

## Solubility of ZnS Concentrate Containing Pyrite and Chalcopyrite in HNO<sub>3</sub> solutions

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In this study, the dissolution of ZnS concentrate in HNO<sub>3</sub> solutions was investigated, taking into consideration the effect of acid concentration, stirring speed and reaction temperature. It was observed that the dissolution rate increased with increasing acid concentration and reaction temperature, but no effect of stirring speed was observed. Using the experimental data, we attempted to establish a kinetic model for the dissolution process. Employing graphical and statistical methods, the following kinetic model including the effect of the above chosen parameters, was established.  $-\ln(1-X) = 4412.71 \cdot (C)^{1.25} \cdot \exp(-48150/RT) \cdot t^{0.74}$  The activation molar energy of the dissolution process was found to be 48.15 kJ · mol<sup>-1</sup>.

*Key words:*

Sphalerite, nitric acid, dissolution kinetics.

### Introduction

Zinc is found in many different minerals in the world. A small quantity of zinc is present in almost every volcanic rocks. It is estimated that Zn constitutes 0.013 % of earth's crust<sup>1</sup>. About 6,000,000 ton/year of the world's production of Zn originates from the treatment of sulphide concentrates containing sphalerite (ZnS) as the predominant zinc mineral<sup>2</sup>.

The dissolution of mineral ores in aqueous solutions may be a physical, chemical or electrochemical process. The crystalline nature of the mineral, its state of subdivision, its defect structure, and other factors play an important role in the dissolution. Sphalerite (ZnS), usually together with sulphide minerals constitutes complex sulphide ores.

There are many studies related to dissolution of ZnS in various media. *Kammel* et al.<sup>4</sup> investigated the leaching of nine sphalerite samples in Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> / H<sub>2</sub>SO<sub>4</sub> solutions. They found that the dissolution rate of sphalerite increased by increasing the amount fraction of iron in samples containing iron up to  $x = 1$  % iron. Dissolution rates diminished by decreasing the amount fraction of iron in samples containing up to  $x = 1-10$  % iron, when Cu<sup>+2</sup> was added in leaching solutions. *Geveci* et al.<sup>5</sup> studied the leaching of complex sulphide ores in acidic FeCl<sub>3</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solutions and found that Zn was dissolved completely in Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solutions at about 100 °C and at these conditions, the leaching rate of copper was lower than that of zinc. Also, 100 % of the zinc and 98 % of the copper in the sample could be leached under pressure in autoclave at 140 °C. *Perez* et al.<sup>2</sup> investigated the leaching of Cu-Zn sulphide ores in Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> / H<sub>2</sub>SO<sub>4</sub>

and HCl / FeCl<sub>3</sub> solutions. They found that the dissolution rate of Zn was faster than that of Cu and stated that this situation was the result of a galvanic reaction between chalcopyrite and sphalerite. *Warren* et al.<sup>6</sup> studied the reaction mechanism of sphalerite in FeCl<sub>3</sub>/HCl solutions. They determined that the leaching rate was decreased proportionally with  $[\text{Fe}^{+3}]_T^{0.5}$  and  $[\text{Cl}^-]_T^{0.43}$  in low FeCl<sub>3</sub> concentrations, and  $[\text{Fe}^{+3}]_T$  and  $[\text{Cl}^-]_T$  in high FeCl<sub>3</sub> concentration. *Vasilev* et al.<sup>7</sup> examined the dissolution kinetics of four sphalerite samples in HCl solutions up to 10 mol L<sup>-1</sup> and found that dissolution rate increased with increasing amounts of iron, but the activation energy decreased. Similar results have been confirmed by other authors<sup>8-10</sup>. The leaching kinetics of sphalerite containing pyrite was investigated in Cl<sub>2</sub>-saturated water by *Ekinci* et al.<sup>11</sup>, and it was found that the sphalerite leaching was controlled by diffusion through the product layer. The activation molar energy was calculated to be 22.68 kJ mol<sup>-1</sup>.

