

# **Kinetics of Sphalerite leaching by Sodium Nitrate in Sulfuric Acid**

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#### **Abstract**

In the present work, the extraction of zinc from a sphalerite concentrate using sodium nitrate as an oxidant in a sulfuric acid solution was investigated. The effective parameters such as the temperature, sulfuric acid and sodium nitrite concentrations, stirring speed, particle size, and solid/liquid (S/L) ratio were analyzed. The dissolution rate increased with increase in the sulfuric acid and sodium nitrite concentrations and temperature but decreased with increase in the particle size and S/L ratio. Moreover, the stirring speed had a significant effect on the leaching rate. Under the optimum conditions, 74.11% of zinc was obtained. The kinetic data obtained was analyzed by the shrinking core model (SCM). A new SCM variant captured the kinetic data more appropriately. Based on this model, the activities of the reactants control the diffusion but the two concentrations affect the second order reaction rate or diffusion in both directions. At 75 °C, the  $R^2$  values in the surface chemical reactions and diffusion were 0.78 and 0.89, respectively. Using the new model, however, the  $R^2$  value 0.989 was obtained. The reaction orders with respect to [H<sub>2</sub>SO<sub>4</sub>], [NaNO<sub>3</sub>], S/L ratio, and particle size were  $1.603$ ,  $1.093$ ,  $-0.9156$ , and  $-2.177$ , respectively. The activation energy for the dissolution was 29.23 kJ/mol. *Corresponding author: abdarban@modares.ac.ir ([A](http://en.wikipedia.org/wiki/Dolomite). Khodadadi).<b[r](http://en.wikipedia.org/wiki/Pyrite)>Work, the extraction of zinc from a sphalerite concentrate using sodium nitrat<br>solution was investigated. The effective parameters su[ch](http://en.wikipedia.org/wiki/Ore) as the temperature,<br>conc* 

**Keywords:** *Sulfide Ores, Leaching, Reaction Kinetics, Modeling.*

## **1. Introduction**

Sphalerite is the chief zinc ore, and is usually associated with galena, pyrite, and other sulfides along with [calcite,](http://en.wikipedia.org/wiki/Calcite) dolomite, and fluorite. Froth flotation is a process for selectively separating the hydrophobic minerals from the hydrophilic ones [1]. Through the flotation process, the sphalerite concentrate produced has a zinc content greater than 50% [2]. The conventional RLE (roasting, leaching, and electro-wining) zinc production process has been in use since 1916. Currently, more than 85% of zinc is produced using this process [3]. However, due to the roasting stage, this method has numerous disadvantages such as high  $SO_2$  production and high energy consumption (and hence, high production cost). To by-pass these problems, a number of researchers have been trying to develop alternative methods for preventing the production of  $SO<sub>2</sub>$  gas such as the direct leaching of sphalerite at the atmospheric pressure in the presence of oxidants. In this context, numerous research

efforts have been carried out using various oxidants like ferric ions [4], hydrogen peroxide [2], and ammonium persulfate [5] in acidic and alkaline solutions. However, most research works has been aimed at investigating the leaching of sulfides using nitric acid as the oxidant; the leaching processes using nitrates have not been sufficiently investigated, even though they oxidize as strongly as nitric acid [6]. Berdenhann [7] has investigated the nickel sulfide dissolution using ferric ions and sodium nitrate, as the oxidants, in acidic media. He has concluded that zinc extraction in the presence of sodium nitrate is higher than that in ferric ions. The copper recovery in the  $Cu<sub>2</sub>S$  leaching using a sulfuric acid solution in sodium nitrate has been reported to be higher than 95% [6]. The oxidation of sphalerite in an acidic medium ( $pH \leq 2$ ) is an electrochemical process that releases zinc ions, and forms the elemental sulfur [8]:

$$
ZnS = Zn2+ + S0 + 2e-
$$
  
E<sup>0</sup> = 0.265 + 0.0295 log[Zn<sup>2+</sup>] (1)

