Investigation of Leaching Kinetics of Smithsonite Ore

Laçin, Oral*+; Dönmez, Bünyamin; Eti, Feride Ebru
Department of Chemical Engineering, Atatürk Üniversity, 25240 Erzurum, TURKEY

ABSTRACT: *The leaching kinetics of smithsonite ore in acetic acid solutions, an environmental friend, and natural reagent was investigated. The influence of parameters such as reaction temperature, particle size, solid-liquid ratio and acid concentration was studied in order to reveal the leaching kinetics of smithsonite ore. In this study, experimental and statistical methods were carried out in order to analyze the kinetics data to investigate a kinetics model which describes the dissolution. The results indicate that the unreacted shrinking core model for fluid-solid heterogeneous reactions was favorable for the leaching process. The apparent activation energy of the leaching process was found as 74 kJ/ mol. It was determined that the leaching rate of smithsonite was controlled by the chemical reaction below:* $(1-x)^{1/3}=3.7\times10^{5}e^{-74/RT}t$.

KEYWORDS: *Smithsonite ore; Leaching; Reaction kinetics; Acetic acid.*

INTRODUCTION

In recent years, as a result of an increase in the consumption of raw materials, the developing countries have started to use their own resources such as mine and natural gas. Turkey is one of the few countries which have a vast variety of mineral sources. For instance, Turkey is rich in terms of smithsonite ore, which is an important source of zinc and its compounds. Also, these products have rather wide usage fields [1,2].

Most common method for the leaching process is a hydrometallurgical method [3,4]. Although there are studies regarding the examination of zinc dissolution with inorganic reagents [5-8], there are few studies concerning the dissolution kinetics of zinc in organic reagents [9-12]. Therefore, it is significant to examine zinc dissolution with carbonaceous compounds in particular [13,14].

In aquatic solutions, acetic acid is weakly dissociated (pKa = 4.76). Also, many metals, as well as their oxides and carbonates, dissolve in aqueous solutions of acetic acid to give simple salts. Today, acetic acid is also widely used as a solvent in the chemical industry and a raw material for many organic syntheses such as the manufacture of vinyl acetate and cellulose acetate [15].

The reaction rate of the process strongly depends on properties of the solid as well as the process conditions. The natural smithsonite also contains some impurities such as aluminum, iron, and calcium. These impurities affect the quality of products. As inorganic acids such as H_2SO_4, HNO_3 or HCI were used, some undesired impurities particularly such as Fe can be dissolved in the leaching solutions. Therefore, organic reagents used are selective.

When the zinc carbonate is chemically reacted with the acetic acid, zinc acetate, carbon dioxide and water are formed. Zinc acetate formed has rather a wide usage fields such as medicine, mordant dyeing, wood preservative,

** To whom correspondence should be addressed.*
+ E-mail: olacin@atauni.edu.tr
1021-9986/2018/1/205-212 8/$/5.80
DOI:

disinfectant and porcelain industry [2,16]. Thus, it is believed that the kinetic data for the reaction of smithsonite by acetic acid are very important for industrial applications.

Therefore, the aim of this work is to study the leaching behavior of smithsonite by acetic acid solutions as a different approach.

EXPERIMENTAL SECTION

The smithsonite ore used in the work was provided from Kayseri in Turkey. After crushing and washing, the ore was ground and then sieved using ASTM standard sieves, giving particle size fractions of -425+250 (338) μm, -250+180 (215) μm, -180+150 (165) μm and -150+90 (120) μm. The ore's chemical composition was analyzed by standard gravimetric and volumetric methods. The results were given in Table 1. An X-ray diffractogram illustrating the contents of the sample was given in Fig. 1. From the chart list in Table 2 peaks in Fig. 1 demonstrated that they belonged to smithsonite ore.

The acetic acid used as leachate in the study was of reagent grade. Dissolution experiments were carried out in a well-mixed spherical glass batch reactor (500 mL) heated by a constant temperature bath and equipped with a mechanical stirrer that had a digital controller unit, a thermometer, and a condenser. Experimental setup was given in Fig. 2. After adding 250 mL of acetic acid solution to the reaction vessel and setting the temperature at the desired value, a charge of a certain amount of solid was approximately added to the reactor while stirring the content of the reactor at a certain speed. After each test, an amount of sample taken from the leach slurry was filtered immediately, and the amount of zinc in the filtrate was analyzed complexometrically by EDTA at the medium of buffer solution (about pH 10) [17].

