Sakarya University Journal of Science

ISSN : 2147-835X
Publisher : Sakarya University

Vol. 28, No. 5, 930-936, 2024
DOI: https://doi.org/10.16984/saufenbilder.1410409

Research Article

The Effect of Various Parameters in the Sulfuric Acid Leaching of Low Grade Zinc Oxide Ore of Niğde-Türkiye

Özlem Kaya[1*], Gürol Uysal[2]

[1] Sivas Cumhuriyet University, Faculty of Engineering, Department of Metallurgical and Materials Engineering, Sivas, Türkiye, okaya@cumhuriyet.edu.tr
[2] ETİ Electrometallurgy Inc., Muğla, Türkiye, g.uysal@etimet.com
[*]Corresponding Author

ARTICLE INFO

ABSTRACT

Keywords:
Leaching
Low grade zinc oxide ore
Zinc extraction

Article History:
Received: 29.12.2023
Accepted: 18.08.2024
Online Available: 14.10.2024

The aim of this study was to investigate the main parameters affecting the leaching of low grade zinc oxide ores with sulfuric acid. The influence of leaching time (5 to 480 minutes), sulfuric acid concentration (25 to 125 g/L), leaching temperature (25 to 90 °C), particle size (-104 µm, -82 µm, -60 µm, -49 µm) and solid/liquid ratio (1/10, 1/7.5, 1/5, 1/4) was investigated. The effects of these process parameters were studied with to achieve maximum zinc extraction with minimum iron extraction and acid consumption. The optimum parameters for sulfuric acid leaching of zinc ore were determined to be 60 min leaching time, 75 g/L sulfuric acid concentration, 80 ºC leaching temperature, 1/10 solid/liquid ratio and -60 µm particle size. Under these optimum conditions, Zn extraction (%), Fe extraction (%) and acid consumption (ton H_2SO_4/ dissolved ton Zn) were obtained 88.68%, 25.83% and 5.47 ton H_2SO_4/ dissolved ton Zn respectively.

1. Introduction

Zinc is a versatile non-ferrous metal that is widely utilized in various industries including galvanization, cosmetics, die casting, and battery manufacturing. Oxidized zinc ores such as smithsonite ($ZnCO_3$), zincite (ZnO), hemimorphite ($Zn_4(SiO_7)(OH)_2H_2O$), willemite (Zn_2SiO_4) and hydrozincite ($ZnCO_3.2Zn(OH)_2$) are the most important sources of zinc metal production after sulfides [1, 2]. Most of the zinc in the world is produced from high grade zinc sulfide ores. In recent years, the demand for zinc and zinc compounds has increased, whereas the number of high grade zinc ore stores has decreased. As a result, new sources of zinc, such as low grade ores, carbonate ores and silicate ores, are being considered, leading to an increasing focus on the processing of low grade oxide ores.

The extraction of zinc from its oxide ores can be performed using both pyrometallurgical and hydrometallurgical methods. The three main steps in the hydrometallurgical method are leaching, purification and electrolysis. Leaching processes constitute the first step of the hydrometallurgical methods and plays an important role in the extraction of metals and compounds in an economical way. The most commonly used hydrometallurgical methods for zinc production are alkaline leaching, acid leaching and ammonia leaching. Acid leaching is considered the most effective method of zinc extraction process because of its advantages, including rapid process, easy leach solution purification and high selectivity [3-5].

Leaching studies on zinc ore with sulfuric acid have been carried out by many researchers. Frenay [6] conducted leaching studies on

