metal values from copper converter and smelter slags by ferric chloride leaching, Hydrometallurgy, 5 (1980) 355—365.

[15] Lal Bihari Sukla, RaN Narayan Kar & Vinita Panchanadikar, Leaching of copper converter slag with Aspergillus niger culture filtrate, BioMetals 1992, 5,169-172.

[16] A.N. Banza, E. Gock, K. Kongolo, Base metals recovery from copper smelter slag by oxidizing leaching and solvent extraction, Hydrometallurgy 67 (2002) 63–69.

[17] I.M. Ahmed, A.A. Nayl, J.A. Daoud, Leaching and recovery of zinc and copper from brass slag by sulfuric acid, Journal of Saudi Chemical Society (2012). Article in press.

[18] LEVENSPIEL O. Chemical reaction engineering [M]. New York: Wiley, 1972: 361−371.

[19] LIU Zhi-xiong, YIN Zhou-lan, HU Hui-ping, CHEN Qi-yuan, Leaching kinetics of low-grade copper ore containing calcium-magnesium carbonate in ammonia-ammonium sulfate solution with per sulfate, Trans. Nonferrous Met. Soc. China 22(2012) 2822−2830.