Dissolution behavior for samples of natural smithsonite was tested under reaction conditions as follows: reaction temperature from 30 to 70 ºC, acid concentration from 1 to 10 M, the solid-liquid ratio from 4 to 80 g/L and particle size from -150+90 to -425+250 μm.

Dissolution tests were performed as a function of studied parameters, and their ranges and values were listed in Table 3.

RESULTS AND DISCUSSION

The reaction between smithsonite and acetic acid is a fluid-solid multiphase reaction. This reaction can be express as follows:

Table 1: Chemical analysis of the smithsonite ore.

Component	[wt.%]
ZnO	57.28
SiO_2	1.8
Al_2O_3	1.5
Fe_2O_3	1.6
CaO	0.9
Loss on ignition	35.5
others	1.42

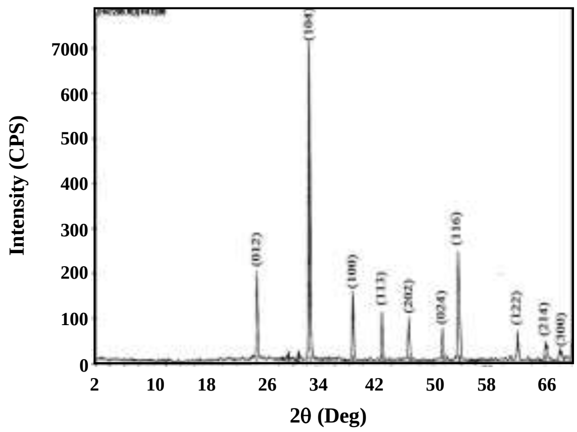

Fig. 1: The diffraction patterns of the smithsonite ore.

$$2CH_3COOH_{(aq)} + 2H_2O_{(l)} \leftrightarrow \quad (1)$$

$$2H_3O^+_{(aq)} + 2CH_3COO^-_{(aq)}$$

$$ZnCO_{3(s)} + 2H_3O^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + CO_{2(g)} + 3H_2O_{(l)} \quad (2)$$

The overall reaction can be written as follows:

$$ZnCO_{3(s)} + 2CH_3COOH_{(aq)} \rightarrow \quad (3)$$

$$Zn^{2+}_{(aq)} + 2CH_3COO^-_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$

Effect of particle size

The experiments were performed for different particle sizes (-425+250 (338) μm, -250+180 (215) μm, -180+150 (165) μm and -150+90 (120) μm) in solutions containing 3.0 M acetic acid at a stirring speed of 500 rpm. The effect of particle size was studied at 50 ºC and the solid-liquid ratio of 8 g/L. As seen in Fig. 3, the dissolution rate partially increased with a decrease in particle size of solid used, which could be attributed to the increase of the contact surface with the decrease of the particle size per unit weight of the solid.

Table 2: Chart List.

C. formula : $ZnCO_3$
C.or mineral name : Smithsonite
Elements : Zn, C, O
System : Rhombohedral

d (Å)	Intensity
3.55	50
2.75	100
2.327	25
2.110	18
1.946	25
1.776	12
1.703	45
1.515	14
1.493	14
1.411	10
1.408	2
1.374	4
1.357	2
1.343	10
1.2524	6
1.2423	2
1.2048	4
1.1833	8
1.1632	2
1.1057	2
1.1028	2
1.0710	6
1.0699	4
1.0552	2
1.0371	< 1

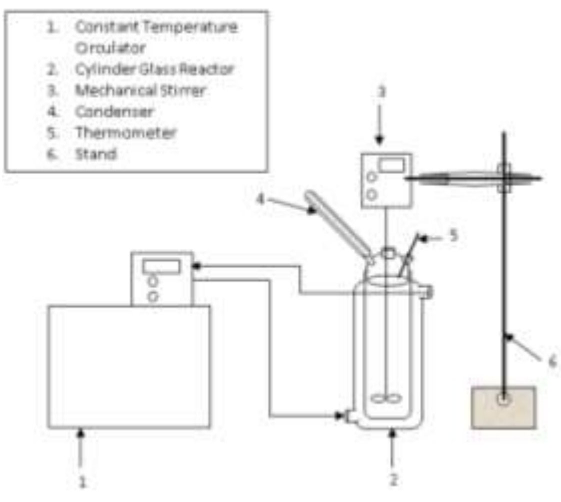

Fig. 2: Schematic view of the experimental setup.