The oxidation of sodium nitrate in an acidic solution occurs according to the following equations [9]:

 $NO_3 + 4H^+ + 3e^- = NO + 2H_2O$ <br>  $E^0 = 0.957$  (2)  $E^0$ 

 $2NO_3 + 4H^+ + 2e^- = 2NO_2 + 2H_2O$ <br>  $E^0 = 0.790$  (3)  $\text{E}^0$ 

Comparison of Eq. 1 with the  $NaNO<sub>3</sub>$  redox reaction shows that the redox potential for sulfide/elemental sulfur is less than that for NaNO<sub>3</sub>. Therefore, the oxidation of sulfide to the elemental sulfur is possible. The leaching of a sulfide concentrate in an acidic solution in the presence of sodium nitrate can be expressed as follows [7]:

 $3MeS + 2NO_3 + 8H^+ = 3Me^{+2} + 3S^0 + 2NO +$  $4H<sub>2</sub>O$  $(4)$ Or  $MeS + 2NO<sub>3</sub><sup>-</sup> + 4H<sup>+</sup> = 3Me<sup>+2</sup> + 3S<sup>0</sup> + 2NO<sub>2</sub> +$  $2H<sub>2</sub>O$ Me: Divalent metal ions: Zn, Cu, etc. (5)

In this work, the kinetics of the sphalerite dissolution by sodium nitrate in sulfuric acid was studied. The influences of the stirring speed, particle size, acid concentration, sodium nitrate

concentration, temperature, and liquid/solid (L/S) ratio were also investigated. Additionally, the kinetic data obtained was analyzed by the shrinking core model (SCM), and the best-fitting equation to the experimental data was determined.

#### **2. Materials and method**

A sphalerite concentrate sample obtained from Bama Lead and Zinc Complex in the Isfahan province in Iran was used. The sample was sieved to four-size fractions. The chemical analysis of each size fraction is presented in Table 1.

For the leaching experiments, a 1-L water glass recipient was used. The temperature was kept constant using a water bath. The calculated volumes of the  $H_2SO_4$  and NaNO<sub>3</sub> solutions were added to the glass reactor, which was then heated to the desired temperature. Subsequently, a sample with a pre-determined weight was added to the reactor. At the specified time intervals, 1 mL of the solution was taken from the leach solution and diluted using distilled water. All the zinc analyses were carried out using an atomic absorption spectrophotometer (model Varian-AA240). The experimental conditions are shown in Table 2. Keeping the other parameters constant, the effect of each parameter on the dissolution rate was evaluated.





\*Constant values used when effect of other parameters was investigated.

# **3. Effect of parameters on dissolution rate 3.1. Effect of solid/liquid ratio**

The effect of the solid/liquid (S/L) ratio on the sphalerite dissolution was studied for three different solid/liquid (S/L) ratios (4, 8, and 12 g/L) at 75 °C in a solution containing  $H_2SO_4$  (2.0) M) and  $\text{NaNO}_3$  (1.0 M). The stirring speed and

particle size were kept constant at 400 rpm and  $-53 + 45$  µm, respectively. As shown in Figure 1, zinc extraction increased with a decrease in the amount of solid; this was caused by the increase in the acid available per unit of solid. To investigate the other leaching parameters, the 8 g/L S/L ratio was chosen.



**Figure 1. Effect of solid/liquid ratio on sphalerite dissolution.**

#### **3.2. Effect of particle size**

To investigate the influence of the particle size on the dissolution rate, leaching experiments were carried out for different particle sizes  $(-106 + 75,$  $-75 + 53$ ,  $-53 + 45$ , and  $-45 \mu$ m), while the other parameters were kept constant. As it can be seen in Figure 2, the dissolution rate increased significantly with decrease in the particle size due

to the presence of the smaller particles, providing larger contact surface areas between the sphalerite and the leaching reagent. Zinc extraction decreased from 74.11 to 69% after 150 min, as the particle size increased from  $-53 + 45$  to  $-75 + 53$ µm. The other leaching parameters were analyzed using  $a - 53 + 45$  µm particle size.