Cite as: Kaya Ö., Uysal G. (2024). The Effect of Various Parameters in the Sulfuric Acid Leaching of Low Grade Zinc Oxide Ore of Niğde-Türkiye, *Sakarya University Journal of Science*, 28(5), 930-936. https://doi.org/10.16984/saufenbilder.1386611

oxidized zinc ores using different solutions, including ammonium hydroxide, sulfuric acid, sulfurous acid, and sodium hydroxide. Caustic soda and sulfuric acid were identified as providing the best leaching results. This study highlighted that smithsonite can be completely leached, whereas hemimorphite is relatively refractory to leaching. He et al. [7] investigated the pressure leaching of high silica Pb-Zn oxide ore using air as a pressurized gas in a sulfuric acid medium. The leaching time, leaching temperature, sulfuric acid concentration, oxygen partial pressure, and solid/liquid ratio were among the parameters studied. Under optimum conditions, the study found that zinc extraction reached 96%. Moreover, the dissolution rates for Si, Pb and Fe were as low as 1%, 2%, and 6%, respectively. Pecina et al. [8] investigated the use of hydrogen peroxide as an oxidant in sulfuric acid solutions for the extraction of zinc from sphalerite concentrate. Acid and peroxide concentrations, particle size, reaction time and temperature are among the parameters studied. This study also investigated the use of complexing agents (citric acid, phosphoric acid, oxalic acid and phosphonic acid) to enhance zinc recovery in an oxidative aqueous medium. Terry and Monhemius [9] studied the acid dissolution kinetics of natural and synthetic willemites and natural hemimorphites. The parameters studied included acid type, surface area, temperature and pH. For willemite the dissolution was found to be mixed chemical/diffusion controlled and for hemimorphite the dissolution was found to be diffusion controlled.

As noted in the literature, detailed studies on the leaching of low grade zinc oxide ores are limited and therefore require more comprehensive investigations. In addition, each ore has its own chemical and mineralogical properties; therefore, the optimum leaching conditions will vary from one ore type to another. The research was specifically focused on investigating the important factors affecting sulfuric acid leaching of low grade zinc oxide ore from Niğde-Türkiye.

2. Materials and Methods

The zinc oxide ore used for the leaching experiments was supplied by a local mining company in Niğde-Türkiye. The chemical composition of the ore was characterized by X-ray fluorescence (XRF) and is presented in Table 1.

Table 1. The chemical composition of zinc oxide ore

Component	Weight (%)
Zn	8.44
Fe	21.70
Pb	1.21
Cu	0.07
Mn	1.96
Ca	1.30
Cd	0.04
Ni	0.11
SiO_2	28.62
S	0.08
As	1.01
K	0.29
Na	<0.10
Moisture	2.02

The X-ray diffraction (XRD) pattern of zinc oxide ore was obtained using a Rigaku DMAX IIIC model X-ray diffractometer with CuKά radiation at 35 kV and 15 mV (Figure 1). As shown in Figure 1, smithsonite ($ZnCO_3$) and zincite (ZnO) are the main zinc oxide minerals in the sample, whereas quartz (SiO_2), goethite (FeOOH) and pyrolusite (MnO_2) are gangue minerals.

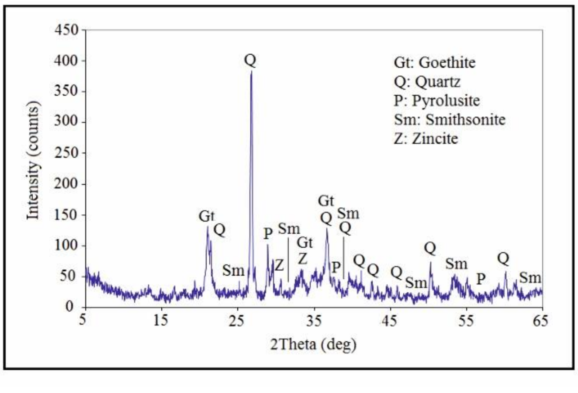

Figure 1. The XRD pattern of zinc oxide ore

Leaching tests were performed using sulfuric acid from Merck with 95-98% analytical purity. In the experiments, a 1000 mL glass beaker was used. The beaker was covered by a cap with four holes that were drilled for place the thermometer, mechanical stirrer, pH meter or back cooler and for taking samples. The experiments were performed with 50 g of sample in a beaker placed in a thermostatically controlled water bath. Figure 2 shows the experimental setup for leaching.