Effect of reaction temperature

The experiments were carried out at the 30-70 ºC temperature range in 3.0 M acetic acid stirring speed of 500 rpm and the solid-liquid ratio of 8 g/L for -180+150 µm. Typical rate curves were shown in Fig. 4. From this figure, it was observed that the dissolution rate was very sensitive to reaction temperature.

Effect of acid concentration

To observe the effect of the acid concentration, in the range of 1.0-10.0 M, the experiments were performed at 50 ºC with an agitation speed of 500 rpm, the solid-liquid ratio of 8 $g.L^{-1}$ for -180+150 µm. From Fig. 5(a) and 5(b), for the concentration range of 1.0-3.0 M, it was observed that the increase in acid concentration increased the dissolution rate of smithsonite, but for 3.0-10.0 M, the increase in concentration decreased the dissolution rate.

Table 3: Parameters and theirs values selected.

particle size (μm)	-150+90	-180+150	-250+180	-425+250		
solid-liquid ratio (g.L^{-1})	4	8	20	40	80	
acid concentration (M)	1	2	3	4	6	10
reaction temperature (ºC)	30	40	50	60	70	
reaction time (min)	5	10	30	60	90	

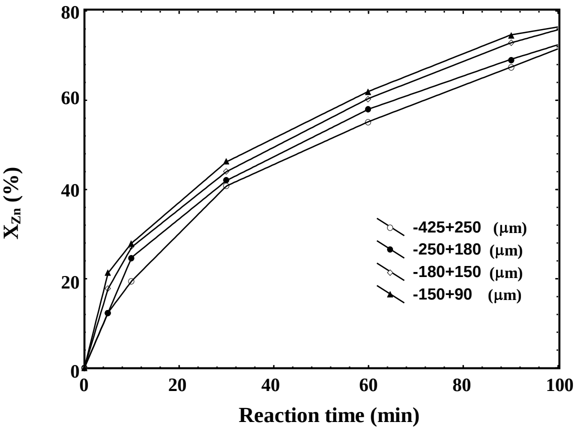

Fig. 3: Effect of particle size on the leaching of smithsonite.

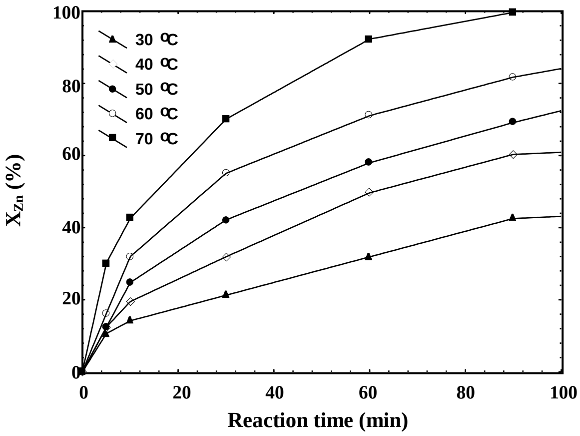

Fig. 4: Effect of reaction temperature on the leaching of smithsonite.

It could be attributed to the intensity of the negative effect of water decrease, after a certain value of acid concentration, was more dominant than that of the positive effect of the increase of acid concentration.

Again, when the acid concentration exceeds a definite value, the number of hydrogen ions in the medium might decrease due to a decrease in water amount more and more [18]. In addition, this behavior could be explained by the fact that appearance rate of production increases as the acid concentration in the medium increased, appearance rate of production increases and as the product reached the saturation value near the solid particle, it formes a difficult soluble solid film layer around the particle. Consequently, the dissolution process is slowing down [13].