**Figure 2. Effect of particle size on sphalerite dissolution.**

## **3.3. Effect of stirring speed**

The influence of the stirring speed on the sphalerite dissolution was studied at 0, 200, 400, and 600 rpm and 75 ˚C in a solution containing  $H_2SO_4$  (2.0 M) and NaNO<sub>3</sub> (1.0 M). As shown in Figure 3, the stirring speed had an important effect on the dissolution of the sphalerite. The zinc recovered under similar experimental conditions, however, without agitation, was

approximately 30%. It was almost 74.11% when a 400 rpm stirring speed was induced, which shows that the rate of the sphalerite dissolution depends on the stirring speed. Hence, there is an indication that the reaction is controlled by the film diffusion. In analyzing the effects of the other parameters, 400 rpm was chosen as the optimal operating stirring speed.



**Figure 3. Effect of stirring speed on sphalerite dissolution.**

# **3.4. Effect of temperature**

To determine the influence of temperature, leaching experiments were performed at the five temperatures 45, 55, 65, 75, and  $85^{\degree}$ C. The fixed laboratory parameters at this stage were the stirring speed of 400 rpm, sulfuric acid (2.0 M), sodium nitrate (1.0 M), particle size of  $-53 + 45$ 

µm, and phase ratio of 8 g/L. With an increase in the temperature, the sphalerite dissolution rate increased. As it can be seen in Figure 4, after 150 min,with an increase in the temperature from 45 to 75 ˚C, the dissolution rate increased from 63.47 to 74.11%.



**Figure 4. E of temperature on sphalerite dissolution.**

### **3.5. Effect of H2SO<sup>4</sup> concentration**

The effect of the  $H_2SO_4$  concentration on the sphalerite dissolution was studied for the 0.5, 1.0, 1.5, 2.0, and 2.5 M  $H_2SO_4$  concentrations at 75 °C in a solution containing  $NaNO<sub>3</sub>$  (1.0 M). The results obtained are given in Figure 5. An increase in the  $H_2SO_4$  concentration results in a moderate increase in the zinc extraction. However, at a high acid concentration (2.0 and 2.5 M), the effect is not significant. Zinc leaching increased from 47 to

74.11% after 150 min as the acid concentration was increased from 0.5 to 2.0 M. With an increase in the acid concentration to 2.5 M, the dissolution rate increased to 2.5%, ultimately reaching 76%. With an increase in the acid concentration, the hydrogen ion concentration in the leaching solution increased, raising the redox potential for the oxidant, and enhancing the dissolution rate.



**Figure 5. Effect of acid concentration on sphalerite dissolution.**

### **3.6. Effect of NaNO<sup>3</sup> concentration**

The effect of  $NaNO<sub>3</sub>$  concentration on the zinc extraction is shown in Figure 6. Experiments were carried out at the five different NaNO<sub>3</sub> concentrations 0.1, 0.5, 1.0, 1.5, and 2.0 M. The results obtained show that an increase in the oxidant concentration accelerates the sphalerite dissolution. At low concentrations of sodium nitrate, the sphalerite dissolution rate was very

weak, confirming that without the oxidant, the sphalerite dissolution did not occur.

The X-ray diffraction (XRD) analysis of the solid residue obtained from the leaching experiment is shown in Figure 7. As demonstrated, the elemental sulfur and sphalerite appear in the graph, which confirms that the elemental sulfur is formed during the leaching process.



