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## Copper ammonia leaching from smelter slag

**Abstract:** Copper smelter slag can be considered as an important source for using in the copper hydrometallurgy. Ammonia leaching seems to be attractive for processing copper slag. Under the influence of ammonia, copper, which is part of the minerals of copper, forms soluble ammonia complexes, while iron precipitates as insoluble compounds. In the present work, the possibility of leaching the copper smelter slag (1.26 wt.% Cu) of the Balkhash smelter using  $\text{NH}_4\text{OH}$  solutions was considered. The effect of experimental factors (leaching duration, reagent concentration, temperature, stirring rate, as well as a solid-to-liquid ratio) on the extraction of copper into solution was studied. It was found that the extraction of copper into solution increases with increasing temperature (in the studied range 298 – 333 K), pulp density (up to 10 pct) and stirring rate (up to 800 rpm). The concentration of  $\text{NH}_4\text{OH}$  almost does not affect on the level of copper extraction in the range of 1-4 M. The following experimental conditions provide the recovery of 65% of Cu into ammonia solution: 1M  $\text{NH}_4\text{OH}$ ,  $T = 333$  K, particle size 90% < 200 mesh, solid-to-liquid ratio 10 pct, stirring rate 800 rpm, and leaching duration 180 min, 65% of copper is extracted into the solution. Shrinking core model with mixture kinetics was used to describe the process of ammonia leaching of copper from smelter slag. The activation energy and pre-exponential factor for the reactions of copper dissolution were calculated to be  $16.2 \pm 0.7$  kJ/mol and  $0.138 \pm 0.001$  min<sup>-1</sup>, respectively. The relatively low value of the activation energy indicates that the rate of the overall leaching process is controlled mainly by the processes of mass transfer rather than by the rate of chemical reactions of copper dissolution.

**Key words:** copper smelter slag, ammonia leaching, shrinking core model, copper dissolution, ammonia complexes of copper.

## Introduction

Being the solid waste by-product of copper pyrometallurgical production, the copper smelter slag contains a significant amount of valuable metals, primarily, copper and zinc [1-5]. This slag is usually dumped directly, or used as ballast or additive in building or road industry [6-8]. Considering the environmental and economic aspects, it is critical to find ways to recover valuable metals from the slag. However, this task is not easy to implement, because copper slag consists of a matrix of fayalite ( $\text{Fe}_2\text{SiO}_4$ ) and includes minor components of target valuable metals.

Hydrometallurgy is considered as the promising way to recover such metals from the copper slag [9-14]. Among other hydrometallurgical processes, sulfuric acid leaching is recognized as the most convenient process for this because of the producing huge amount of acid on the metallurgical plants. However, using this process leads to the dissolution of iron pre-

sents in the slag that causes problems in the subsequent treatment of the leachate. In addition, sulfuric acid solutions are highly corrosive.

Ammonia leaching is being proposed for using in copper metallurgy as an alternative to sulfuric acid leaching [15-19]. The main advantages of ammonia leaching of copper- and zinc-containing sources are as follows: (i) raw material with high carbonation can be leached by ammonia solutions; acidic leaching can not be used for processing these types of material due to high consumption of acid (ii) equipment corrosion are eliminated (iii) complexation capacity of iron with ammonia is very low, and iron, leached, precipitates in the form of insoluble compounds. Thus, ammonia leaching has a suitable selective capacity for the non-ferrous metals to the iron (iv) unlike acids, ammonia does not react with alumina silicates, and ferrosilicates (v) the residual ammonia in the soil after leaching can act as fertilizers. The main disadvantage of ammonia leaching is the high evaporation capacity of ammonia.

Despite the fact that ammonia hydrometallurgy has been developing for a long time, there is a very limited number of works devoted to ammonium leaching of non-ferrous metals from metallurgical slag [20-24]. In the present paper, we attempted to use ammonia leaching to extract copper from copper smelting slag sample of the Balkhash copper smelter (Central Kazakhstan). The aim of the work was to investigate the influence of experimental factors on the copper extraction from the smelter slag into the solution during ammonia leaching, as well as to determine the conditions that provide an acceptable level of copper recovery.

