

Investigation of leaching kinetics of zinc from a low-grade ore in organic and inorganic acids

S.M. Seyed Ghasemi and A. Azizi*

School of Mining, Petroleum & Geophysics Engineering, Shahrood University of Technology, Shahrood, Iran

Received 8 September 2016; received in revised form 24 October 2016; accepted 4 November 2016

*Corresponding author: aazizi@shahroodut.ac.ir (A. Azizi).

Abstract

The leaching kinetics of a low-grade zinc oxide ore in different acid media was investigated with respect to the experimental variables including acid concentration, temperature, liquid to solid (L/S) ratio, and stirring speed. The results obtained showed that the leaching reagent concentration and the reaction temperature exerted significant effects on the extraction of zinc, whereas the L/S ratio and stirring speed exhibited a relatively moderate effect on the leaching rate. The maximum leaching rate with inorganic acids was obtained to be 90.76%, while the maximum zinc recovery with citric acid was determined to be 88.68%. It was found that the zinc leaching process followed the kinetic law of the shrinking core model. It was distinguished that the dissolution rate was controlled by diffusion through the fluid film in the HNO₃ medium with the activation energy of 4.38 kJ/mol, whereas when dissolution was performed in the presence of HCl, H₂SO₄, and citric acid, an intermediate process (i.e. a physico-chemical process) was the rate-controlling step.

Keywords: *Leaching Kinetics, Zinc Recovery, Low-Grade Oxide Ore, Shrinking Core Model.*

1. Introduction

Metals play an important role in the industrial development and improved living standards. Society can draw on metal resources from the Earth's crust as well as the metals discarded after use. New routes to metal recycling are continually investigated not only for reducing costs but also to prevent the environmental pollution [1]. Zinc is one of the most widely used metals that finds applications in paints, cosmetics, food, constructions, automobiles, pharmaceutical, detergent, textile, leather, electrical equipment or metallic coatings for corrosion protection as well as an endless list of other capital applications [2-5]. According to Sethurajan et al., the zinc demand and usage have increased many folds in the recent years; in 2015, the demand for and usage of Zn has exceeded its supply by 151,000 tons [6]. Consequently, there is a depletion of high-grade Zn sulfide ores, which are the common source of Zn metal production. Thus in the recent years, extraction of Zn from non-sulfidic ores

such as carbonate ores, silicate ores, and secondary resources is explored [6-9]. The widely used method implemented to treat and recycle zinc involves hydrometallurgical unit operations. Hydrometallurgical extraction of metals is often less costly, and it is less harmful to the environment because it does not emit SO₂ and some other hazardous gases. In addition, metals can be obtained directly in pure form from leach solutions or recovered from impure leach solutions. Leaching processes constitute the first step of the hydrometallurgical methods, and leaching kinetics plays an important role in the extraction of metals and compounds in an economical way [8, 10-11].

Mineral acids such as HCl, H₂SO₄, and HNO₃ are commonly used as the leaching reagents, from which, H₂SO₄ is the most preferred lixiviant [6, 10, 12-22]. In addition to inorganic acids, organic acids have been applied as leaching reagents in the recent years [4, 16, 23-30]. The results

obtained indicate that during the leaching process of zinc oxidized ores, sulfuric acid leaching is the most viable and versatile process. However, mineral acids cause environmental pollution, and may dissolve undesired impurities, especially those containing high contents of iron, calcium, and silicon; the excessive acid consumption and complex purification process would cause a significant concern [1, 8]. Organic acids are not usually used as the leachants due to their low dissolution efficiencies but they are attractive due to the ease of biodegradation. They can be used in mildly acidic conditions (pH 3–5) [1].

Despite the fact that extensive works have been carried out on the hydrometallurgical treatment of low-grade zinc oxide ores, there are less reports on the leaching kinetic of zinc oxide ores, especially on the low-grade oxide ores [4, 10, 11, 21, 29]. Hence, this study was aimed to investigate the leaching kinetics of zinc from a low-grade zinc oxide ore with the acid solutions including H_2SO_4 , HCl, HNO_3 , and $C_6H_8O_7$. The dissolution kinetics was examined according to the heterogeneous reaction models, and the best

fitted equation to the experimental data was determined.

2. Experimental

2.1. Materials

In order to conduct the leaching experiments, the required oxide samples were supplied from the Goushfil mine tailings in Iran. Then the samples were crushed in a jaw crusher, and thereafter, were ground by a laboratory ball mill until 80% of the particles were less than 150 microns in diameter. The chemical composition of the samples was then characterized by Oxford X-ray fluorescence apparatus ED2000 (80 kV, 40 mA, calibrated with Si-standard), and the results obtained were tabulated in Table 1. The phases of the representative sample were also detected by X-ray diffraction (XRD) analysis, and the main phases included dolomite ($CaMg(CO_3)_2$), barite ($BaSO_4$), calcite ($CaCO_3$), pyrite (FeS_2), quartz (SiO_2), goethite ($FeO(OH)$), smithsonite ($ZnCO_3$), and cerussite ($PbCO_3$).

H_2SO_4 (96-98%), HNO_3 (65%), HCl (37%), and citric acid monohydrate ($C_6H_8O_7$, 99%) were used as the leaching reagents.

Table 1. Chemical composition of low-grade zinc oxide ore (mass fraction, %).

Composition	ZnO	PbO	Al_2O_3	Fe_2O_3	BaO	SiO_2	CaO	SO_3	MgO	K_2O	MnO	TiO_2	SrO
Content	5.91	5.32	4.95	15.68	15.76	24.77	15.42	7.79	1.24	0.92	0.86	0.35	0.48

2.2. Leaching experiments

The leaching experiments were conducted on the representative samples in a 500-mL beaker, which was heated on a hot plate equipped with a digital controlled magnetic stirrer and a thermometer for temperature control under different conditions including the citric acid concentration of 0.25-1 M, inorganic acid concentration of 10-25%, temperature of 50-80°C, stirring speed of 200-500 rpm, and liquid to solid (L/S) ratio of 10-25 mL/g. For each test, 3 g of the representative sample was placed in the beaker containing the desired volume of the selected leaching reagents. The leaching solutions were mixed using a magnetic stirrer with a certain speed at the required temperature. When the leaching process finished within a required time interval, the sample was filtered and the liquid phase was analyzed for its zinc content. The zinc concentration was determined using a Unicam Atomic Absorption Spectrometry (AAS). The leaching rate was calculated via the following equation:

$$R = \frac{C_1 \times V}{C_0 \times m} \times 100 \quad (1)$$

where R is the recovery percentage of zinc; C_1 (g/L) is the concentration of zinc ion in the leach solution; V (L) is the volume of leach solution; C_0 (%) is the metal content of zinc in the oxide ore sample, and m (g) is the mass of the low-grade zinc oxide ore used in the experiment.

3. Results and discussion

3.1. Effect of acid concentration

The dissolution rate of zinc was investigated using the H_2SO_4 , HCl, HNO_3 , and citric acid ($C_6H_8O_7$) solutions at 70 °C, a stirring speed of 500 rpm, and an L/S ratio of 20. In this work, the effects of the inorganic acid (H_2SO_4 , HCl, and HNO_3) concentrations on the leaching performance of zinc was evaluated by regulating the concentration to 10, 15, 20, and 25%, while citric acid was investigated in the range of 0.25-1 M with steps of 0.25 M. The results obtained are given in Figure 1 as a fraction of zinc recovery vs. leaching time. As it can be seen, the fraction of zinc dissolved was changed when the acid concentration was increased. As considered, H_2SO_4 had the lowest capability in leaching zinc. It can also be seen that the highest zinc recoveries were obtained in the

concentrations of 20%, 0.75 M, 25%, and 30% for HNO₃, C₆H₈O₇, HCl, and H₂SO₄, respectively. Under the optimal condition, zinc dissolution was very fast with citric acid at a concentration of 0.75 M. It attained 50.62% at the first 30 min and reached 79.25% in 90 min. The lowest kinetic dissolution was obtained with H₂SO₄ with a reaction time of 30 min but it increased gradually attaining 61.37% in 90 min. Therefore, the

reaction rate was slower at H₂SO₄ compared with the other inorganic acids since it needed further time and concentration to reach a high dissolution efficiency. These behaviors are probably because more H⁺ ions can react with carbonate ions in solution to promote the reaction. A comparison between the acids showed that nitric acid had the highest zinc dissolution efficiency, followed by citric acid, hydrochloric acid, and sulfuric acid.