**Figure 6. Effect of sodium nitrite concentration on sphalerite dissolution.**



#### **4. Kinetic analysis**

Leaching is a heterogeneous process, involving the mass transfer of the reactant and product ions. The dissolution of various mineral particles was investigated using different models. As the dissolution proceeds, the particles shrink with time until the total surface area of the particles diminishes, and the overall dissolution rate is reduced. If a product layer is formed around the particles, the dissolution process can be analyzed by SCM, though the model can be used even if there is no layer formation. Additionally, during the dissolution of the particles in some reactions, a loss of reagents or the exit of products may block the filling of pores with either impurity already present in the ore (clays, etc.) or re-precipitated leaching products. This leads to a "blocked-pore" kinetic model [10]. Similarly, the sphalerite dissolution in an acidic medium is a heterogeneous process, and most sulfide mineral leachings follow SCM [1]. According to this model, the reaction of the sphalerite can be expressed as follows: **Archive of Case of C** 

 $A (fluid) + bB (solid) \rightarrow fluid product + solid product$ 

The reaction rate is controlled by the following two equations.

When the resistance to diffusion through the product layer controls the reaction rate, the following equation expresses the dissolution rate [11, 12]:

$$
1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}} = \frac{2M_BDC_A}{P_Bar_0^2}t = K_d t
$$
 (6)

When the the reaction progress is unaffected by the presence of an ash layer, the reaction rate is proportional to the available surface of the unreacted core. In this case, the reaction rate is controlled by the surface chemical reactions. The following equation expresses the dissolution rate  $[1\overline{1, 12}]$ :

$$
1 - (1 - X)^{\frac{1}{3}} = \frac{K_c M_B C_A}{p_B a r_0} = K_r t
$$
 (7)

where X is the fraction reacted,  $K<sub>C</sub>$  is the kinetic constant,  $M_B$  is the molecular weight of the solid,  $C_A$  is the concentration of the dissolved lixiviant, a is the stoichiometric coefficient of the reagent in the leaching reaction,  $r_0$  is the initial radius of the solid particle, t is the reaction time,  $\rho_B$  is the the solid density, and  $K_r$  is the rate constant.

Numerous researchers who have investigated the kinetics of the sphalerite dissolution process under various conditions have pointed out that it is either a reaction- or diffusion-controlled process [13, 14]. However, in a few cases, neither of the two equations mentioned has been able to explain the sphalerite dissolution rate.

Bobeck [15] used Eq. 8, which is included in both Eqs. 6 and 7:

$$
\[1 - (1 - X)^{\frac{1}{3}}\] + B \left[1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}}\right] = Kt \tag{8}
$$

where

$$
B=K_{\rm r}\!/K_{\rm d}.
$$

Dehghan et al. [16] have reviewed the sphalerite dissolution kinetics in an acidic ferric chloride solution and concluded that the sphalerite leaching is not appropriately captured by Eqs. 6 and 7; they used a new type of SCM, which provided a better fit to the kinetic data. Moreover, Dehghan et al. have found that both the interfacial transfer and diffusion through the product layer affect the reaction rate. The model equation is given as:

$$
\frac{1}{3}\ln(1-X) + \left[ (1-X)^{-\frac{1}{3}} - 1 \right] = K_m t \tag{9}
$$

Compared to the models presented above, a new variant of SCM proposed by Dickinson and Heal [17] has provided a better expression for the sphalerite leaching using the kinetic data for sodium nitrate in sulfuric acid. According to this model, which is a more complete type of the diffusion-control model (Eq. 6), both the solid and acid concentrations have a role in controlling the

reaction rate, and diffusion occurs in two directions. An equation for this model is given as follows:

$$
\frac{1}{5}(1-X)^{-5/3} - \frac{1}{4}(1-X)^{-4/3} + \frac{1}{20} = K_{p}t
$$
\n
$$
K_{p} = \frac{DV_{m}C_{0A}C_{0B}}{r_{0}^{2}}
$$
\n(10)

Where,  $K_p$  is a kinetic constant,  $V_m$  is the volume of the produced layer, D is the diffusion coefficient, and  $C_0$  is the concentration of the penetrating species at the surface (A, solid and B, fluid).