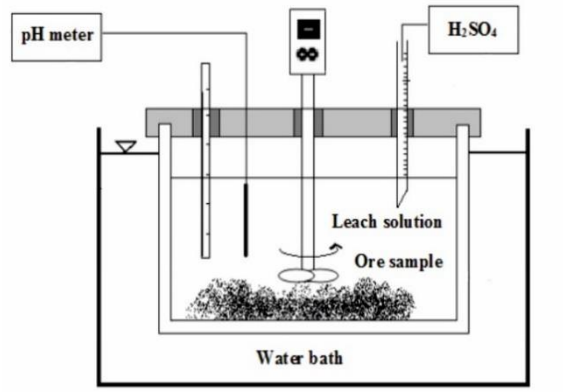

Figure 2. The experimental setup for leaching

While the method used in the leaching experiments was the same, the experiments investigated the effect of different parameters on the sulfuric acid leaching of zinc oxide ore. After the completion of each leaching experiment, the leach solution was filtered, and the solid leach residue was then washed with distilled water. The washed solid residue was dried at 105 ± 5 °C. The total dissolved weight (%) was calculated from the dried solid residue. To determine the Zn extraction (%) and Fe extraction (%), the leach solution was analyzed using Atomic Adsorption Spectrometry (AAS). The sulfuric acid consumption was determined by alkalimetric titration with NaOH.

3. Results and Discussion

3.1. Effect of leaching time

Leaching experiments were carried out in the range of 5-480 min. In the experiments, an H_2SO_4 concentration of 75 g/L, leaching temperature of 40 ^oC, particle size of -82 µm and solid/liquid ratio of 1/10 were kept constant. Leaching experiments at different times are presented in Figure 3.

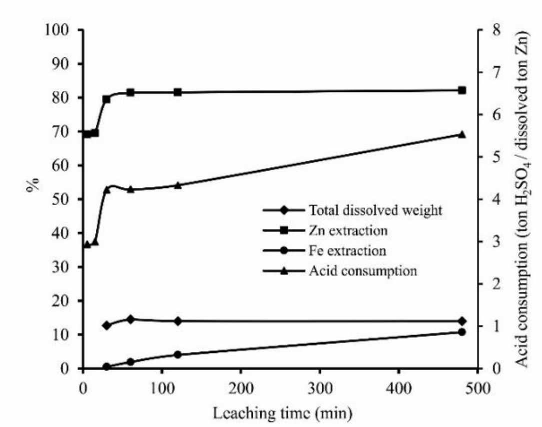

Figure 3. Effect of leaching time on the sulfuric acid leaching

As shown in Figure 3, the Zn extraction (%) increased to 81.45% with leaching times up to 60 min and remained almost constant with longer leaching times. This suggests that the majority of zinc dissolution occurs within the initial 60 min of leaching. In contrast, Fe extraction (%) increased from 0.49% after 30 min to 10.73% after 480 min of leaching. The increase in iron extraction over time indicates a progressive dissolution of iron from the ore. The iron content in the ore plays a significant role in determining zinc extraction, with higher iron content leading to lower zinc extraction.

According to Frenay [6], this is the result of smithsonite particles covered with hydroxides of iron. Simultaneously, the acid consumption (ton H_2SO_4/dissolved ton Zn) increased with increasing leaching time. While the acid consumption at the end of 5 minutes leaching is 2.93 ton H_2SO_4/dissolved ton Zn, it increases to 5.53 ton H_2SO_4/dissolved ton Zn at the end of 480 minutes leaching. This indicates a relationship between leaching time and acid consumption.

From Figure 3 it can be seen that 81.45% Zn extraction, 14.46% total dissolved weight, 1.89% Fe extraction and 4.23 ton H_2SO_4/dissolved ton Zn are achieved with the 60 min leaching time. Considering the high values of Zn extraction (%), total dissolved weight (%) and the low values of Fe extraction (%), acid consumption (ton H_2SO_4/dissolved ton Zn), a leaching time of 60 min was considered optimal.