Effect of solid-liquid ratio

This effect was investigated for five different solid to liquid ratios in solutions containing 3.0 M acid and 50 ºC at stirring speed of 500 rpm for -180+150 μm. As could be seen in Fig. 6, leaching rate was decreased with the increase of solid to liquid ratio.

KINETICS ANALYSIS

For kinetics analysis of fluid-solid multiphase reaction, an important task is to find the rate-controlling factors and kinetic parameters. For this purpose, the shrinking unreacted core model which is a readily accessible theory has been used here to describe the smithsonite leaching in acetic acid solutions.

For smithsonite ore, the leaching process can be analyzed in a few steps: the diffusion of acetic acid from the bulk solution to the external surface of a smithsonite particle, the chemical reaction at the interface and the diffusion of product species into the bulk solution. Since it is not the diffusion of product species, there are only two controlling steps, namely, fluid film diffusion and chemical reaction.

If the process is controlled by the resistance of fluid layer, the kinetic equation can be written as follows [19]:

$$k_d t = \frac{3 b k_l C_A}{R \rho_B} t = X_B \tag{4}$$

If this is controlled by the resistance of chemical reactions, the kinetic equation can be written as follows [19]:

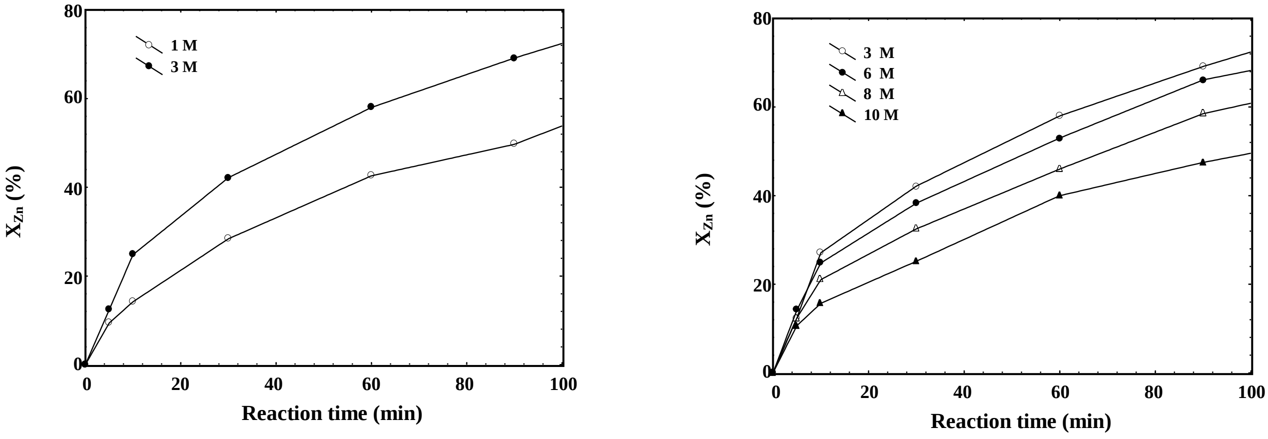

Fig. 5: a) Effect of acid concentration on the leaching of smithsonite, b) Effect of acid concentration on the leaching of smithsonite.

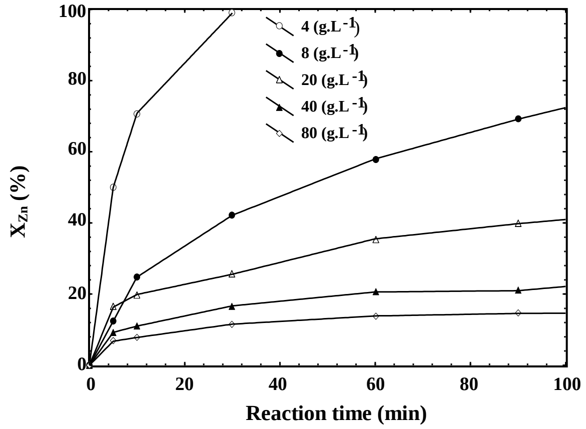

Fig. 6: Effect of solid to liquid ratio on the leaching of smithsonite.

$$kt = \frac{bk_S C_A}{R\rho_B} t = \left[1-\left(1-X_B\right)^{1/3}\right] \quad (5)$$

The kinetics of the leaching for smithsonite ore in acetic acid solutions is statistically studied by using heterogeneous and homogeneous reaction models. The fit of all the experimental data into the integral rate is tested by multiple regressions using Statistica Package 7.0 Program, and the multiple regression coefficients obtained for integral rate expression are calculated (Table 4). From Table 4, it is seen that the highest value of the regression coefficient correcting the rate expression is for chemical reaction control. This value is calculated 0.994.