In Figure 8,  $\frac{1}{2}(1-X)^{-\frac{1}{3}} - \frac{1}{2}(1-X)$ 20  $(1-X)^{\frac{-4}{3}} + \frac{1}{20}$ 4  $(1-X)^{-5/3} - \frac{1}{4}$ 5  $\frac{1}{-}(1-X)^{-5}$   $\frac{1}{3}$   $\frac{1}{-}(1-X)^{-3}$ 4 3  $(-X)^{\frac{-5}{3}} - \frac{1}{2}(1-X)^{\frac{-4}{3}} + \frac{1}{20}$ has

been plotted *vs.* time at different temperatures. The slope of this line is the specified kinetic constant.



As it can be seen in Table 3, the popular modes of SCM (Eqs. 6 and 7) were compared to the new mode (Eq. 10). According to the results given in this table, SCM with diffusion through the product layer, compared to the chemical reaction-

controlled model, showed a better fit to the data but the new SCM mode suggested by Dikenson provided an even better fit due to a more linear relationship between the left side of Eq. 10 and time.

<b>Surface reaction</b>	<b>Diffusion</b>	New variant of SCM
D4		
0.8421	0.9590	0.9809
0.8366	0.9508	0.9952
0.8210	0.9374	0.9921
0.7833	0.8924	0.9898
0.7718	0.8804	0.9994

**Table 3. Correlation coefficient values for different temperatures.**

The temperature-dependence of the reaction rate constant can be determined through the Arrhenius equation [18]:

$$
K_{p} = A \exp\left(\frac{-E_{a}}{RT}\right) \tag{11}
$$

where A is the frequency factor,  $E_a$  is the activation energy of the reaction, R is the universal gas constant, and T is the absolute

temperature. With respect to Eq. 11, if the plot of In  $k_P$  *vs.* 1/T is drawn, the slope of the line is  $E_a/R$ . If this value is multiplied by R, the activation energy value is obtained. As it can be seen in Figure 9, the slope of the line is 3.5052, and we obtained the activation energy value of 29.23 kJ/mol.



**Figure 9. Arrhenius plot of data presented in Figure 8.**

The activation energy for a diffusion-controlled process is different from that for a process controlled by a chemical reaction. The activation energy for a process controlled by a diffusion mechanism is 4-12 kJ/mol; for a chemical reaction mechanism, the activation energy is greater than 40 kJ/mol [19]. However, other studies have offered the following different results: the activation energies of 2-5 and 12-26 kJ/mol for the diffusion-controlled process, and 40-80 kJ/mol for the process controlled by a chemical reaction [19-21]. Babu [5] has obtained an activation energy of 41 kJ/mol for the diffusion-controlled process, and Dehqan [16] has obtained it to be 49.2 kJ/mol. In addition, Adabayo [14] and Arawi [22] have, respectively, obtained the activation energies of 28 and 16 kJ/mol for two processes controlled by a chemical reaction.

Hence, the magnitude of the activation energy cannot determine the control mechanism of the process; it can only be used as a guide for determining the leaching process.

Therefore, we can conclude that if the activation energy is less than 30 kJ/mol, the process is not controlled by a chemical reaction, and it is more likely to be controlled by diffusion. Moreover, in the diffusion-controlled process, there is a close correlation between the stirring speed and the reaction rate caused by the thickness reduction of the product layer. Thus three factors confirm that our process is controlled by a diffusion mechanism, as follow: its low activation energy (29.23 kJ/mol), the correlation between the stirring speed and Zn extraction (Figure 5), and the fit of Eq. 10 to the experimental data. In the next stage of our experiments, the reaction order with respect to the sulfuric acid and sodium nitrate concentrations, particle size, and S/L ratio was determined. Ln  $k_p$  *vs.* ln $[H_2SO_4]$  was plotted (Figure 10). The slope of the line obtained conveys the reaction order with respect to the sulfuric acid concentration, and is proportional to  $[H_2SO_4]^{1.6032}$ , with a correlation coefficient of 0.986.

Ln  $k_p$  *vs.* ln[NaNO<sub>3</sub>] was plotted (Figure 11). The reaction order with respect to sodium nitrate was 1.093, and the slope of the line obtained is proportional to  $[NaNO<sub>3</sub>]^{1.093}$ .