3.2. Effect of sulfuric acid concentration

The effect of different concentrations of sulfuric acid (25, 40, 55, 75, 100 and 125 g/L) on the leaching was studied under the following conditions: leaching time of 60 min, leaching temperature of 40 ^oC, particle size of -82 µm and solid/liquid ratio of 1/10. Leaching experiments with different concentrations of sulfuric acid are shown in Figure 4.

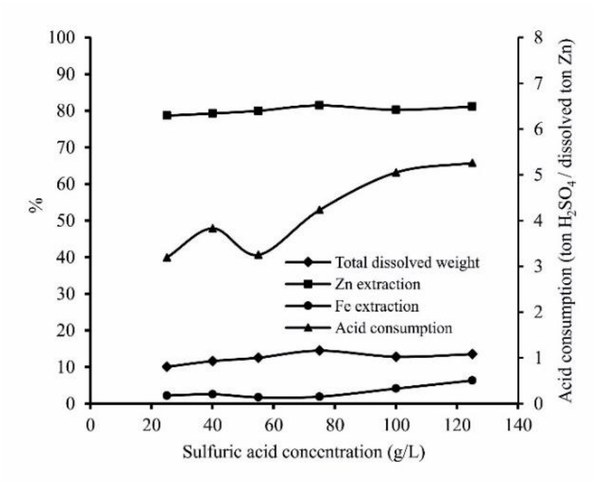

Figure 4. Effect of acid concentration on the sulfuric acid leaching

The general dissolution reactions for the main zinc oxide minerals, smithsonite ($ZnCO_3$) and zincite (ZnO), with sulphuric acid are given by equations (1) and (2): [4, 10-11]

$$ZnCO_3 + H_2SO_4 \rightarrow ZnSO_4 + H_2O + CO_2 \quad (1)$$

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O \quad (2)$$

Figure 4 indicates that with an increase in the sulfuric acid concentration from 25 g/L to 125 g/L, the Zn extraction (%) increased from 78.68% to 81.14%, the Fe extraction (%) increased from 2.19% to 6.30% and the total dissolved weight (%) increased from 10.04% to 13.49%. As the sulfuric acid concentration increases, the chemical reactions between zinc (Zn), iron (Fe) and sulfuric acid become more complete, resulting in higher extraction of both Zn and Fe into the leaching solution [7].

Figure 4 shows that there is a positive correlation between the sulfuric acid concentration and both the total dissolved weight (%) and Zn extraction (%). This suggests that an increase in acid concentration increases the leaching efficiency of zinc oxide ores. The maximum values for the total dissolved weight (%) and Zn extraction (%) were obtained at a sulfuric acid concentration of 75 g/L. Above this concentration, both the values remained constant. Similar trends have been observed in previous studies by Espiari et al. [1] and Bodas [12]. Espiari et al. [1] found that zinc recovery increased up to 88% with sulfuric acid concentration up to 2 M and remained almost constant at higher acid concentrations. Bodas [12] reported that zinc extraction increased with sulfuric acid concentration up to 4.5 M and then became constant.

The maximum Zn extraction (81.45%) and total dissolved weight (14.46%) were obtained with 75 g/L of sulfuric acid. The lowest Fe extraction of 1.89% at 75 g/L sulfuric acid is desirable, as it minimizes the dissolution of iron during the leaching. This is important for maintaining the selectivity of the leaching process and avoiding contamination of the leaching solution with unwanted metals. Higher sulfuric acid concentrations can result in increased zinc extraction, but an optimum concentration needs to be identified to balance extraction efficiency and acid consumption. A sulfuric acid concentration of 75 g/L was identified as the optimum condition for achieving a balance among high Zn extraction (%), total dissolved weight (%) and low Fe extraction (%), acid consumption (ton H_2SO_4/dissolved ton Zn).

3.3. Effect of leaching temperature

Leaching experiments were carried out over a wide temperature range (25°C-90°C) to understand the effect of temperature on the leaching process. Leaching temperature experiments were performed with a leaching time of 60 min, H_2SO_4 concentration of 75 g/L, particle size of -82 µm, solid/liquid ratio of 1/10. Leaching experiments at different temperatures are shown in Figure 5.