Presently, over 80 % of total Zn output is from the roast-leach-electrowinning process<sup>12</sup>, which has been applied for many years. Direct leaching of concentrate provides some advantages since it will eliminate the roasting step. Some of these advantages are the elimination of SO<sub>2</sub> formation and high extraction yield of zinc because insoluble zinc ferrite does not form<sup>11</sup>. These will result in avoiding SO<sub>2</sub> emission into the atmosphere.

The acids, such as HCl and H<sub>2</sub>SO<sub>4</sub> as a leaching reactive, are not effective to dissolve ZnS concentrate containing CuFeS<sub>2</sub> and FeS<sub>2</sub> in moderate conditions<sup>13</sup>, but HNO<sub>3</sub> is very effective and also a strong oxidizing agent. It is thought that when this concentrate is dissolved in HNO<sub>3</sub> solution, Zn<sup>2+</sup>,

$\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  will pass into the solution, and  $\text{Pb}^{2+}$ , available in little amounts in the concentrate, will precipitate in the form of  $\text{PbSO}_4$ , due to its very low solubility, and can be separated easily from the solution. After this treatment,  $\text{Fe}^{3+}$  in the solution can be precipitated by adjusting pH about 4.  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  can be converted to their metallic forms by cementation by Zn processes and electrowinning, respectively. Nitrous oxides forming during the leach process can be captured, and they can be reconverted to nitric acid by oxidation with air and an absorption to the aqueous solution.<sup>13,14</sup>

In this study, the leaching of ZnS concentrate containing  $\text{CuFeS}_2$  and  $\text{FeS}_2$  in  $\text{HNO}_3$  solutions, was investigated by using quantities such as acid concentration, reaction temperature and stirring speed.

## Material and methods

The concentrated zinc sulphide concentrate used in these experiments was obtained from the Rize-Çayeli region in Turkey. The concentrate was sieved by using 273  $\mu\text{m}$  ASTM standard sieves. It was determined by X-ray diffraction that the concentrate contained mainly ZnS,  $\text{CuFeS}_2$  and  $\text{FeS}_2$  (Figure 1); and by chemical analysis that the concentrate contained a small amount of galena ( $\text{PbS}$ ). The chemical composition of the concentrate was determined by volumetric and gravimetric methods<sup>15,16</sup>. Trace elements were analysed by using an AAS and the analysis result is given in Table 1.

The dissolution experiments were carried out in a glass reactor (250 mL) equipped with a me-

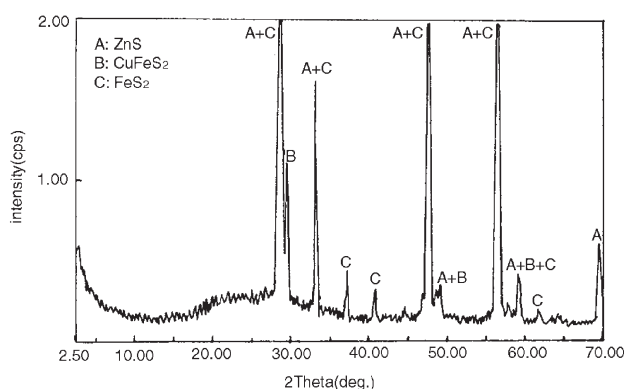


Fig. 1 – X-ray diffractogram of the ZnS concentrate

Table 1 – The chemical composition of zinc sulphur concentrate.