Ln  $k_p$  *vs.* ln[S/L] was plotted (Figure 12); it can be used to determine the reaction order with respect to the S/L ratio. The reaction order was found to be  $-0.9156$ , and the slope of the line obtained is proportional to  $(S/L)^{-0.9156}$ .

Finally, as it can be seen in Figure 13, the reaction order with respect to the particle size was – 2.1777, and the slope of the line obtained is proportional to  $[Size]$ <sup>-2.1777</sup>.



**Figure 11. Determination of reaction order with respect to ln[NaN03].**



**Figure 12. Determination of reaction order with respect to ln[S/L].**



**Figure 13. Determination of reaction order with respect to ln[Size].**

# **5. Dissolution rate equation**

By determining the activation energy of the dissolution process and the reaction orders with respect to the experimental conditions, the following equation could be used to describe the kinetics of the sphalerite dissolution by sodium nitrate in sulfuric acid:

$$
\frac{1}{5}(1-X)^{-\frac{5}{3}} - \frac{1}{4}(1-X)^{-\frac{4}{3}} + \frac{1}{20} =
$$
\n
$$
K_0 \left[H_2 SO_4\right]^{1.6032} \left[NaNO_3\right]^{1.093}
$$
\n
$$
(r_0)^{-2.1777} \left(\frac{S}{L}\right)^{-0.9156} \exp\left(\frac{-29233}{RT}\right)t
$$

As shown in Figure 14, plotting

$$
[H_2SO_4]^{1.6032}[NaNO_3]^{1.093}(r_0)^{-2.1777}\left(\frac{S}{L}\right)^{-0.9156}\exp\left(\frac{-29233}{RT}\right)t
$$
  
\n*vs.*  
\n
$$
\frac{1}{5}(1-X)^{-5/3} - \frac{1}{4}(1-X)^{-4/3} + \frac{1}{20}
$$
  
\ngives a k<sub>0</sub> value of 829423.



The extraction rates obtained under the experimental conditions and those calculated by the model were compared. Under the optimum dissolution conditions, which were determined to be  $H_2SO_4$  (2.0 M), NaNO<sub>3</sub> (1.0 M), 75 °C, 8 g/L S/L ratio, 150 min leaching time, and  $-45 + 53$ µm particle size, the extracted zinc was calculated using the following equation:

$$
\frac{1}{5}(1-X)^{-\frac{5}{3}} - \frac{1}{4}(1-X)^{-\frac{4}{3}} + \frac{1}{20} =
$$
  
82.9×10<sup>4</sup> [2]<sup>1.6032</sup> [1]<sup>1.093</sup> (49)<sup>-2.1777</sup> (8)<sup>-0.9156</sup>  
exp $\left(\frac{-29233}{8.314*348}\right)$ (150)

According to the equation, the extracted zinc, X, was 75.3%, while the zinc extracted under the experimental conditions was 74.11%. This demonstrates a significant correlation between the experimental and calculated values.

#### **6. Conclusions**

- In this work, the kinetics of the sphalerite concentrate leaching by sulfuric acid and sodium nitrate were studied. The effects of the experimental parameters such as the temperature, sulfuric acid and sodium nitrite concentrations, stirring speed, particle size, and S/L ratio were analyzed.

The dissolution rate increased with increase in the sulfuric acid and sodium nitrite concentrations and temperature. However, it decreased with increase in the particle size and S/L ratio. Moreover, the stirring speed had a significant effect on the leaching rate.

The optimum leaching conditions were determined to be: size,  $(-75 + 53)$  µm; [NaNO<sub>3</sub>], 1 mol/L;  $[H_2SO_4]$ , 2 mol/L; T, 75 °C; and S/L, 8 g/L. Under these conditions, 74.11% of zinc was extracted in 150 min.

- The kinetic data was analyzed by SCM. The new SCM variant fits the kinetic data more appropriately.