The results from Figure 5 show a positive relationship between leaching temperature and both total dissolved weight (%) and Zn extraction (%). Increasing the leaching temperature from 25°C to 80°C resulted in a gradual increase in the total dissolved weight (4.22% to 24.68%) and Zn extraction (76.85% to 87.95%). These results are consistent with those of Santos et al. [13], who observed a significant increase in zinc extraction from 36% to 90% when the temperature was increased from 70°C to 90°C during the leaching of zinc silicate ores.

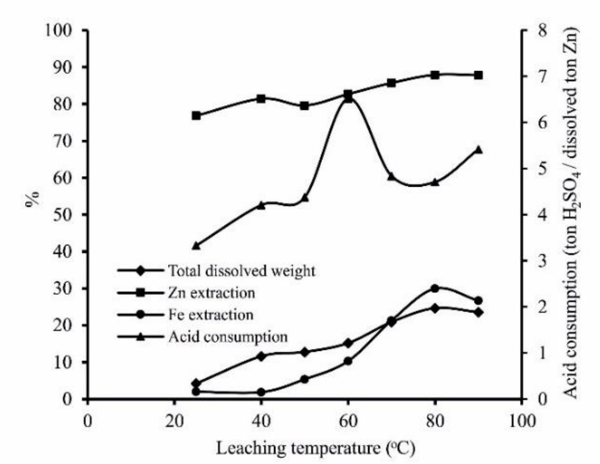

Figure 5. Effect of leaching temperature on the sulfuric acid leaching

As the leaching temperature increased from 25°C to 80°C, an increase in acid consumption was observed from 3.33 to 4.71 ton H_2SO_4/dissolved ton Zn. This indicates that too much acid is being used in the leaching process at higher temperatures. It can be seen that the leaching temperature was also effective for Fe extraction (%). At a leaching temperature of 80°C, Fe extraction reached 29.96%. Although it is known that iron dissolution affects selectivity, an optimum leaching temperature of 80 ^{o}C was chosen to increase Zn extraction, while other parameters were investigated. Figure 5 shows that at a leaching temperature of 80 ^{o}C, 24.68% total dissolved weight, 87.95% Zn extraction, 29.96% Fe extraction and 4.71 ton H_2SO_4/dissolved ton Zn acid consumption were achieved. Thus, leaching temperature of 80 ^{o}C is considered to be the optimum leaching temperature.

3.4. Effect of particle size

Four different particle sizes (-104, -82, -60 and -49 µm) were used to determine the effect of particle size on the leaching process. The leaching experiments were conducted under the conditions: leaching time of 60 min, H_2SO_4 concentration of 75 g/L, leaching temperature of 80 ^{o}C and solid/liquid ratio of 1/10. The leaching experiments with different particle sizes are shown in Figure 6.