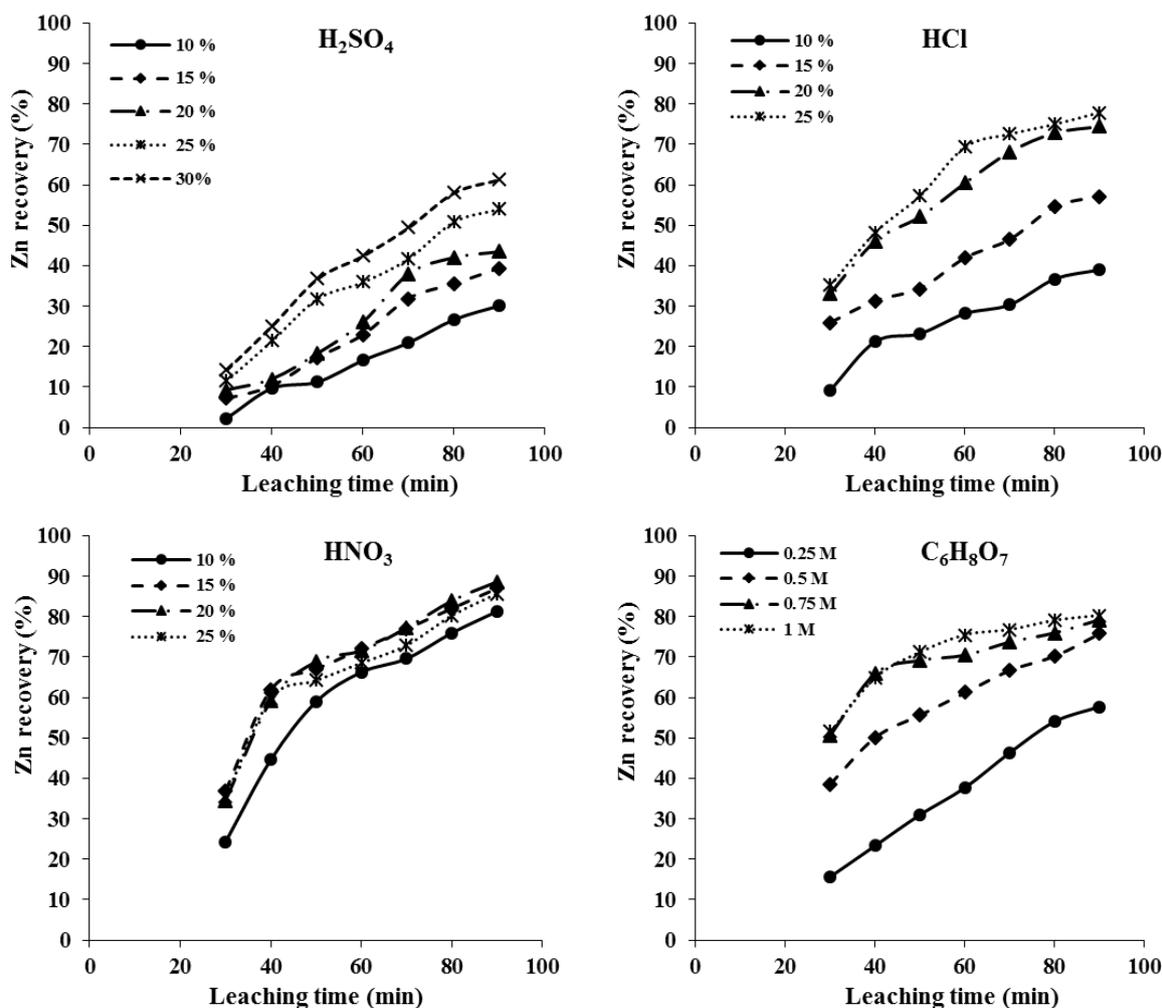


Figure 1. Effect of acid concentrations (H₂SO₄, HCl, HNO₃, C₆H₈O₇) on dissolution of zinc; operation conditions: temperature = 70 °C, L/S = 20 mL/g, agitation speed = 500 rpm.

3.2. Effect of L/S ratio

The effect of L/S ratio on the dissolution rate of zinc was investigated using different L/S ratios (10, 15, 20, and 25 mL/g) at 70 °C, an H₂SO₄ concentration of 30%, an HCl concentration of 25%, an HNO₃ concentration of 20%, a C₆H₈O₇ concentration of 0.75 M, and a stirring speed of 500 rpm (Figure 2). The results obtained indicated that agitation had a more pronounced effect on the dissolution of zinc, especially in HNO₃ and HCl solutions. As considered, the leaching rate of zinc

increased with increasing L/S ratio for the leaching agents. As it can be seen in Figure 2, the maximum zinc dissolution was obtained at an L/S ratio of 20 mL/g. It was observed that after 90 min of dissolution, the leaching fraction of zinc increased from 49.97 to 61.37% for H₂SO₄, 62.95 to 77.92% for HCl, 69.43 to 88.68 for HNO₃, and 65.25 to 79.25% for citric acid when the L/S ratio increased from 10 to 20 mL/g, but with further increment of L/S ratio up to 25 mL/g, the leaching

rate reduced. This result indicates that an optimal

L/S ratio is beneficial for the extraction of zinc.

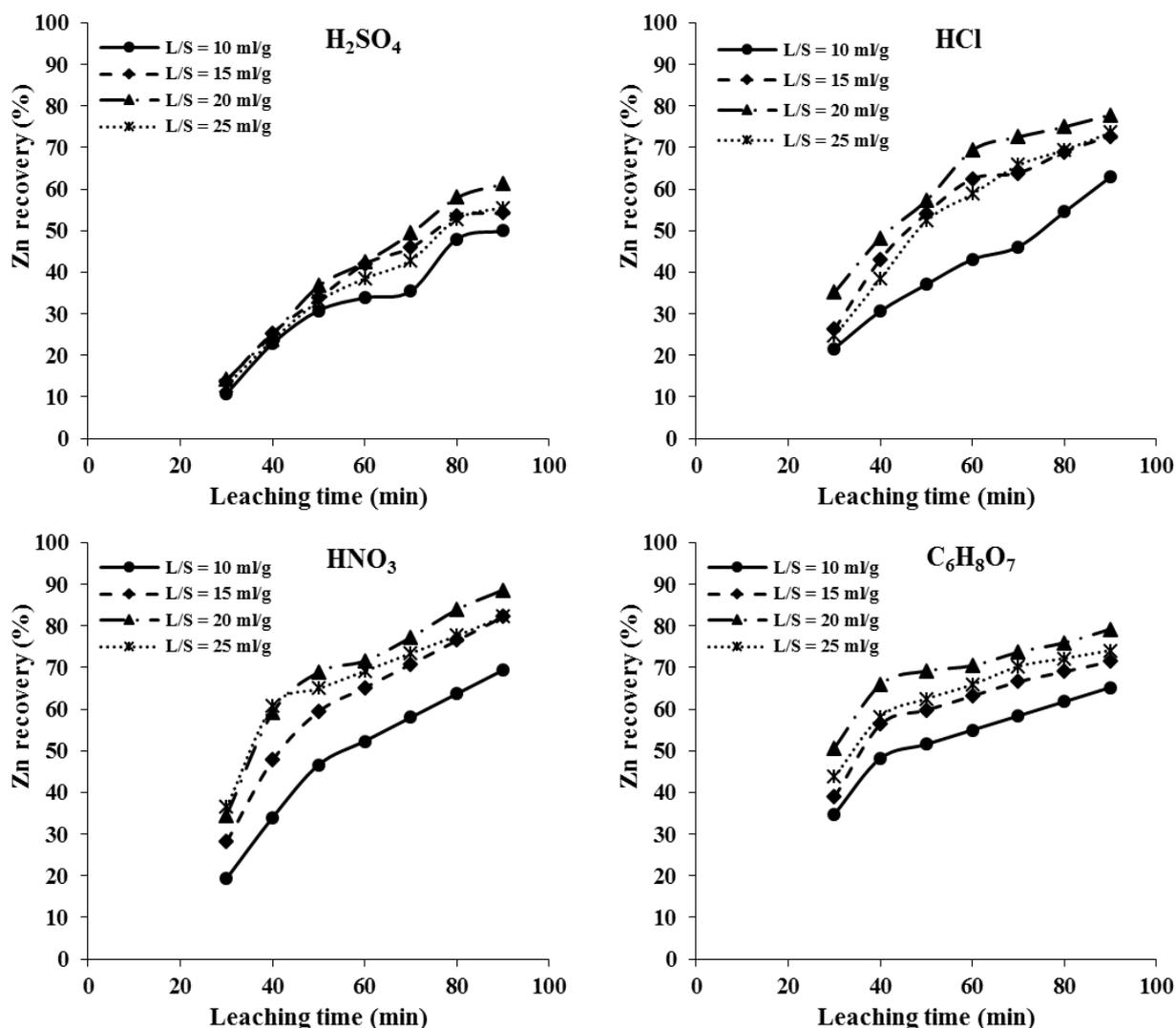


Figure 2. Effect of L/S ratio on dissolution of zinc; operation conditions: temperature = 70 °C, HCl concentration = 25%, HNO₃ concentration = 20%, C₆H₈O₇ concentration = 0.75 M, agitation speed = 500 rpm.