### Materials and Methods

*Slag sample.* Copper smelter slag, used in this research, was obtained from copper smelter plant of «Kazakhmys Smelting» (Balkhash, Central Kazakhstan). The major phases of the slag sample were identified by X-ray powder diffractometry (XRD) as (Fe<sub>2</sub>SiO<sub>4</sub>), ferrosilite (FeSiO<sub>3</sub>), and magnetite (Fe<sub>3</sub>O<sub>4</sub>). The copper-containing minor phases were chalcocite (Cu<sub>2</sub>S), chalcopyrite (CuFeS<sub>2</sub>), covellite (CuS), and cuprite (Cu<sub>2</sub>O). Zinc was mainly presented in the form of its ferrite (ZnFeO<sub>2</sub>). The chemical composition of the slag sample determined by ICP-AES (Perkin Elmer, Optima 8000) after complete microwave-assisted dissolving in nitric acid was, wt. %: Fe 14.72, Si 40.28, Zn 2.73, Cu 1.26, Al 1.32, S 0.97, Ca 0.83.

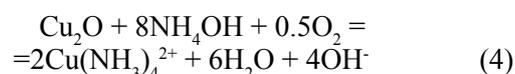
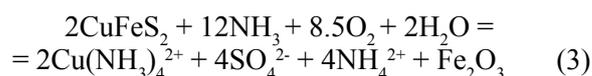
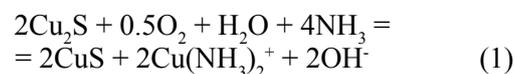
Crushed, ground, and sieved (-0.074 mm) slag sample was used for the leaching experiments.

*Leaching experiment.* The leaching tests were performed in a 1-L flask. The slag sample (20 g) was placed in the flask filled with an ammonia-ammonium aqueous solution with pre-determined concentrations of NH<sub>4</sub>OH, as well as a liquid-to-solid ratio. The flask was stirred at 500 min<sup>-1</sup> at a predetermined temperature with continuous air bubbling (300 mL×min<sup>-1</sup>). After leaching, quantitative analysis of metal ions (Fe, Cu, Zn) in the leachate was performed by using ICP-AES (Perkin Elmer, Optima 8000). All experiments were repeated 3 times.

*Variable parameters.* The following parameters were varied during the experiments to determine the conditions that provide the highest copper recovery into solution (limit values are shown in brackets): concentration of NH<sub>4</sub>OH (1-4 M), temperature (298 – 333 K), leaching duration (40-240 min), and liquid-to-solid ratio (6-20 pct).

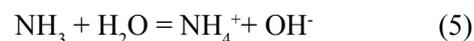
### Results and Discussion

*Leaching behavior of copper-containing phases.* Copper minerals of the slag react with aqueous ammonia in the presence of oxygen with the formation of ammonia complexes of copper (Eqs.1-4):



According to the Eh-pH diagram for the copper-ammonia-water system, Cu(I) and Cu(II) complexes with ammonia are ionic species stable in alkaline aqueous media [22]. In the solutions with an ammonia concentration of 0.01 to 5 M, the complex Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> predominates.

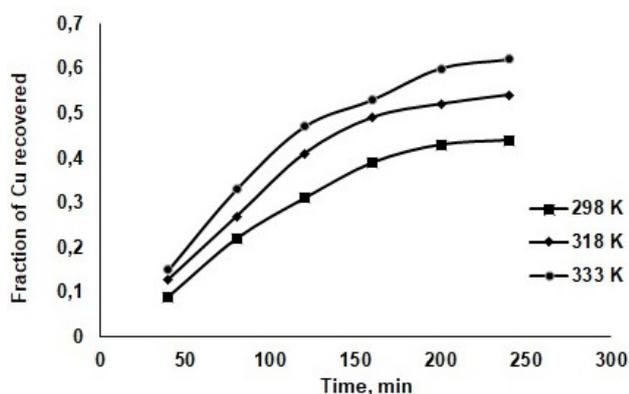
Complexation of copper ions can only happen with NH<sub>3</sub> and not with NH<sub>4</sub><sup>+</sup> ions. Therefore, the conditions should be maintained to shift the equilibrium between NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> to the left side in the Eq.5:



Obviously, increasing the pH of the medium (i.e., increasing the concentration of hydroxyl ions) is desirable for rising the free ammonia concentration. Once the pH is greater than 9.25, NH<sub>3</sub> is the dominant species in the system.