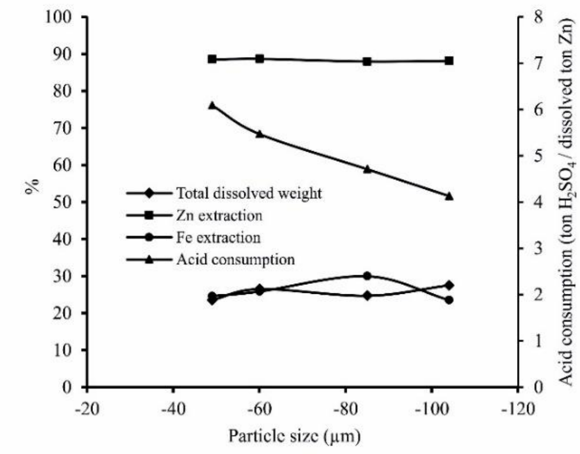

Figure 6. Effect of particle size on the sulfuric acid leaching

Figure 6 shows that decreasing the particle size had no noticeable effect on the total dissolved weight (%), Zn extraction (%), Fe extraction (%) and acid consumption (ton H_2SO_4/dissolved ton Zn). Contrary to the expectation that decreasing the particle size would positively influence the leaching process, the experimental results show that the highest total dissolved weight (26.50%) and zinc extraction (88.68%) were observed at the -60 µm particle size. This can be explained by the possibility that some other factors (surface area, agglomeration effect, and mineralogical properties) interact with the particle size to influence the leaching efficiency. An acid consumption of 5.47 ton H_2SO_4/dissolved ton Zn was achieved at this particle size. Based on these observations, a particle size of -60 µm was selected as the optimum for zinc leaching under the given conditions.

3.5. Effect of solid/liquid ratio

Four different solid/liquid ratios (1/10, 1/7.5, 1/5 and 1/4) were investigated for their effect on the leaching process. Leaching experiments were performed under conditions in which the leaching time, H_2SO_4 concentration, leaching temperature and particle size were kept constant at 60 min, 75 g/L, 80 ^{o}C and -60 µm respectively. Leaching experiments with different solid/liquid ratios are shown in Figure 7.

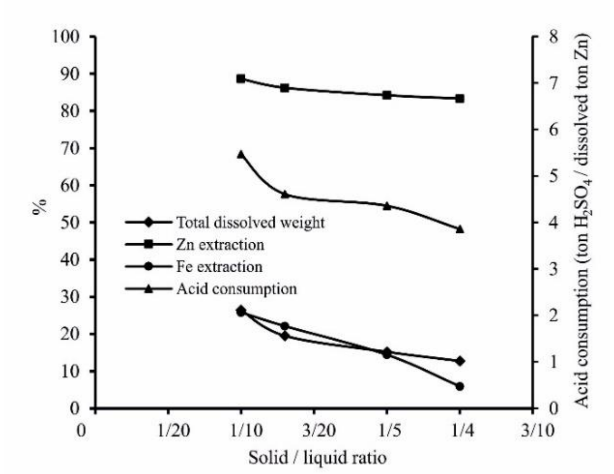

Figure 7. Effect of solid/liquid ratio on the sulfuric acid leaching

Figure 7 shows the inverse relationship between the solid/liquid ratio and total dissolved weight (%). As the solid/liquid ratio decreased from 1/4 to 1/10, the total dissolved weight (%) increased from 12.75% to 26.50%. A decrease in the solid/liquid ratio resulted in increased values of Zn extraction (%), Fe extraction (%), and acid consumption (ton H_2SO_4/ dissolved ton Zn). This indicates that a lower solid/liquid ratio results in a more efficient leaching process but requires higher acid consumption.

The experiments showed that the highest values for both the total dissolved weight (%) and Zn extraction (%) were obtained with a solid/liquid ratio of 1/10, giving 26.50% total dissolved weight and 88.68% Zn extraction. Based on these results, a solid/liquid ratio of 1/10 was chosen as optimal for the studied conditions. These results are consistent with the study by Espiari et al. [1], who reported that the leaching rate increased as the solid/liquid ratio decreased. They achieved a maximum zinc recovery of 98% at a solid/liquid ratio of 1/4.

4. Conclusion

This study investigated the extraction of zinc by sulfuric acid leaching from low grade oxidized zinc ore. Five main parameters including leaching time and temperature, acid concentration, particle size and solid/liquid ratio were optimized. The following conclusions were drawn:

(1) Smithsonite ($ZnCO_3$) and zincite (ZnO) were identified as the major zinc oxide minerals in the studied ore. The solubility of zinc in sulfuric acid was confirmed from these minerals.

(2) Zn and Fe extraction increased with an increase in leaching time, sulfuric acid concentration, and leaching temperature. This indicated a positive correlation between these factors and the efficiency of Zn and Fe extraction.

(3) Decreasing both the particle size and solid/liquid ratio contributed to an increase in Zn extraction (%). This suggests that finer particle sizes and lower solid/liquid ratios improve leaching efficiency.