3.3. Effect of stirring speed

The leaching rate of zinc in different acid solutions was investigated as functions of the stirring speed under the following conditions: temperature = 70 °C, H₂SO₄ concentration = 30%, HCl concentration = 25%, HNO₃ concentration = 20%, C₆H₈O₇ concentration = 0.75 M, and L/S ratio = 20 mL/g. The experimental data was plotted in Figure 3 for different agitation speeds ranging from 200 to 500 rpm. As it can be seen in this figure, zinc dissolution with acid reagents was strongly dependent on the stirring speed. As considered, the leaching rate of zinc increased with increasing the stirring for inorganic leaching agents (H₂SO₄, HCl, and HNO₃).

It can also be observed in Figure 3 that after 90 min of dissolution, the zinc recovery increased from 42.19 to 61.37% for H₂SO₄, 52.87 to 77.92% for HCl, and 70.24 to 88.68% for HNO₃ when the stirring speed increased from 200 to 500 rpm. This result indicates that a high stirring speed is beneficial for the extraction of zinc. A value of 500 rpm was kept for further use in this study, whereas, for citric acid, when the stirring speed increased from 200 to 400 rpm, zinc recovery enhanced from 61.27 to 85.77%, and with a further growth it reduced. According to Larba et al., this behavior is due to the mechano-chemical effect of the magnetic stirrer [1]. Therefore, a stirring speed of 400 was found to be optimal for leaching of zinc using citric acid.

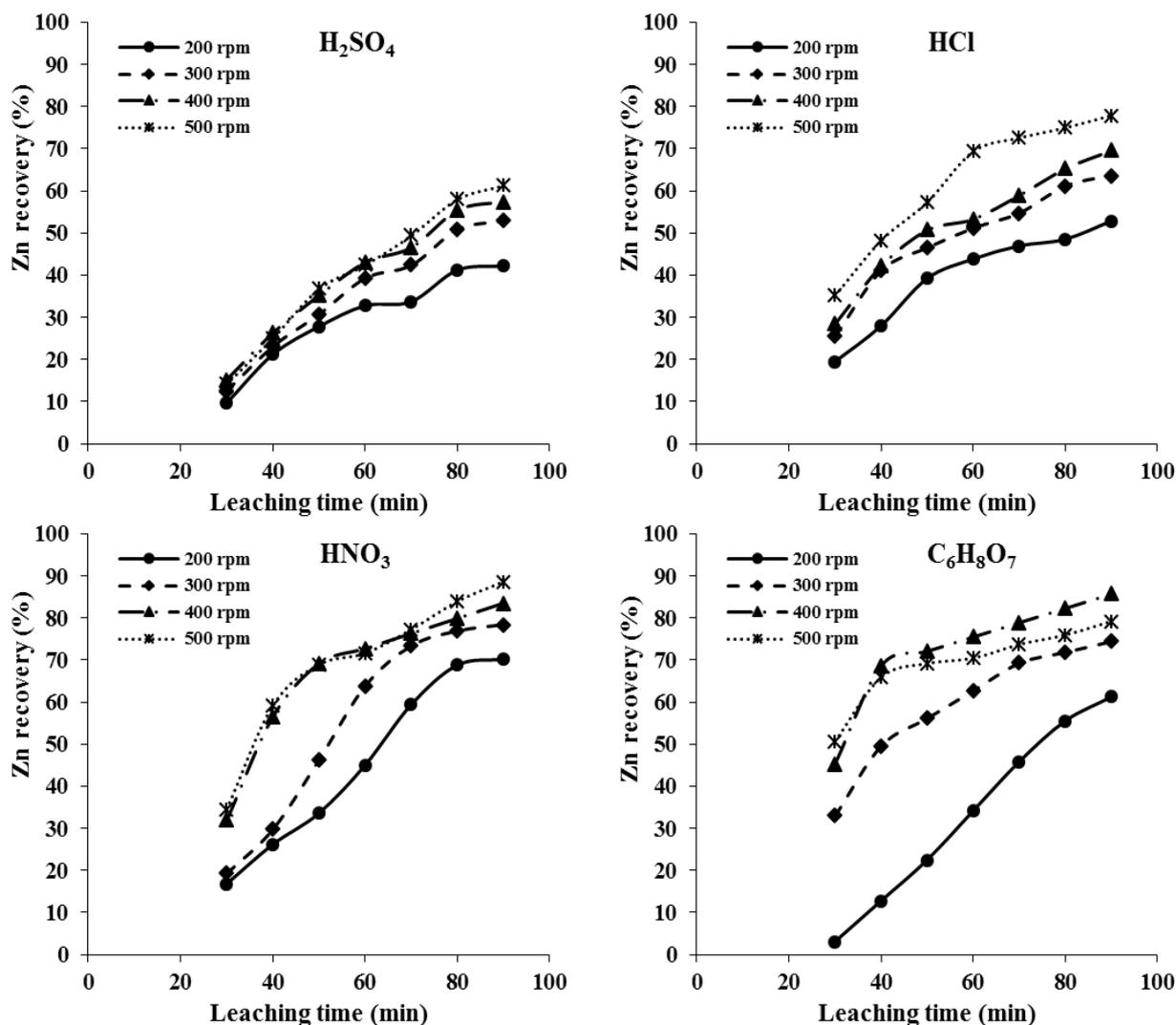


Figure 3. Effect of agitation speed on dissolution of zinc; operation conditions: temperature = 70 °C, L/S ratio = 20 mL/g, HCl concentration = 25%, HNO₃ concentration = 20%, and C₆H₈O₇ concentration = 0.75 M.

3.4. Effect of temperature

The effect of temperature on the rate of zinc dissolution from low-grade zinc oxide ore was investigated over a temperature range of 50-80 °C, at an L/S ratio of 20 mL/g, and a stirring speed of 500 rpm when inorganic acids were used as the leaching reagents and 400 rpm when citric acid was applied as the leaching agent. Also the concentrations of H₂SO₄, HCl, HNO₃, and citric acid were adjusted to 30%, 25%, 20%, and 0.75 M, respectively. The results obtained are presented in Figure 4. As it can be seen in this figure, zinc dissolution with acids was highly temperature dependent. The results obtained

indicate that temperature has a more pronounced effect on the dissolution of zinc with citric acid than that observed with the inorganic acids. It was seen that after 90 min of dissolution, the zinc leaching rate by citric acid was only 61.19% at 50 °C but quickly increased to 88.68% when the temperature was increased to 80 °C. It was also observed that zinc recovery enhanced from 40.27 at 50 °C to 65.21 at 80 °C, 59.52% at 50 °C to 81.62 at 80 °C, and 79.79% at 50 °C to 90.76 at 80 °C when sulfuric acid, hydrochloric acid, and nitric acid were used as the leaching reagents, respectively.