Mass fraction	Zn	Cu	Fe	Pb	Ag	Au	Moisture
w/%	49.50	2.80	8.58	0.67	$1.33 \cdot 10^{-2}$	$1.1 \cdot 10^{-4}$	8.70

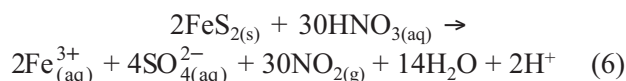
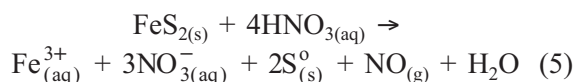
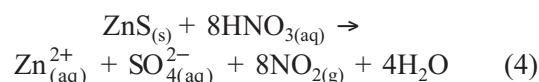
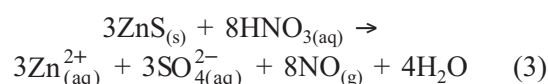
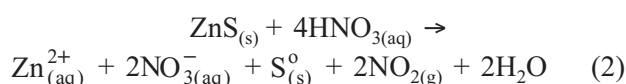
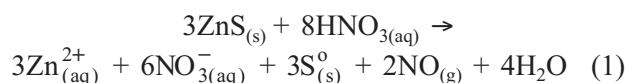
chanical stirrer having a digital controller unit and timer, a thermostat and a cooler. The temperature of the reaction medium could be controlled within  $\pm 0.5$  °C. First 100 mL nitric acid of known concentration was introduced into the reactor. After the desired reactor temperature was reached, a predetermined amount of the zinc sulphide concentrate was added into solution while the content of the vessel was stirred at a certain speed. At the end of the experiment, the contents of the vessel were filtered, and the filtrate solution was then analysed volumetrically for Zn and Cu.<sup>15,16</sup>

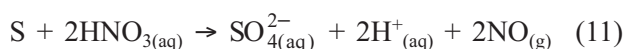
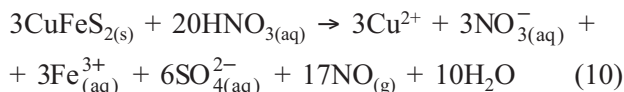
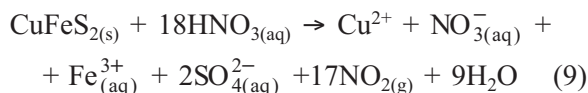
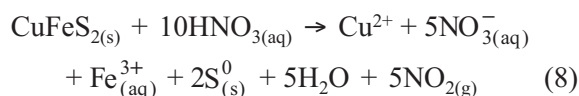
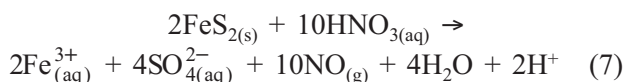
## Results and discussion

### Dissolution Reactions

Dissolution of sphalerite, chalcopyrite, pyrite and galena in acidic  $\text{FeCl}_3$  solutions have been investigated by other researcher, and it has been found that sulphide sulphur reacts with  $\text{Fe}^{3+}$  in two stages. In the first stage, sulphide sulphur is converted to  $\text{S}^0$  and in the second stage  $\text{S}^0$  to  $\text{SO}_4^{2-}$ <sup>13,17–21</sup> that the concentrate contained a small amount of galena ( $\text{PbS}$ ).

On the other hand, the kinetics of pyrite oxidation with nitric acid solutions has been studied by Kadioglu et. al.; the authors have determined that pyrite oxidation takes place in two stages. In the first stage, elemental sulphur is formed and in the second stage the elemental sulphur is converted to  $\text{SO}_4^{2-}$ . They have expressed that elemental sulphur increases by increasing acid concentration and temperature<sup>22</sup>. In according to the works cited above, when ZnS concentrate is added into the nitric acid solution, the reactions taking place in the medium, can be written as follows:





**Effects of parameters**

The quantities presented in Table 2 are measured against the conversion fraction of Zn, which is defined as follows:

$X$  = the amount of dissolved Zn / the amount of Zn in original sample.

Results are presented in the form of  $X$  versus time graphs in Figure 2–4. Figure 2 shows that increases of the temperature has a positive effect on the dissolution rate, as expected, due to the expo-

Table 2 – Quantities and their values corresponding to their levels to be studied in experiments.