From the results of the statistical analyses, it is found that the leaching of smithsonite ore in acetic acid solutions is controlled by chemical reaction. Also, it is determined that the rate expression obeyed the formula expressed in Eq. (5).

The plots of $1-(1-X_B)^{1/3}$ vs. t for the reaction temperature are shown in Fig. 7. From the slopes of the straight lines, the apparent rate constants are evaluated.

The temperature effect on the leaching rate is expressed by the Arrhenius equation as follows [19]:

$$k = k_o e^{-E/RT} \quad (6)$$

The plot of lnk vs. ln(1/T) is plotted for each value of the temperature in Fig. 8. From this graphic, the activation energy and frequency factor are calculated as 74 kJ/mol and 3,7*10^5 s^{-1} respectively.

The activation energy of fluid film diffusion controlled processes varies between 4.18 and 12.55 kJ/mol, while for a chemical reaction controlled process it is usually greater than 41.84 kJ/mol [5]. The value of activation energy calculated also supports that the leaching of smithsonite in acetic acid solutions is chemically controlled.

If the values obtained from Eq. (6) are written in Eq. (5), the equation representing the kinetics of this process can be expressed as follows:

$$1-\left(1-X_B\right)^{1/3} = 3.7\times10^5 e\left(-74/RT\right) xt \quad (7)$$

Thus, the Eq. (7) represents the model of the dissolution kinetics of smithsonite ore in acetic acid solutions.

There are various kinetic models published in the literature on the leaching of smithsonite. These models are presented in Table 5.

Table 4: The regression coefficient calculated for the homogeneous and heterogeneous models.

Kinetic equations	Regression coefficient
X_B	0.966
$1\text{-}3(1\text{-} X_B)^{2/3}+2(1\text{-} X_B)$	0.984
$1\text{-}(1\text{-} X_B)^{1/3}$	0.994
$1\text{-}(1\text{-} X_B)^{1/2}$	0.979
$1\text{-}(1\text{-} X_B)^{2/3}$	0.975
$-\ln(1\text{-} X_B)$	0.984
$X_B /1\text{-} X_B$	0.973

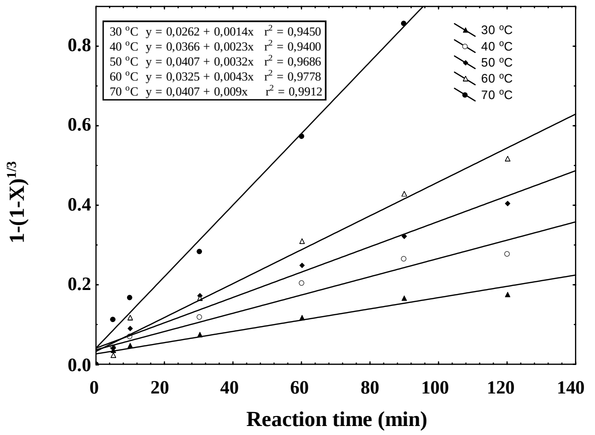

Fig. 7: 1-(1-x)$^{1/3}$ plot vs. time at various reaction temperatures.