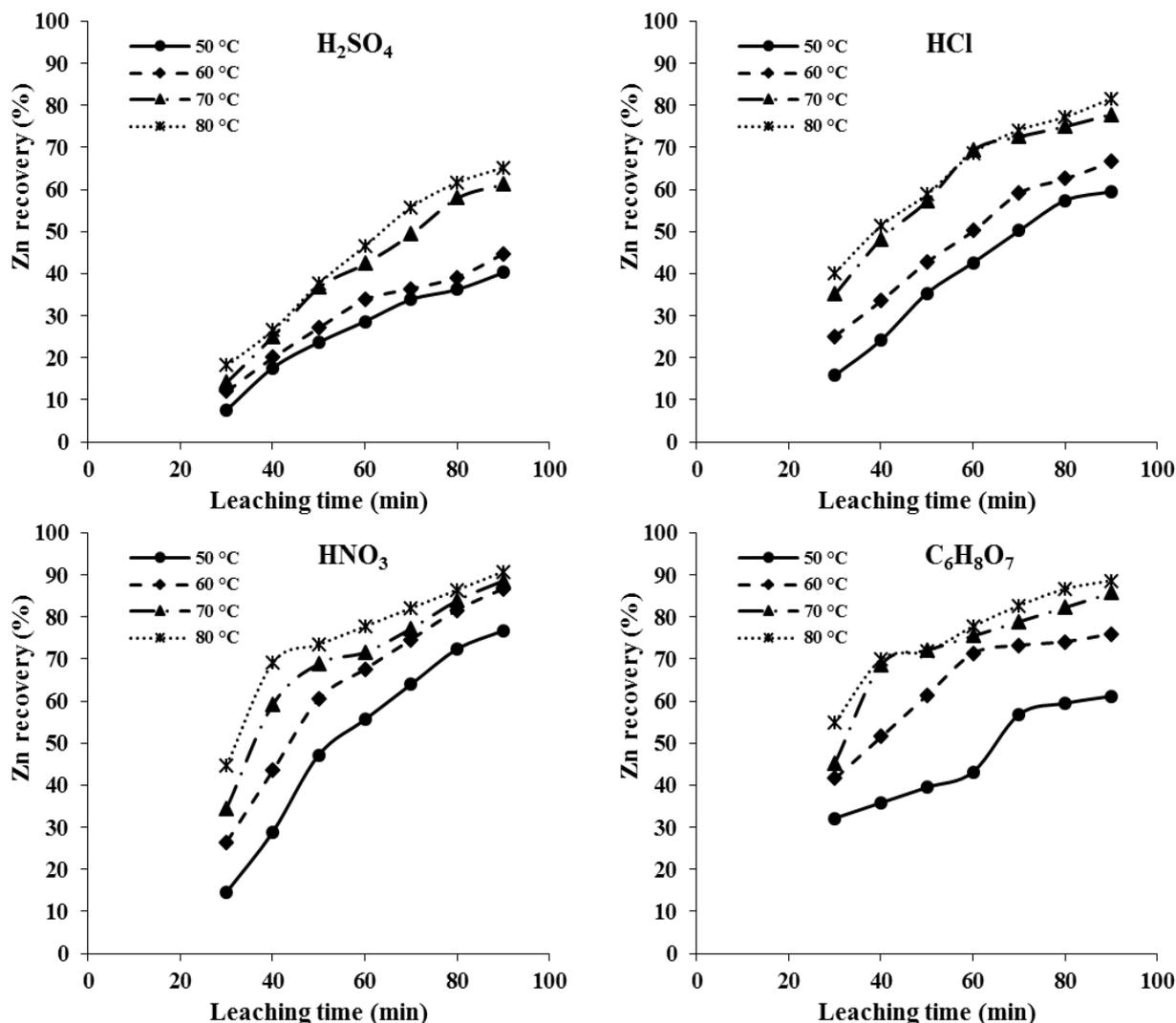


Figure 4. Effect of temperature on dissolution of zinc; operation conditions: agitation speed = 500 rpm for inorganic acids and 400 rpm for citric acid, L/S ratio = 20 mL/g; HCl concentration = 25%, HNO₃ concentration = 20%, and C₆H₈O₇ concentration = 0.75 M.

3.5. Leaching kinetic study

The rate of a reaction between a solid and a fluid such as the system considered here can be expressed by the heterogeneous kinetics models. In a heterogeneous system, the overall rate expression becomes complicated because of the interaction between the physical and chemical processes [31]. In order to interpret the results of zinc dissolution in the different acidic media studied, the kinetics was assessed on the basis of the shrinking core model (SCM). SCM was chosen because it approximated real particles more closely than did the other conversion models in a wide variety of situations [32]. In this model, the solid reactant is considered to be non-porous with a spherical shape, and it is initially surrounded by a fluid film through which mass transfer occurs between the solid and the bulk of the fluid. As the reaction proceeds, a product layer

forms around the unreacted core. However, it is assumed that the initial outside radius of the solid does not change while the leaching reaction continues [32-34]. According to the SCM model, the leaching rate is governed by the following physical and chemical phenomena: rate of transport of fluid reactant to and products from the particle surface (i.e. diffusion through the fluid film), rate of diffusion of the fluid reactant and products through the porous product layer that is formed on the unreacted core of solid (i.e. diffusion through the product layer), and the reaction rate at the surface of unreacted core (i.e. surface chemical reaction). Each one of these phenomena affects the rate of the overall leaching reaction. One or more of these factors might control the reaction rate [35].

The overall leaching process may be controlled by the intrinsic chemical reaction or the external

mass transfer. The following expressions can be used to describe the dissolution kinetics of the leaching process, assuming that the Zn-containing minerals have a spherical size.

If the reaction rate is controlled by diffusion of the leaching agent through the liquid film formed, then the fraction of zinc reacting at any time, t , in a film diffusion control situation can be expressed as [6, 11, 32]:

$$1 - (1 - x)^{\frac{2}{3}} = k \times t \quad (2)$$

If the reaction rate is controlled by diffusion through a product layer, then diffusion of the reagent or dissolved species through a solid reaction product at any time, t , can be calculated as follows [32]:

$$1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x) = k \times t \quad (3)$$

If the process is controlled by a surface chemical reaction, then Eq. (4) can be used to describe the dissolution kinetics of zinc [32]:

$$1 - (1 - x)^{\frac{1}{3}} = k \times t \quad (4)$$

where x is the fraction of zinc reacted, t is the reaction time (min or h), and k is the apparent rate constant (min^{-1} or h^{-1}). The rate of the process is controlled by the slowest step of the sequential ones.

To determine the kinetic parameters and rate-controlling step of zinc leaching from the Iranian low-grade oxide ore in the acid solutions investigated in this study, the shrinking core model was tested at various temperatures. The validity of the experimental data in the integral rate was tested by the graphical method. To test the possibility of diffusion through a solid reaction product, liquid film, and surface chemical reaction, the left-hand side of Eqs. (2), (3), and (4) were plotted against time; the results obtained are shown in Figures 5-7. The leaching experiments were carried out at temperatures ranging from 50 to 80 °C in steps of 10 °C under the following operational optimum conditions: an L/S ratio of 20 mL/g, an H_2SO_4 concentration of 30%, an HCl concentration of 25%, an HNO_3 concentration of 15%, a $\text{C}_6\text{H}_8\text{O}_7$ concentration of 0.75 M, an agitation speed of 500 rpm when inorganic acids were used as the leaching reagents, and a stirring speed of 400 rpm when citric acid was used as the leaching reagent.

Using the slopes of the straight lines, the apparent rate constants, k (Figures 5-7), were evaluated. The rate constants were calculated using the slopes of the straight lines, and their correlation coefficients were given in Figures 5-7. When these figures are compared, it is revealed that the low R^2 values obtained for the diffusion through the product layer indicate that this model is not the rate-controlling step. However, the largest regression coefficients were obtained for the liquid film diffusion and the chemical reaction models, indicating that these models act as the rate-controlling step in this leaching system. On the other hand, it can be seen that R^2 values for the kinetic models in Eqs. (2) and (4) are much closer to each other, and thus it is difficult to distinguish between the two models of surface chemical reaction (Eq. (4)) and liquid film diffusion (Eq. (2)). This is due to the small difference between the two models, as pointed out by Levenspiel (1999) [32]. On the other hand, in the leach processes, the dissolution ratio depends directly on the activation energy. Hence, activation energy was employed to determine the rate-controlling step of zinc leaching in the acid solutions. The activation energy and the reaction rate constant can be calculated by the Arrhenius equation:

$$K = A \times e^{\frac{-E_a}{R \times T}} \quad (5)$$

where K is a reaction rate constant (min^{-1}), A is the frequency factor (min^{-1}), E_a is activation energy of the reaction (J mol^{-1}), R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is the leaching temperature in Kelvin (K).

For the two reaction models of surface reaction control (Eq. (4)) and liquid film diffusion control (Eq. (2)), the Arrhenius equation was plotted as $\text{Ln}(K)$ vs. $(1/T)$ for each temperature and lixiviant, and the activation energies were calculated using the slopes of the straight lines, where the slope is $-E_a/R$. For example, the Arrhenius plot ($\text{Ln}(K)$ vs. $1/T$) or zinc dissolution by the hydrochloric acid solution based on the solid product diffusion model is shown in Figure 8. The values for the activation energies calculated from the Arrhenius plot is shown in Table 2.