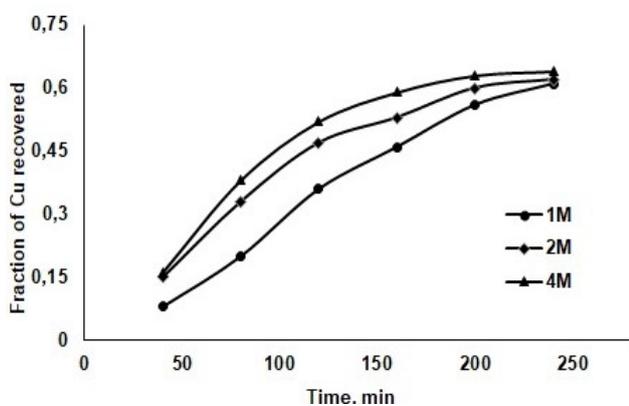
*Effect of temperature.* The leaching tests were performed at 298, 318 and 333 K while NH<sub>4</sub>OH concentration, S:L ratio, and stirring rate were set at 1M, 10 g: 1 L (10 pct) and 800 rpm, respectively. Fig.1 demonstrates that comparatively higher Cu recovery was obtained as the reaction temperature increased.

At a temperature of 333 K, copper recovery into solution reached 62% after 4 hours of leaching. A further increase in temperature is impractical due to the loss of ammonia in the environment. As has been demonstrated by Liu et al. [24], copper (II) oxide easily reacts with ammonia at ambient temperature with the formation of a soluble copper complex. Apparently, it is precisely due to the leaching of Cu<sub>2</sub>O that the presence of dissolved copper in the solution is ensured at 298 K.



**Figure 1** – Effect of temperature and leaching duration on copper recovery into solution (1M  $\text{NH}_4\text{OH}$ , particle size 90% < 200 mesh, S:L = 10 pct, stirring rate 800 rpm)

*Effect of  $\text{NH}_4\text{OH}$  concentration.* The influence of  $\text{NH}_4\text{OH}$  concentration on copper recovery into the solution has been investigated by varying the reagent concentration from 1 to 4 M at constant values of temperature (333 K), solid-to liquid ratio (10 pct), and stirring rate (800 rpm). The results obtained are present in Fig. 2.



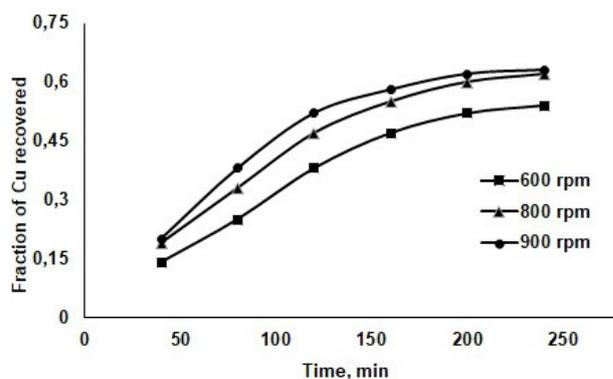
**Figure 2** – Effect of  $\text{NH}_4\text{OH}$  concentration and leaching duration on copper recovery into solution (333 K, particle size 90% < 200 mesh, S:L = 10 pct, stirring rate 800 rpm)

As can be seen from Fig. 2, an increase in the concentration of  $\text{NH}_4\text{OH}$  leads to an increase of copper extraction into solution; however, 4 hours after the start of leaching, the concentration of the reagent practically ceases to affect the degree of copper recovery, which reaches a plateau at 62%.

The following aspects should be taken into account when discussing the effect of  $\text{NH}_4\text{OH}$  concentration on the leaching of copper from slag. Firstly,

it is the stoichiometry of the reactions (Eqs. 1-4). According to the above-mentioned equations, 1M of copper requires from 1M (for chalcocite) to 8 M (for chalcopyrite) moles of ammonia to leach. If we take into account that the copper content in the slag is 1.26 wt.%, and the solid-to-liquid ratio at leaching (10 pct), then the theoretical ammonia consumption for copper leaching will be about 0.10 mol per 1 litre of solution (without taking into account the equilibrium constants of the reactions of copper minerals with ammonia). Another point is related to the fact that an increase in the concentration of ammonia in solution leads to a decrease in the concentration of oxygen. Oxygen, in turn, is an important component of the reaction mixture (see Eqs. 1-4).