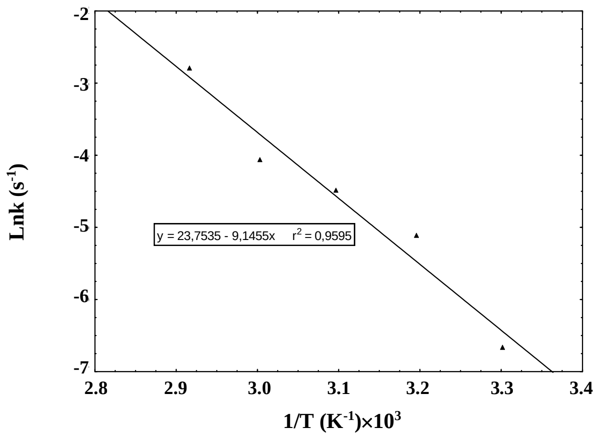

Fig. 8: Arrhenius plot for the leaching of smithsonite.

As seen in Table 5, it is observed that the kinetics models and their values have varied according to the type of reagent.

CONCLUSIONS

Smithsonite ore is an alternative source for the sulfurous ores. The kinetics of the reaction between smithsonite ore and acetic acid is investigated at the various parameter levels. Based on the results obtained in this research, the following conclusions can be drawn:

- In the process, it is observed that the reaction rate is rather sensitive to both temperature and solid-liquid ratio.
- It is shown that the leaching rate increases for the acid concentration range 1.0-3.0 M and decreases for range 3.0-10.0 M.
- From results of dissolution, it is proved that the kinetics obeys a shrinking-core model with the surface chemical reaction as the rate-controlling step. The activation energy of the process is found to be 74 kJ/mol.
- It is seen that about 99 % of the smithsonite ore is dissolved in 3.0 M acetic acid solution at a temperature 70 ºC with a particle diameter of -180+150 µm and a solid/liquid ratio of 8 g/L for 90 min.
- In terms of human health and environmental pollution, using such organic acids with this nontoxic technique can be a major improvement for the research and usage of such processes.
- After leaching of $ZnCO_3$, zinc acetate can be produced from their solutions, which is used in important fields such as medicine, mordant dyeing, wood preservative, disinfectant and porcelain industry.
- Inorganic and organic reagents for the dissolution of smithsonite ore are compared (Table 5). It is observed that the kinetics models and their values have varied according to the type of reagent.

Table 5: The Various Kinetic Models on the Leaching of Smithsonite with Some Reagent.

Reagent	Temp. (ºC)	Time (min)	Mechanism	Kinetics Model	Ref.
Acetic Acid	30-80	90	chemical reaction control	$1-(1-X_B)^{1/3}=3.7\times10^5 e(-74/RT)xt$	This Study
Gluconic Acid	30-70	120	chemical reaction control	$1-(1-x)^{1/3} = 3.7 \times 10^5 e^{-47.92/R_g T} t$	[9]
Methane Sulfonic Acid	20-80	60	Mixed Control	$(1/3)\ln(1-x)+(1-x)^{-1/3}-1= 6.97(C)^{2.1901}(PS)^{-0.7018}(SS)^{0.9306} \exp(-32.66/RT)$ t.	[11]
Sulfamic Acid	20-70	60	chemical reaction control	$1-(1-X)^{1/3}=[k_0.(C)^{0.488}(r_0)^{-0.361} (SS)^{3.509}\exp(-42.86/RT)]$ t	[10]
Hydrochloric Acid	25-45	60	chemical reaction control	$1-(1-X)^{1/3}=k0(HCl)^{0.70}(S/L)^{-0.76}r_0^{-0.95}\exp(-59.58/RT)]$ t	[6]
Ammonium chloride	70-90	250	Mixed Control	$1-2/3\alpha-(1-\alpha)^{2/3}+\beta[1-(1-\alpha)^{1/3}= 570.92d_0^{-2} C^{1.33}\exp(-21.3/RT)]$ t	[8]

Symbol

$X_B = X$	Converted fraction
T	Temperature, K
E	Activation energy, kJ/mol
t	Reaction time, s
k_d	Diffusion rate constant, s^{-1}
k	Reaction rate constant, s^{-1}
k_0	Frequency factor, s^{-1}
k_s	Rate constant for the surface reaction, cm/s
R	Universal gas constant, kJ/mol.K
ρ_B	Molar density of B in the solid, mol/cm^3
R	average radius of solid particles, cm
b	Stoichiometric coefficient
C_A	Bulk concentration of the fluid, mol/cm^3
k_l	Mass transfer coefficient for the liquid film, cm/s

Received : Aug. 25, 2016 ; Accepted :Mar. 6, 2017

REFERENCES

[1] Zhao Y., Stanforth R., Production of Zn Powder by Alkaline Treatment of Smithsonite Zn-Pb Ores, *Hydrometallurgy*, **56**: 237-249 (2000).