As shown in Table 2, the calculated activation energy for each acid solution was less than 40 kJ/mol. The typical activation energy for a chemically controlled process is greater than 40 kJ/mol (usually $> 10 \text{ kcal/mol}$), whilst the activation energy for the diffusion controlled

process is from 4.2 to 12.6 kJ/mol [10-11, 34, 36-38]. In addition, according to Habashi (1983), the processes of intermediate control are also known; in these processes, the diffusion rate equals the rate of chemical reaction. The activation energy of such processes is typically 5-7 kcal/mol (i.e. 21-29.4 kJ/mol) [37]. Therefore, according to the activation energy values determined in this work, the rate of leaching process is controlled by diffusion through the liquid film. In order to further investigate this point, the leaching kinetics of zinc in acid solutions with activation energy greater than 10 kJ/mol was investigated in two stages based on the chemical reaction model. The results obtained are shown in Figures 9-11. As it can be seen, the leaching rate is controlled by the surface chemical reaction in the first 20 min with

activation energies of 50.24 and 60.94 kJ/mol and diffusion through the fluid film in the range of 20-90 min with activation energies of 20.89 and 9.88 kJ/mol for H₂SO₄ and HCl, respectively. Also the kinetic analysis of the results obtained indicates that the dissolution of zinc in citric acid in 70 min is controlled by the diffusion process with the activation energy of 22.21 kJ/mol, but thereafter, the leaching rate is according to the surface chemical reaction control with activation energy of 43.43 kJ/mol. This demonstrates that the rate-controlling step used to describe the dissolution of zinc in hydrochloric acid, sulfuric acid, and citric acid solutions is a physico-chemical process.

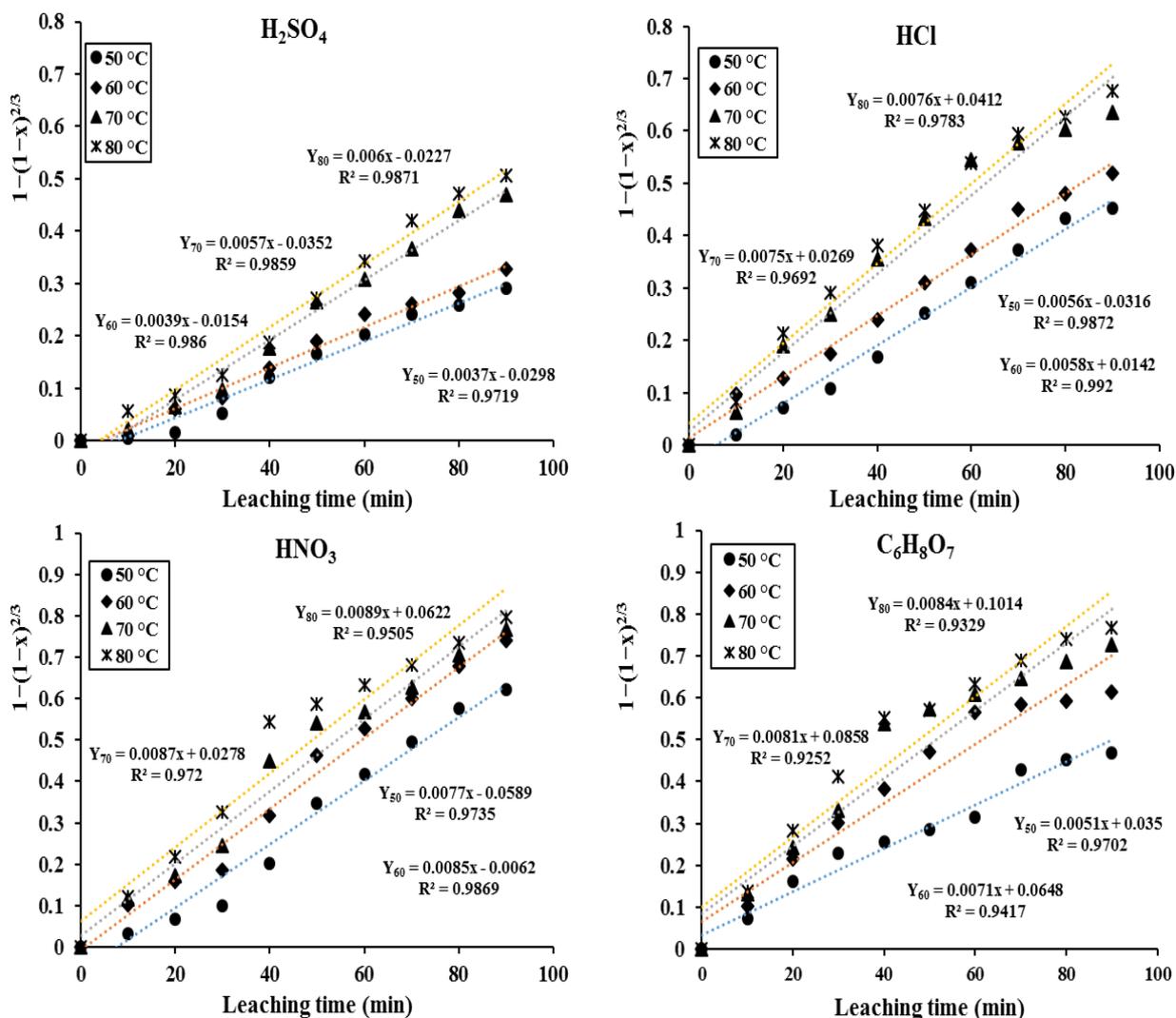


Figure 5. Plot of $1-(1-x)^{2/3}$ vs. leaching time at different temperatures for dissolution reactions of zinc with H₂SO₄, HCl, HNO₃, and citric acid solutions.

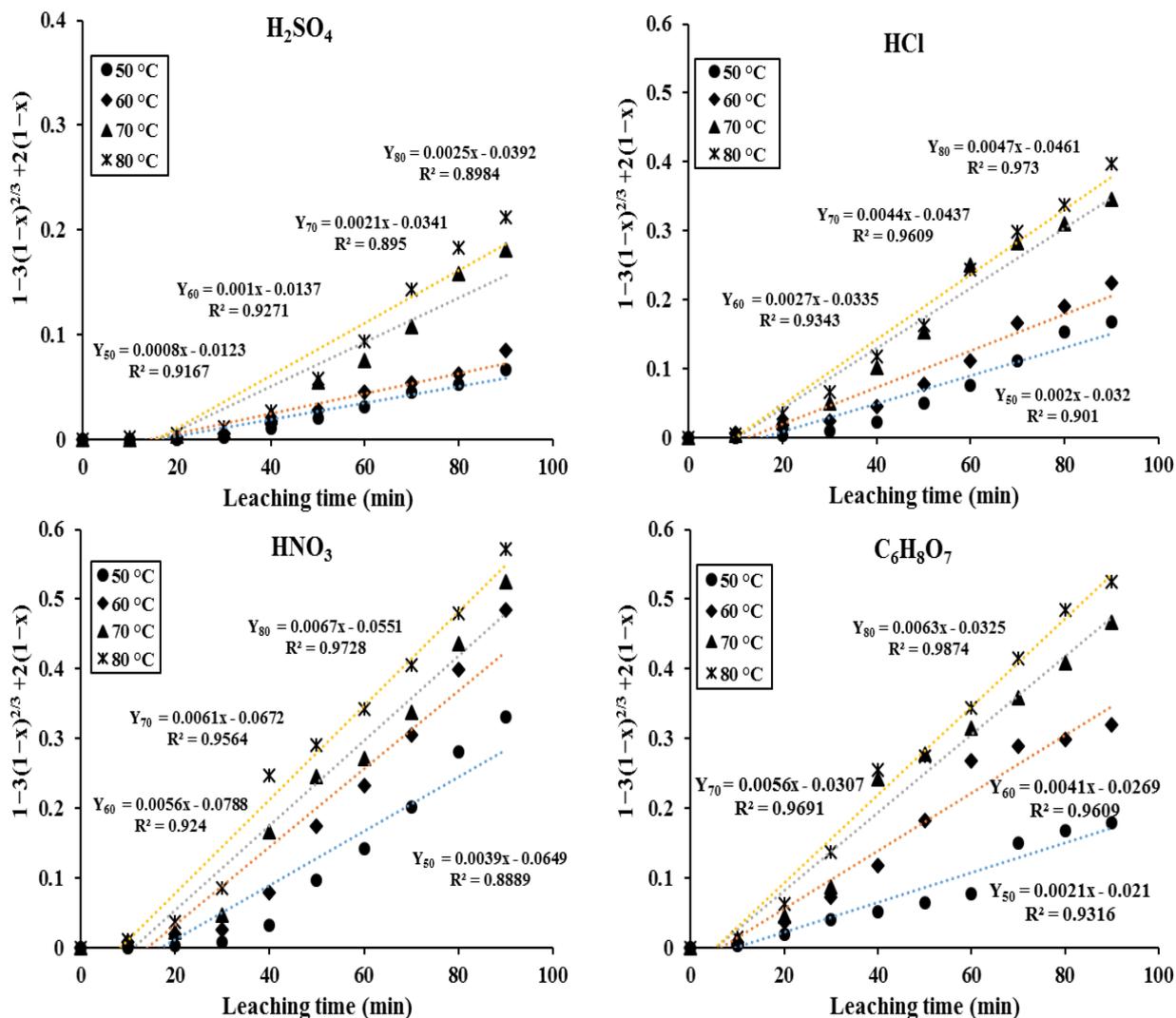


Figure 6. Plot of $1-3(1-x)^{2/3}+2(1-x)$ vs. leaching time at different temperatures for dissolution reactions of zinc with H₂SO₄, HCl, HNO₃, and citric acid solutions.