- The reaction orders with respect to the  $H_2SO_4$ and $NaNO<sub>3</sub>$  concentrations,  $S/L$  ratio, and particle size were found to be 1.603, 1.093, −0.9156, and −2.177, respectively.

- The activation energy was calculated to be 29.23 kJ/mol.

- The dissolution rate can be expressed by Eq. 4, which represents a semi-empirical mathematical model.

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# **References**

[1]. Uçar, G. (2009). Kinetics of sphalerite dissolution by sodium chlorate in hydrochloric acid. Hydrometallurgy 95: 39-43.

[2]. Aydogan, s. (2006). Dissolution kinetics of sphalerite with hydrogen peroxide in sulphuric acid medium. Chemical Engineering Journal. 123: 65-70.

[3]. Zhi, F., Qing, J. and Wang, C. (2013). Atmospheric oxygen-rich direct leaching behavior of zinc sulphide concentrate. Trans. Nonferrous Met. Soc. China. 23: 3780-3787.

[4]. Akcil, A. and Ciftci, H. (2002). A study of the selective leaching of complex sulfides from the Eastern Black Sea Region, Turkey, Minerals Engineering. 15: 457–459.

[5]. Babu, M.N., Sahu, K.K. and Pandey, B.D. (2002). Zinc recovery from sphalerite concentrate by oxidative leaching with ammonium, sodium and potassium persulfates. Hydrometallurgy. 64: 119-129.

[6]. Rajko, Z. and Vracar, A. (2003). Leaching of copper (I) sulphide by sulphuric acid solution with addition of sodium nitrate, Hydrometallurgy. 70: 143- 151.

[7]. Berdenhan, R. and Vanvuuren, C. (1999). Technical note the leaching behavior of a nickel concentrate in an oxidative sulphuric acid solution. Minerals Engineering. 12: 687-692.

[8]. Pecina, T., Telhma, F. and Pedro, C. (2008). Leaching of a zinc concentrate in  $H_2SO_4$  solutions containing  $H_2O_2$  and complexing agents, Minerals Engineering. 21: 23-30.

[9]. Miroslav, D. and Sokić, A. (2009). Kinetics of chalcopyrite leaching by sodium nitrate in sulphuric acid, Hydrometallurgy. 95: 273-279.

[10]. Shafaei, S.Z. (1996). Hydrometallurgical processing of angouran oxidized zinc. PhD thesis, the University of Leeds, pp. 142-200.

[11]. Zhenghui, W., Dreisinger, D., Urchb, H. and Fassbender, S. (2014). The kinetics of leaching galena concentrates with ferric methane sulfonate solution. Hydrometallurgy. 142: 121-130.

[12]. Xiong, L.Z., Lan, Z., Shao, Y., Xiong, F. and Chenc, Y.C. (2014). Leaching and kinetic modeling of calcareous bornite in ammonia ammonium sulfate solution with sodium persulfate. Hydrometallurgy. 144: 86-90.

[13]. Rath, P.C., Paramguru, R.K. and Jena, P.K. (1981). Kinetics of dissolution of zinc sulphide in aqueous ferric chloride solution. Hydrometallurgy. 6: 219-225.

[14]. Adebayo, A.O., Ipinmoroti, K.O. and Ajayi, O. (2006). Leaching of Sphalerite with Hydrogen Peroxide and Nitric Acid Solutions. Minerals & Materials Characterization & Engineering. 5 (2): 167- 177.

[15]. Bobeck, G.E. and Su, H. (1985). The kinetics of dissolution of sphalerite in ferric chloride solution. Metall. Trans. B 16B: 413-424.

[16]. Dehghan, R. and Kolahdoozan, M. (2008). Leaching and kinetic modelling of low-grade calcareous sphalerite in acidic ferric chloride solution, Hydrometallurgy. 96: 275-282.

[17]. Dickinson, C.F. and Heal, G.R. (1999). Solidliquid diffusion controlled rate equations. Thermochim. Acta 340-341: 89-103.