[2] Rotsan E.F., Debuys H.V., Madey D.L., Pinnel S.R., Evidence Supporting Zinc as an Important Antioxidant for Skin, *Int. J. Dermatol.*, **41**: 606-611 (2002).

[3] Dönmez B., Ekinci Z., Çolak S., Çelik C., Optimization of the Chlorination of Gold in Decopperized Anode Slime in Aqueous Medium, *Hydrometallurgy*, **52(1)**: 81-90 (1999).

[4] Demir F., Lacin O., Donmez B., Leaching Kinetics of Calcined Magnesite in Citric Acid Solutions, *Ind. & Eng. Chem. Res.*, **45**(4):1307-1311 (2006).

[5] Abdel-Aal E.A., Kinetics of Sulfuric Acid Leaching of Low-Grade Zinc Silicate Ore, *Hydrometallurgy*, **55**: 247-254 (2000).

[6] Dhawana N., Safarzadeh M.S., Birinci M., Kinetics of Hydrochloric Acid Leaching of Smithsonite, *Russ. J. Non Ferr. Met.*, **52**(3): 209–216. (2011).

[7] Abalı Y., Bayca S.U., Gumus R., Dissolution Kinetics of Smithsonite in Boric Acid Solutions, *Physicochem. Probl. of Miner. Process.*, **53**: 161-172 (2017).

[8] Ju, S., Motang, T., Shenghai, Y., and Yingnian, L., Dissolution Kinetics of Smithsonite Ore in Ammonium Chloride Solution, *Hydrometallurgy*, **80**: 67–74 (2005).

[9] Hursit M, Lacin O, Sarac H, Dissolution Kinetics of Smithsonite ore as an Alternative Zinc Source with an Organic Leach Reagent, *J. Taiwan Inst. Chem. Eng.*, **40**: 6-12 (2009).

[10] Dan-Dan Wu, Shu-Ming Wen, Jing Yang, Jiu-Shuai Deng, Li Jiang, Dissolution Kinetics of Smithsonite in Sulfamic Acid Solution, *Asian J. of Chem.*, **25(18):** 10556-10560 (2013).

[11] Feng Q., Wen S., Zhao W., Bai X., Chen Y., Dissolution Regularities Of Smithsonite In Methane Sulfonic Acid, *Russ. J. Non Ferr. Met.*, **56**(4): 365-371, (2015).

[12] Irannajad M., Meshkini M., Azadmehr A.R., Leaching Of Zinc From Low Grade Oxide Ore Using Organic Acid, *Physicochem. Probl. Miner. Process.*, **49**(2): 547-555 (2013).

[13] Laçin O., Dönmez B., Demir F., Dissolution Kinetics of Natural Magnesite in Acedic Acid Solutions, *Int. J. of Miner. Process*., **75**: 91-99 (2005).

[14] Demir F., Dönmez B., Çolak S., Leaching Kinetics of Magnesite in Citric Acid Solutions, *J. Chem. Eng. Jpn*., **36**(6): 683-688 (2003).

[15] Hawley G.G., "The Condensed Chemical Dictionary" (9th Ed.), Van Nostarnd Reinhold Company, Newyork, 528 (1977).

[16] Davidson L., "Zinc in the Mineral Fortification of Foods", Leatherhead Publishing, London, England, 187-197 (1999).

[17] Gulensoy, H., "Kompleksometrik Titrasyonlar ve Kompleksometrinin Temelleri", *Fatih Yayınevi*, Istanbul, Turkey (in Turkish).

[18] Marinovic V., Despic A. R., Hydrogen Evolution from Solutions of Citric Acids, *J. Electroanal. Chem*., **431**: 127-132 (1997).

[19] Levenspiel, O., "Chemical Reaction Engineering", 3rd Ed., *John Wiley and Sons Inc.*, New York (1999).