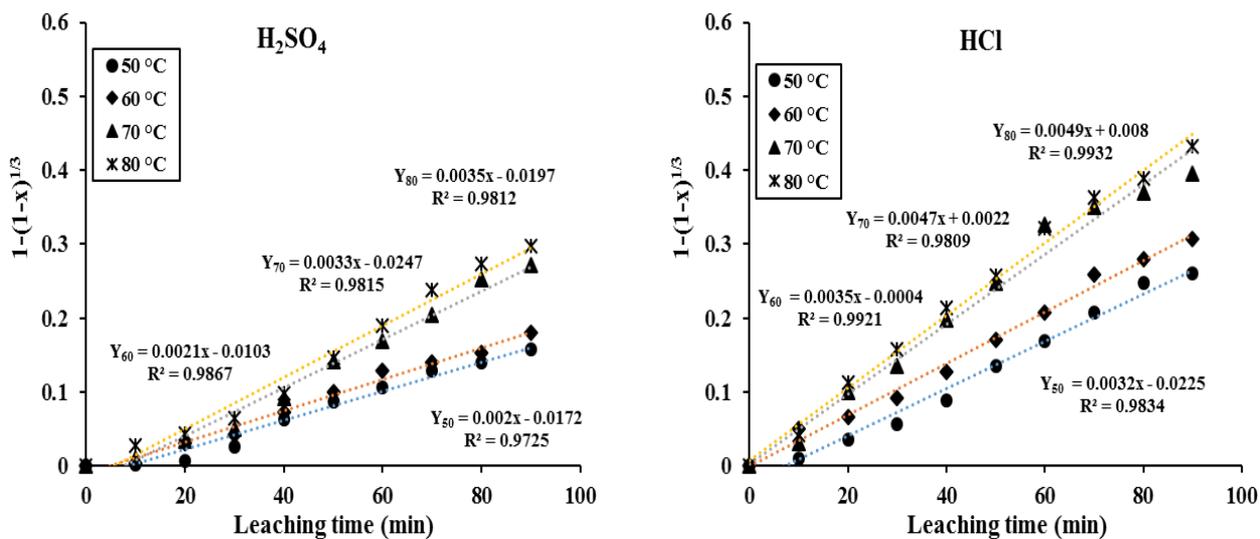


Figure 7. Plot of $1-(1-x)^{1/3}$ vs. leaching time at different temperatures for dissolution reactions of zinc with H₂SO₄, HCl, HNO₃, and citric acid solutions.

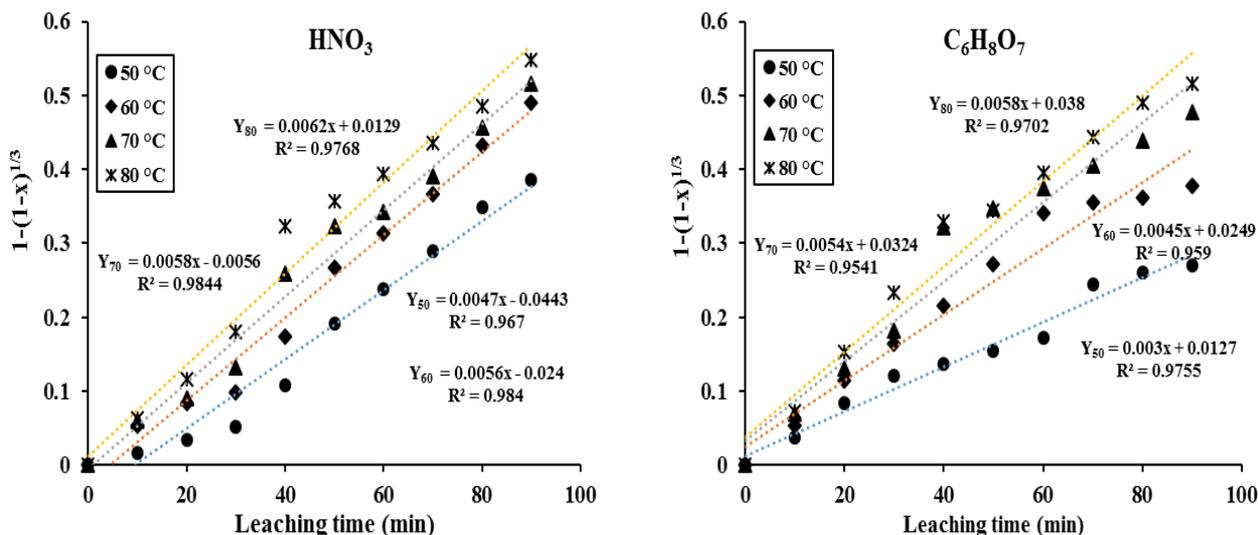


Figure 7. Continued.

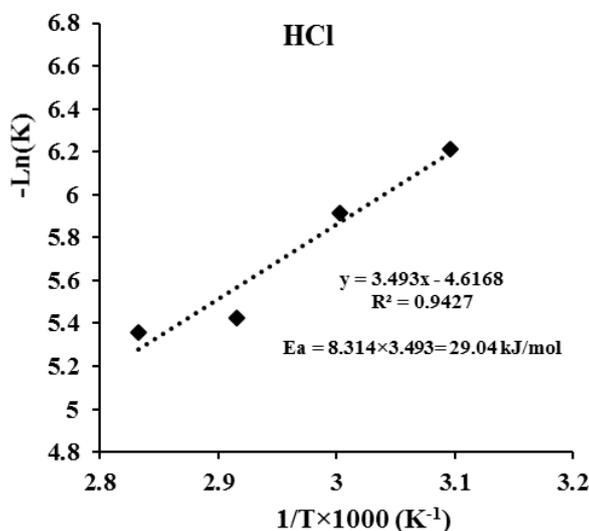


Figure 8. Arrhenius plot for leaching of low-grade zinc oxide ore in HCl solution based on solid product diffusion model.

Table 2. Activation energies calculated for leaching of zinc from low-grade oxide ore in acid solutions.

Leaching reagent	Shrinking core model	Activation energy (kJ/mol)
Citric acid		15.6
Sulfuric acid	$1-(1-x)^{2/3}$	17.33
Hydrochloric acid		11.13
Nitric acid		4.38
Citric acid		20.65
Sulfuric acid	$1-(1-x)^{1/3}$	20.18
Hydrochloric acid		14.93
Nitric acid		8.27
Citric acid		34.49
Sulfuric acid	$1-3(1-x)^{2/3}+2(1-x)$	39.44
Hydrochloric acid		29.04
Nitric acid		16.34

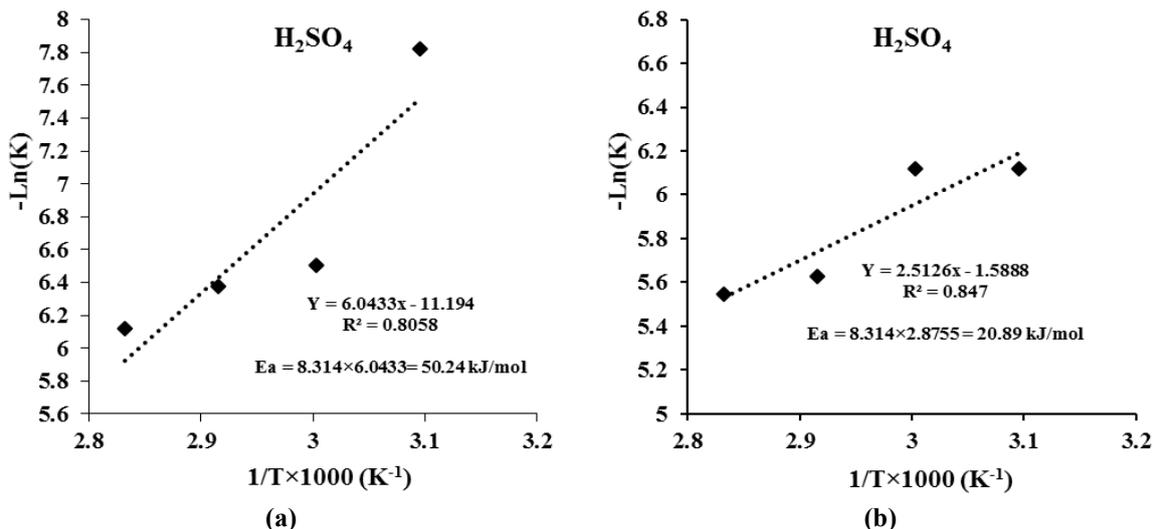


Figure 9. Arrhenius plots for leaching low-grade zinc oxide ore using H₂SO₄ solution based on surface chemical reaction model in ranges of 0-20 min (a), and 20-90 min (b).