[18]. Safarzadeh, M., Moradkhani, D. and Ojaghi, M., (2008). Kinetics of sulfuric acid leaching of cadmium from Cd-Ni zinc plant residues, Journal of Hazardous Materials. 163: 880-890. Sphale, K.K. and Pandey, B.D. (2002).<br>
Meall. Trans. B 16B: 413-424.<br>
comparison sphalerite concentrate by oxidative<br>
Leaching and Kincitic modelling of low-grade<br>
ammonium, sodium and potassium<br>
calcareous sphalerite in a

[19]. Habashi, F. (1980). Principles of Extractive Metallurgy, second ed., Gordon and Breach Science Publ., New York.

[20]. Abdel-Aal, E.A. and Rashad, M.M., (2004). Kinetic study on the leaching of spent nickel oxide catalyst with sulfuric acid, Hydrometallurgy. 74: 189- 194.

[21]. Romankiw, L.T. and De Bruyn, P.L. (1963). Kinetics of dissolution of zinc sulfide in aqueous sulfuric acid. In: Wadsworth, M., Davis, F.T. (Eds.), Unit Processes in Hydrometallurgy, 62 Dallas, TX.

[22]. Harvey, J.T., Tai, Y. and Paterson, J.G. (1993). A kinetic investigation into the pressure oxidation of Engineering. 6: 949-967.

**سینتیک انحالل اسفالریت در محلول اسیذسولفوریک در حضور نیترات سذیم**

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**بخش مهنذسی معذن، دانشگاه تربیت مذرس، ایران**

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## **چکیذه:**

در پژوهش حاضر، استخراج روی از کنسانتره اسفالریت در محلول اسید سوری مصری ویتشیی ی که به عنـوان اکسـیدان مـورد بررسـی قـرار گرفـت. پارامترهای تأثیرگذار نظیر دما، غلظت اسیدسولفوریک، غلظت اسید نیتریک، دور همزن، اندازه ذرات و نسبت جامد به مـایع مـورد بررسـی قـرار گرفتنـد از نتـایج حاصل مشخص شد که نرخ انحلال با افزایش غلظت اسیدسولفوریک و اسید نیتریک و نیز دما افزایش می یابد و ب ا افـزایش انـدازه ذرات و نسـبت جامـد بـه مـایع کاهش می ابد. در نهایت، در شرایط بهینه، میزان استخراج روی برابر ۷۴/۱۱٪ به دست آمد. سینتیک فرآیند نیز توسط مدل هستهی کوچک شـونده مـورد آنـالیز قرار گرفت. یک نوع جدید از این مدل بهترین تطابق را با دادههای آرمایشگاهی نشان داد. بر مبنای این مدل اکتیویتهی حلال و جسم جامد هر دو بر نـرخ انحـلال نأثیر میگذارند و دیفیوژن در دو جهت بر فرآیند تأثیر میگذارد. در دمای ۷۵ درجه سانتیگراد میـزان  $\mathrm{R}^2$  بـرای دو مکانیسـم واکـنش شـیمیایی و دیفیـوژن بـه ترتیب برابر با ۰/۷۸ و ۰/۸۹ به دست آمد اما برای مدل جدید برابر ۰/۹۸۹ به دست آمد. همچنین مرتبههـای واکـنش بـا توجـه بـه غلظـتهـای اسیدسـولفوریک، نيترات سديم، نسبت جامد به مايع و اندازه ذرات به ترتيب برابر با ١/٤٠٣، ١/٤٦٣، و١/٩٧٧ - ب دست آمدنـد. انـرژي اکتيواسـيون نيـز برابـر ٢٩/٢٣ کیلوژول بر مول به دست آمد. ج**کیده:**<br>کلمهای می استخراج روی از کاملا می استفراد این این سیما سولفوریک و در حضور اسببه لیتربک به معموان اکسیمان مورد<br>کلمات کلیدی: کبو کلم اینکه این روی از کاملا می استخراج روی برابر ۱۳۴۸٪ به دست افزاین شرایط این سیاسی ش