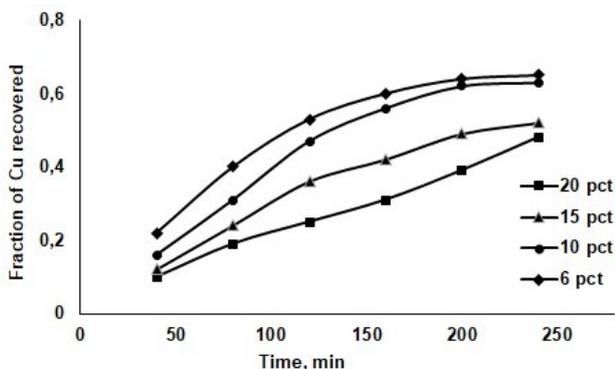
*Effect of stirring rate.* Stirring is a very important process in the ammonia leaching of copper from slag. The experiments carried out in the absence of stirring showed a very low (up to 18%) recovery of copper into solution even with prolonged (up to 5 hours) leaching. This circumstance indicates that the limiting stage of copper leaching reactions is the mass transfer of oxygen and ammonia to the surface of copper minerals. The effect of stirring rate on copper recovery at constant values of  $\text{NH}_4\text{OH}$  concentration (1M), temperature (333 K), and solid-to liquid ratio (10 pct), is presented in Fig. 3.



**Figure 3** – Effect of stirring rate and leaching duration on copper recovery into solution (1M  $\text{NH}_4\text{OH}$ , 333 K, particle size 90% < 200 mesh, S:L = 10 pct)

The value of copper recovery increases with stirring rate up to 800 rpm; above this rate, copper recovery does not affect by the stirring rate. Apparently, up to a value of 800 rpm, the leaching process is controlled by mass transfer, and above this value, the leaching rate is controlled by inner diffusion of the rate of chemical reactions.

*Effect of solid-to-liquid ratio.* Solid-to-liquid ratio, or pulp density, is a very important parameter in hydrometallurgy. The decrease in pulp density, as a rule, intensifies the leaching process. On the other hand, at low pulp density, there is an overrun of the leaching agent and the content of the target metal in the solution after leaching is reduced. Therefore, it was important to find the minimum value of the pulp density, providing an acceptable extraction of copper into solution. The results of the experiments on determining the influence of solid-to-liquid ratio on the copper recovery at the constant values of  $\text{NH}_4\text{OH}$  concentration (1M), temperature (333 K), and stirring rate (800 rpm), is presented in Fig.4.



**Figure 4** – Effect of solid-to-liquid ratio and leaching duration on copper recovery into solution (1M  $\text{NH}_4\text{OH}$ , 333 K, particle size 90% < 200 mesh, 800 rpm)

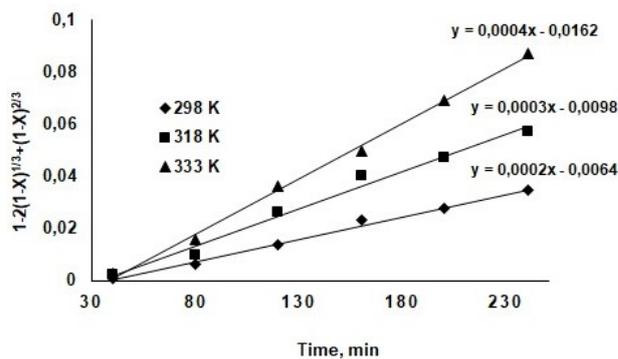
Increasing pulp density from 6 to 20 pct negatively affects the copper recovery. But, the values of copper recovery at 6 and 10 pct are almost the same. In both cases, the copper recovery values reach a plateau (64-65%) with a leaching time of 180 minutes.

*Process kinetics.* The shrinking core model was widely applied for the rate expression of leaching reactions in hydrometallurgy [25]. In this work, mixture kinetics model proposed by Ekmekyapar et al. [26] was used. The model is expressed by the following equation:

$$1 - 2(1-X)^{1/3} + (1-X)^{2/3} = k\tau \quad (6)$$

where X is the fraction of the recovered component, k is the apparent rate constant, and  $\tau$  is the leaching duration.

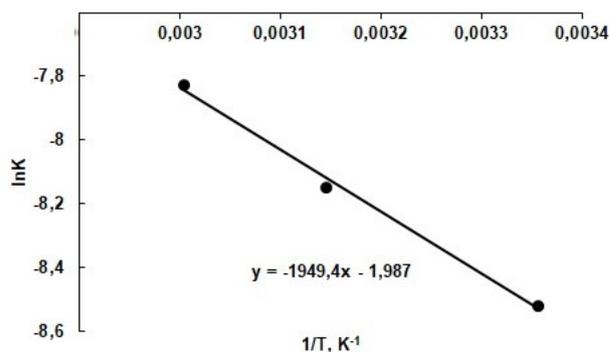
The straight lines in the Fig.5 demonstrate that the leaching process is controlled by mixture kinetics.