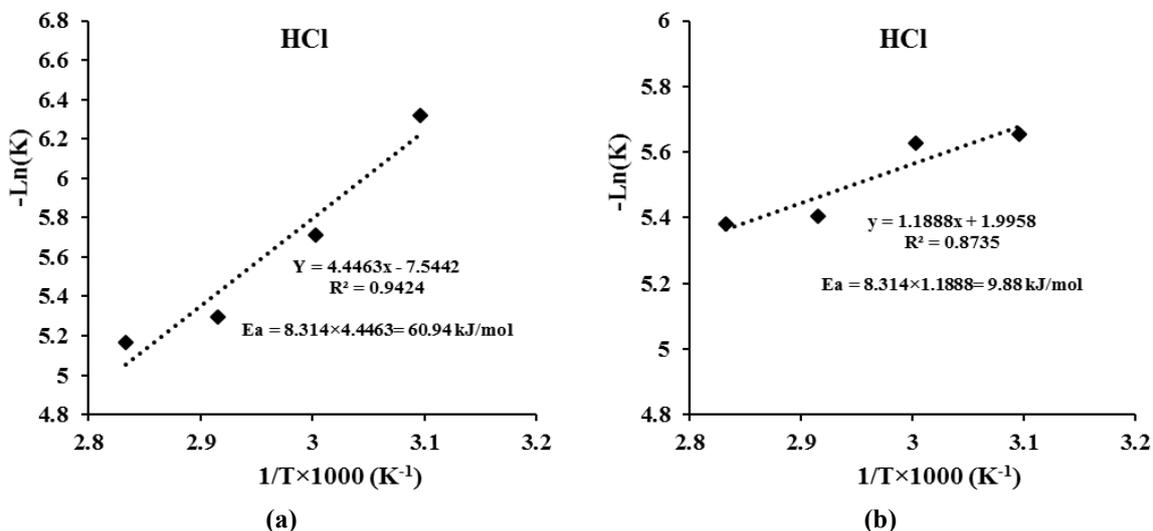


Figure 10. Arrhenius plots for leaching low-grade zinc oxide ore using HCl solution based on surface chemical reaction model in the range of 0-20 min (a) and 20-90 min (b).

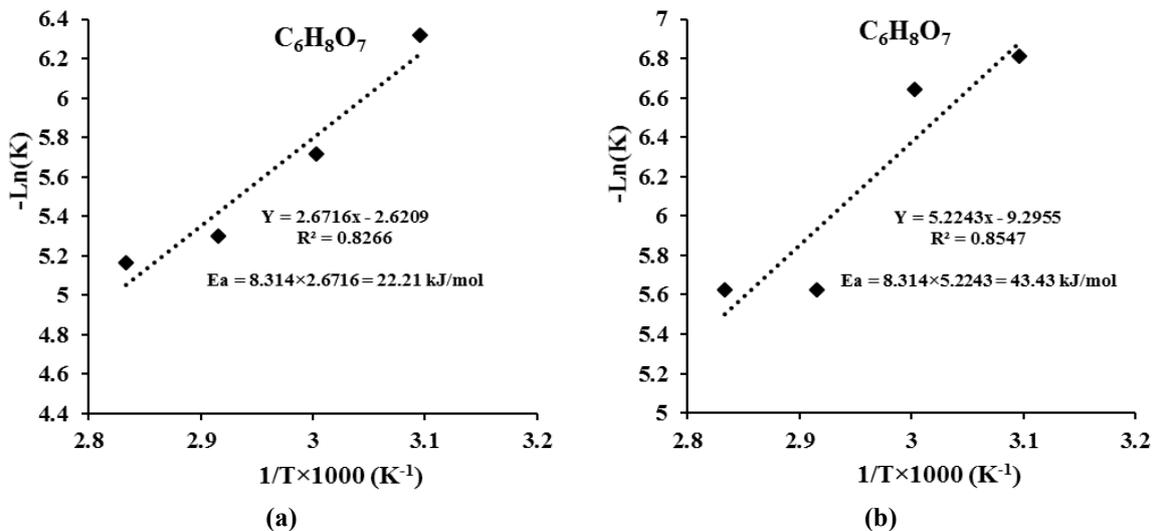


Figure 11. Arrhenius plots for leaching low-grade zinc oxide ore using citric acid solution based on surface chemical reaction model in ranges of 0-70 min (a) and 70-90 min (b).

4. Conclusions

The purpose of this work was to investigate the leaching kinetics of an Iranian low-grade zinc oxide ore in different acid solutions including HCl, H₂SO₄, HNO₃, and citric acid with respect to the experimental variables such as acid concentration, temperature, L/S ratio, and stirring speed. The following conclusions can be drawn from this work:

- (1) The leaching reagent concentration and reaction temperature exerted more pronounced effects on the leaching rate of zinc, whereas the L/S ratio and stirring speed exhibited a relatively moderate effect on the dissolution of zinc.
- (2) Nitric acid had the highest zinc dissolution, followed by citric acid, hydrochloric acid, and sulfuric acid.
- (3) The dissolution kinetics of zinc was examined according to heterogeneous models, and it was distinguished that the leaching process followed the kinetic law of the shrinking core model to describe the leaching of zinc in the acid solutions.
- (4) It was found that diffusion through the fluid film $(1 - (1-x)^{2/3})$ was the rate-controlling steps in the HNO₃ medium with the activation energy of 4.38 kJ/mol, whereas the dissolution rate was controlled by the physico-chemical process in the presence of HCl, H₂SO₄, and citric acid.
- (5) The leaching rate of zinc in H₂SO₄ and HCl is controlled by the surface chemical reaction in the first 20 min with the activation energies of 50.24 and 60.94 kJ/mol, respectively, whereas in the range of 20-90 min, the diffusion process was the rate-controlling step with the activation energies of 20.89 and 9.88 kJ/mol for H₂SO₄ and HCl, respectively.
- (6) it was determined that the dissolution of zinc in citric acid solution is controlled by the diffusion process with the activation energy of 22.21 kJ/mol in 70 min, while in the last 20 min of dissolution, the leaching rate is controlled by the surface chemical reaction with activation energy of 43.43 kJ/mol.

Acknowledgments

The authors acknowledge Mr. Paymard from Bama Mining and Industrial Company for providing the samples and his valuable comments and help during this research work.

References

[1]. Larba, R., Boukerche, I., Alane, N., Habbache, N., Djerad, S. and Tifout, L. (2013). Citric acid as an alternative lixiviant for zinc oxide dissolution. *Hydrometallurgy*. 134-135: 117-123.

[2]. Gimenez-Romero, D., Garcia-Jareno, J.J. and Vicente, F. (2004). Analysis of an impedance function of zinc anodic dissolution. *J Electroanal Chem*. 572 (2): 235-247.

[3]. Lang, G.G. and Horanyi, G. (2005). The formulation and modeling of the anodic dissolution of zinc through adsorbed intermediates. *J Electroanal Chem*. 583 (1): 148-154.

[4]. Hursit, M., Lacin, O. and Sarac, H. (2009). Dissolution kinetics of smithsonite ore as an alternative zinc source with an organic leach reagent. *J Taiwan Inst Chem Eng*. 40 (1): 6-12.

[5]. Xin, W., Srinivasakannan, C., Xin-hui, D., Jin-hui, P. and Da-jin, Y. (2013). Leaching kinetics of zinc residues augmented with ultrasound. *Sep Purif Technol*. 115: 66-72.

[6]. Sethurajan, M., Huguenota, D., Jain, R., Lens, P.N.L., Hornc, H.A., Figueiredo, L.H.A. and van Hullebusch, E.D. (2016). Leaching and selective zinc recovery from acidic leachates of zinc metallurgical leach residues. *J Hazard Mater* (in press). doi:10.1016/j.jhazmat.2016.01.028.

[7]. Jha, M.K., Kumar, V. and Singh, R.J. (2001). Review of hydrometallurgical recovery of zinc from industrial wastes. *Resour Conserv Recycl*. 33 (1): 1-22.