(4) The following optimum conditions for maximum zinc extraction:
Leaching time: 60 minutes
Sulfuric acid concentration: 75 g/L
Leaching temperature: 80°C
Particle size: -60 µm
Solid/liquid ratio: 1/10

(5) Under the optimized conditions, the study achieved maximum Zn extraction of 88.68%, with a minimum Fe extraction of 25.83% and acid consumption of 5.47 ton H_2SO_4/dissolved ton Zn. The highest total dissolved weight was obtained as 26.50%.

Article Information Form

Funding
Authors would like to thank for the financial support provided by TUBITAK (the Scientific and Technical Research Council of Turkey) for the Project no: 109M112.

Authors' Contribution
The authors contributed equally to the study.

The Declaration of Conflict of Interest/ Common Interest
No conflict of interest or common interest has been declared by the authors.

The Declaration of Ethics Committee Approval
This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

References

[1] S. Espiari, F. Rashchi, S.K. Sadrnezhaad, "Hydrometallurgical treatment of tailings with high zinc content", Hydrometallurgy, vol. 82, pp. 54-62, 2006.

[2] J. Deng, Q. Sun, P. Lin, G. Song, S. Wen, J. Deng and D. Wu, "Dissolution kinetics of zinc oxide ore with an organic Acid" International Journal of Metallurgical & Materials Engineering, vol.1: 109, 7 pages, 2015.

[3] M. Hurşit, O. Laçin, H. Saraç, "Dissolution kinetics of smithsonite ore as an alternative zinc source with an organic leach reagent", Journal of the Taiwan Institute of Chemical Engineers, vol. 40, pp. 6-12, 2009.

[4] E.A. Abdel-Aal, "Kinetics of sulfuric acid leaching of low-grade zinc silicate ore, Hydrometallurgy, vol. 55, pp. 247-254, 2000.

[5] Y. Zhang, Y. Hua, X. Gao, C. Xu, J. Li, Y.Li, Q., Zhang, L. Xiong, Z. Su, M. Wang, J. Ru, "Recovery of zinc from a low-grade zinc oxide ore with high silicon by sulfuric acid curing and water leaching", Hydrometallurgy, vol. 166, pp. 16-21, 2016.

[6] J. Frenay, "Leaching of oxidized zinc ore in various media", Hydrometallurgy, vol.15, pp. 243-253, 1985.

[7] S. He, J. Wang, J. Yan, "Pressure leaching of high silica Pb-Zn oxide ore in sulfuric acid medium", Hydrometallurgy, vol. 104, no. 2, pp. 235-240, 2010.

[8] T. Pecina, T. Franco, P. Castillo, E. Orrantia, "Leaching of a zinc concentrate in H_2SO_4 solutions containing H_2O_2 and complexing agents", Minerals Engineering, vol. 21, no.1, pp. 23-30, 2008.

[9] B. Terry, A. J. Monhemius, "Acid dissolution of willemite ($(Zn, Mn)_2SiO_4$) and hemimorphite ($Zn_4Si_2O_7(OH)_2.H_2O$)", Metallurgical Transactions B, vol. 14B, pp. 335-346, 1983.

[10] T. Havlik, M. Turzakova, S. Stopic, B. Friedrich, "Atmospheric leaching of EAF dust with diluted sulphuric acid", Hydrometallurgy, vol. 77, pp. 41-50, 2005.

[11] H. Xu, C. Wei, C. Li, G. Fan, Z. Deng, M. Li, X. Li, "Sulfuric acid leaching of zinc silicate ore under pressure", Hydrometallugy, vol. 105, pp. 186-190, 2010.

[12] M.G. Bodas, "Hyrometallurgical treatment of zinc silicate ore from Thailand", Hydrometallurgy, vol. 40, pp. 37-49, 1996.

[13] F.M. Santos, P.S. Pina, R. Porcaro, A.V. Oliveira, C.A. Silva, V.A. Leão, "The kinetics of zinc silicate leaching in sodium hydroxide", Hydrometallurgy, vol. 102, pp. 43-49, 2010.