**Figure 5** – Plot of  $(1-2(1-X)^{1/3}+(1-X)^{2/3}) = k\tau$  vs time (1M  $\text{NH}_4\text{OH}$ , particle size 90% < 200 mesh, 800 rpm, S:L = 10 pct)

The apparent rate constants for the reactions of copper dissolution have been found as 0.0002, 0.0003 and 0.0004  $\text{min}^{-1}$  for 298, 318 and 333 K, respectively.

In order to determine the activation energy of the reactions of copper dissolution (Eqs. 1-4),  $\ln k$  versus  $1/T$  was plotted (see Fig.6).



**Figure 6** – Arrhenius plot (1M  $\text{NH}_4\text{OH}$ , particle size 90% < 200 mesh, 800 rpm, S:L = 10 pct)

The slope of the Arrhenius plot gives the  $E/R$  value, from which activation energy was calculated as  $16.2 \pm 0.7$  kJ/mol. The relatively low value of the activation energy indicates that the leaching process is controlled mainly by diffusion processes rather than by the rate of chemical reactions.

For the calculating pre-exponential factor, the Arrhenius equation was used:

$$k = A e^{\frac{-E_a}{RT}} \quad (7)$$

where  $k$  is the apparent rate constant,  $A$  is the pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the universal gas constant, and  $T$  is the absolute temperature.

According to the Eq.7, pre-exponential factor for the reaction of copper ammonia leaching was calculated to be  $0.138 \pm 0.001 \text{ min}^{-1}$ .

## Conclusions

From the results of this study, the following conclusions were made regarding the characterization of copper smelter slag obtained from the Balkhash copper plant and the ammonia leaching of this slag.

In the copper smelter slag, copper mainly presents as copper sulfides ( $\text{Cu}_2\text{S}$ ,  $\text{CuFeS}_2$ ,  $\text{CuS}$ ) and oxide ( $\text{Cu}_2\text{O}$ ).

Temperature, stirring rate, as well as pulp density have an impact on the copper recovery into solution when ammonia leaching of the slag, while the concentration of  $\text{NH}_4\text{OH}$  almost does not affect on the level of copper extraction. The stirring rate influences the process below 800 rpm, and pulp density has an impact on the process above 10 pct.

At the conditions of 1M  $\text{NH}_4\text{OH}$ ,  $T = 333 \text{ K}$ , particle size  $90\% < 200$  mesh, solid-to-liquid ratio 10 pct, stirring rate 800 rpm, and leaching duration 180 min, 65% of copper is extracted into the solution.

Shrinking core model with mixture kinetics adequately describes the process of ammonia leaching of copper from smelter slag.

The activation energy of the chemical reactions is calculated to be  $16.2 \pm 0.7 \text{ kJ/mol}$  indicating that the leaching process is controlled mainly by mass transfer processes rather than by the rate of chemical reactions.