[8]. Abkhoshk, E., Jorjani, E., Al-Harashseh, M.S., Rashchi, F. and Naazeri, M. (2014). Review of the hydrometallurgical processing of non-sulfide zinc ores. *Hydrometallurgy*. 149: 153-167.

[9]. Han, J., Liu, W., Qin, W., Peng, B., Yang, K. and Zheng, Y. (2015). Recovery of zinc and iron from high iron-bearing zinc calcine by selective reduction roasting. *J Ind Eng Chem*. 22: 272-279.

[10]. Abdel-Aal, E.A. (2000). Kinetics of Sulfuric Acid Leaching of Low-grade Zinc Silicate Ore. *Hydrometallurgy*. 55 (3): 247-254.

[11]. Espiari, S., Rashchi, F. and Sadrnezhad, S. (2006). Hydrometallurgical treatment of tailings with high zinc content. *Hydrometallurgy*. 82 (1-2): 54-62.

[12]. Arslan, C. and Arslan, F. (2002). Recovery of copper, cobalt, and zinc from copper smelter and converter slags. *Hydrometallurgy*. 67 (1-3): 1-7.

[13]. de Souza, C.C.B.M., Oliveira, D.C. and Tenório, J.A.S. (2001). Characterization of used alkaline batteries powder and analysis of zinc recovery by acid leaching. *J Power Sources*. 103 (1): 120-126.

[14]. Niemczewska, J., Cierpiszewski, R. and Szymanowski, J. (2004). Mass transfer of zinc (II) extraction from hydrochloric acid solution in the Lewis cell. *Desalination*. 162: 169-177.

[15]. Havlik, T., Turzakova, M., Stopic, S. and Friedrich, B. (2005). Atmospheric leaching of EAF

dust with diluted sulphuric acid. Hydrometallurgy. 77 (1-2): 41-50.

[16]. Lee, I.H., Wang, Y.J. and Chern, J.M. (2005). Extraction kinetics of heavy metal-containing sludge. J Hazard Mater. 123 (1-3): 112-119.

[17]. Dutra, A.J.B., Paiva, P.R.P. and Tavares, L.M. (2006). Alkaline leaching of zinc from electric arc furnace steel dust. Miner Eng. 19 (5): 478-485.

[18]. Pecina, T., Franco, T., Castillo, P. and Orrantia, E. (2008). Leaching of a zinc concentrate in H₂SO₄ solutions containing H₂O₂ and complexing agents. Miner Eng. 21 (1): 23-30.

[19]. Langová, Š., Leško, J. and Matýsek, D. (2009). Selective leaching of zinc from zinc ferrite with hydrochloric acid. Hydrometallurgy. 95 (3-4): 179-182.

[20]. Zárate-Gutiérrez, R., Lapidus, G.T. and Morales, R.D. (2010). Pressure leaching of a lead-zinc-silver concentrate with nitric acid at moderate temperatures between 130 and 170°C. Hydrometallurgy. 104 (1): 8-13.

[21]. Dhawan, N., Safarzadeh, M.S. and Birinci, M. (2011). Kinetics of hydrochloric acid leaching of smithsonite. Russian Journal of Metall Nonferr Met. 52 (3): 209-216.

[22]. He, S., Wang, J. and Yan, J. (2011). Pressure leaching of synthetic zinc silicate in sulfuric acid medium. Hydrometallurgy. 108 (3-4): 171-176.

[23]. Fred, C.N. and Fogler, H.S. (1998). The Kinetics of calcite dissolution in acetic acid solutions. Chem Eng Sci. 53 (22): 3863-3874.

[24]. Bakan, F., Lacin, O., Bayrak, B. and Sarac, H. (2006). Dissolution kinetics of natural magnesite in lactic acid solutions. Int J Miner Process. 80 (1): 27-34.

[25]. Bayrak, B., Lacin, O., Bakan, F. and Sarac, H. (2006). Investigation of dissolution kinetics of natural magnesite in gluconic acid solutions. Chem Eng J. 117 (2): 109-115.

[26]. Demir, F., Lacin, O. and Donmez, B. (2006). Leaching kinetics of calcined magnesite in citric acid solutions. Ind Eng Chem Res. 45 (4): 1307-1311.

[27]. Marafí, M. and Stanislaus, A. (2011). Waste catalyst utilization: extraction of valuable metals from spent hydroprocessing catalysts by ultrasonic-assisted

leaching with acids. Ind Eng Chem Res. 50 (16): 9495-9501.

[28]. Irannajad, M., Meshkini, M. and Azadmehr, A. (2013). Leaching of zinc from low grade oxide ore using organic acid. Physicochem Probl Miner Process. 49 (2): 547-555.

[29]. Ju, S., Motang, T., Shendhai, Y. and Yingian, L. (2005). Dissolution kinetics of smithsonite ore in ammonium chloride solution. Hydrometallurgy. 80 (1-2): 67-74.

[30]. Wu, D.D., Wen, S.M., Yang, J. and Deng, J.S. (2015). Investigation of dissolution kinetics of zinc from smithsonite in 5-sulphosalicylic acid solution. Can Metall Q. 54 (1): 51-57.

[31]. Habbache, N., Alane, N., Djerad, S. and Tifouti, L. (2009). Leaching of copper oxide with different acid solutions. Chem Eng J. 152 (2-3): 503-508.

[32]. Levenspiel, O. (1999). Chemical reaction engineering. 3rd ed. John Wiley & Sons. New York. 570 P.

[33]. Liu, W., Tang, M.T., Tang, C.B., He, J., Yang, S.H. and Yang, J.G. (2010). Dissolution kinetics of low grade complex copper ore in ammonia-ammonium chloride solution, Trans. Nonferrous Met Soc China. 20 (5): 910-917.

[34]. Ekmekyapar, A., Aktaş, E., Künkül, A. and Demirkıran, N. (2012). Investigation of leaching kinetics of copper from malachite ore in ammonium nitrate solutions. Metall Mater Trans B. 43 (4): 764-772.

[35]. Crundwell, F.K. (1995). Progress in the mathematical modelling of leaching reactors. Hydrometallurgy. 39 (1-3): 321-335

[36]. Habashi, F. (1969). Principles of extractive metallurgy. Vol. 1. Gordon & Breach. New York. pp. 153-163.

[37]. Habashi, F. (1983). Dissolution of minerals and hydrometallurgical processes. Naturwissenschaften. 70 (8): 403-411.

[38]. Ashraf, M., Zafar, Z.I. and Ansari, T.M. (2005). Selective leaching kinetics and upgrading of low-grade calcareous phosphate rock in succinic acid. Hydrometallurgy. 80 (4): 286-292.

بررسی سینتیک لیچینگ روی از یک کانه کم عیار در اسیدهای معدنی و آلی

سید مهیار سید قاسمی و اصغر عزیزی*

دانشکده مهندسی معدن، نفت و ژئوفیزیک، دانشگاه صنعتی شاهرود، ایران

ارسال ۲۰۱۶/۹/۸، پذیرش ۲۰۱۶/۱۱/۴

* نویسنده مسئول مکاتبات: aazizi@shahroodut.ac.ir

چکیده:

سینتیک لیچینگ یک کانه‌ی اکسید روی کم عیار در واسطه‌های مختلف اسیدی با توجه به تأثیر پارامترهای مختلف شامل غلظت اسید، دما، نسبت مایع به جامد و سرعت همزدن مورد بررسی قرار گرفت. نتایج نشان داد که غلظت عامل لیچینگ و دمای واکنش بیشترین تأثیر را بر استخراج روی دارند، درحالی‌که نسبت مایع به جامد و سرعت همزنی تأثیر ملایمی بر نرخ لیچینگ دارند. ماکزیمم نرخ لیچینگ با اسیدهای معدنی ۹۰/۷۶ درصد به دست آورده شد، درحالی‌که ماکزیمم بازیابی روی با استفاده از اسید سیتریک ۸۸/۶۸ درصد به دست آمد. همچنین نتایج نشان داد که فرآیند لیچینگ از قانون سینتیک مدل هسته انقباضی (کوچک شونده) پیروی می‌کند. نرخ لیچینگ در محلول اسید نیتریک به وسیله مدل نفوذ فیلم سیال با انرژی فعال‌سازی ۴/۳۸ کیلوژول بر مول کنترل شد، در حالی‌که نرخ انحلال روی در محلول‌های اسید هیدروکلریک، اسید سولفوریک و اسید سیتریک به وسیله یک فرآیند حد واسط (فرآیند فیزیکوشیمیایی) کنترل شد.

کلمات کلیدی: سینتیک لیچینگ، بازیابی روی، کانه اکسیدی کم عیار، مدل هسته انقباضی.