## References

1. Kaksonen A. H., Särkijärvi S., Puhakka J. A., Peuraniemi E., Junnikkala S., Tuovinen O. H. (2017). Solid phase changes in chemically and biologically leached copper smelter slag. *Miner Eng.*, vol. 106, pp. 97-101.
2. Das B., Mishra B. K., Angadi S., Pradhan S. K., Prakash S., Mohanty J. (2010). Characterization and recovery of copper values from discarded slag. *Waste Manage Res.*, no. 28(6), pp. 561-567.
3. Sueoka Y., Sakakibara M. (2013). Primary phases and natural weathering of smelting slag at an abandoned mine site in southwest Japan. *Minerals*, no. 3(4), pp. 412-426.
4. Miganei L., Gock E., Achimovičová M., Koch L., Zobel H., Kähler J. (2017). New residue-free processing of copper slag from smelter. *J Clean Prod.*, vol. 164, pp. 534-542.
5. Potysz A., van Hullebusch E. D., Kierczak J., Grybos M., Lens P. N., Guibaud G. (2015). Copper metallurgical slags—current knowledge and fate: a review. *Crit Rev Env Sci Tec.*, vol. 45(22), pp. 2424-2488.
6. Onuaguluchi O., Eren Ö. (2012). Recycling of copper tailings as an additive in cement mortars. *Constr Build Mater.*, vol. 37, 723-727.
7. Pappu A., Saxena M., Asolekar S. R. (2007). Solid wastes generation in India and their recycling potential in building materials. *Build Environ*, vol. 42(6), pp. 2311-2320.
8. Murari K., Siddique R., Jain K. K. (2015). Use of waste copper slag, a sustainable material. *J Mater Cycles Waste*, vol. 17(1), pp. 13-26.
9. Nadirov R. K. (2019). Recovery of valuable metals from copper smelter slag by sulfation roasting. *T Indian I Metals*, vol. 72(3), pp. 603-607.
10. Banza A. N., Gock E., Kongolo, K. (2002). Base metals recovery from copper smelter slag by oxidising leaching and solvent extraction. *Hydrometallurgy*, vol. 67(1-3), pp. 63-69.
11. Yang Z., Rui-lin M., Wang-dong N., Hui, W. (2010). Selective leaching of base metals from copper smelter slag. *Hydrometallurgy*, vol. 103(1-4), 25-29.
12. Turan M. D., Sari Z. A., Miller, J. D. (2017). Leaching of blended copper slag in microwave oven. *T Nonferr Metal Soc.*, vol. 27(6), pp. 1404-1410.
13. Kaksonen A. H., Särkijärvi S., Puhakka J. A., Peuraniemi E., Junnikkala S., Tuovinen O. H. (2016). Chemical and bacterial leaching of metals from a smelter slag in acid solutions. *Hydrometallurgy*, vol. 159, pp. 46-53.
14. Meshram P., Bhagat L., Prakash U., Pandey B. D., Abhilash. (2017). Organic acid leaching of base metals from copper granulated slag and evaluation of mechanism. *Can Metall Quart.*, vol. 56(2), pp. 168-178.
15. Çalban T., Çolak S., Yeşilyurt M. (2005). Optimization of leaching of copper from oxidized copper ore in  $\text{NH}_3\text{-(NH}_4)_2\text{SO}_4$  medium. *Chem Eng Commun.*, vol. 192(11), pp. 1515-1524.
16. Bingöl D., Canbazoğlu M., Aydoğan S. (2005). Dissolution kinetics of malachite in ammonia/ammonium carbonate leaching. *Hydrometallurgy*, vol. 76(1-2), pp. 55-62.

17. Meng X., Han, K. N. (1996). The principles and applications of ammonia leaching of metals—a review. *Min Proc Ext Met Rev.*, vol. 16(1), pp. 23-61.
18. Radmehr V., Koleini S. M. J., Khalesi M. R., Mohammadi M. R. T. (2013). Ammonia Leaching: A new approach of copper industry in hydrometallurgical processes. *Journal of The Institution of Engineers (India): Series D*, vol. 94(2), pp. 95-104.
19. Radmehr V., Koleini S. M., Khalesi M. R., Tavakoli M. R. (2012). Ammonia leaching in the copper industry: a review. In *XXVI international mineral processing congress (IMPC) proceedings/New Delhi, India/24–28 September* (pp. 02512-02523).
20. Nadirov R., Syzdykova L., Zhussupova A. (2017). Copper smelter slag treatment by ammonia solution: Leaching process optimization. *J Cent South Univ.*, vol. 24(12), pp. 2799-2804.
21. Roy S., Sarkar S., Datta A., Rehani S. (2016). Importance of mineralogy and reaction kinetics for selecting leaching methods of copper from copper smelter slag. *Sep Sci Technol.*, vol. 51(1), pp. 135-146.
22. Bidari E., Aghazadeh V. (2015). Investigation of Copper Ammonia Leaching from Smelter Slags: Characterization, Leaching and Kinetics. *Metall Mater Trans B*, vol. 46(5), pp. 2305-2314.
23. Peretrutov A. A., Chubenko M. N., Kim P. P., Yakunin Y. I. (2009). Combined solubility of copper and zinc oxides in ammonia-ammonium solutions. *Russ J Phys Chem A*, vol. 83(8), pp. 1422-1425.
24. Liu Z. X., Yin Z. L., Hu H. P., Chen, Q. Y. (2012). Leaching kinetics of low-grade copper ore with high-alkalinity gangues in ammonia-ammonium sulphate solution. *J Cent South Univ.*, vol. 19(1), pp. 77-84.
25. Safari V., Arzpeyma G., Rashchi F., Mostoufi, N. (2009). A shrinking particle–shrinking core model for leaching of a zinc ore containing silica. *Int J Miner Process.*, vol. 93(1), pp. 79-83.
26. Ekmekyapar A., Oya R., Künkül, A. (2003). Dissolution kinetics of an oxidized copper ore in ammonium chloride solution. *Chem Biochem Eng Q*, vol. 17(4), pp. 261-266.