Quantities	Values
Reaction temperature, °C	12, 25*, 35, 44
Acid concentration, mol L <sup>-1</sup>	22.06, 4.21, 6.98* 10.58
Particle diameter, mesh	-273*
Stirring speed, min <sup>-1</sup>	200, 300, 400, 500*, 800

\* The values kept constant

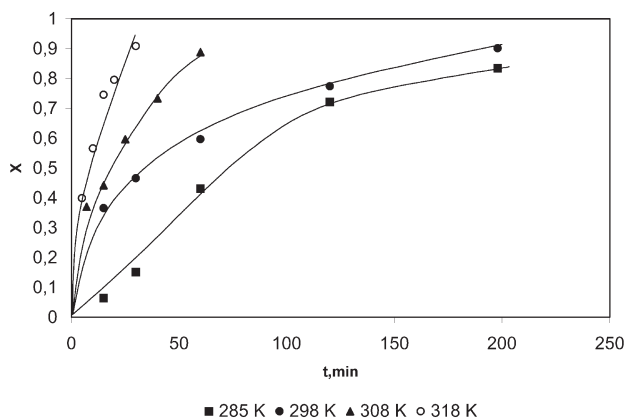


Fig. 2 – Effect of reaction temperature on the dissolution of ZnS concentrate

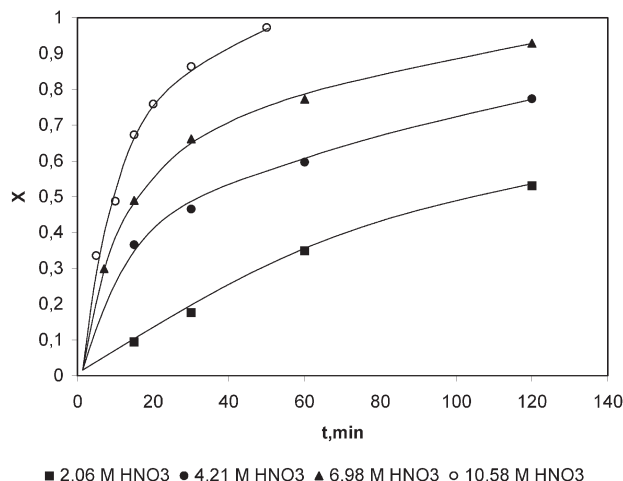


Fig. 3 – Effect of acid concentration on the dissolution of ZnS concentrate

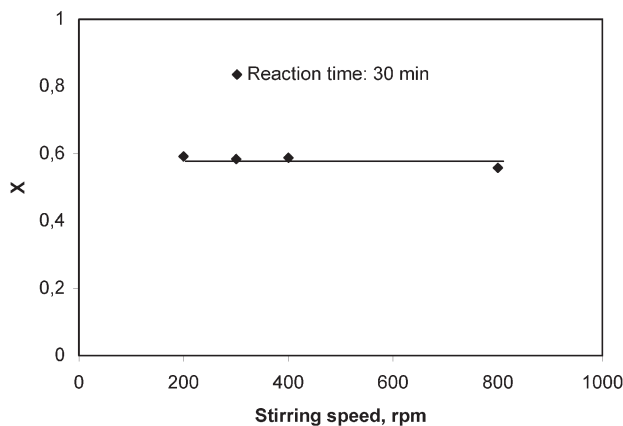


Fig. 4 – Effect of stirring speed on the dissolution of ZnS concentrate

ponential dependence of the rate constant in the Arrhenius equation. The effect of nitric acid concentration shown in Figure 3 showed that the dissolution rate increased with increasing acid concentration. The effect of stirring speed on the dissolution process is shown in Figure 4. It is evident that the dissolution rate is practically independent of the stirring speed.

**Kinetics analysis**

The dissolution kinetics were investigated using heterogeneous fluid-solid reaction models and pseudo-homogeneous reaction models<sup>23,24</sup>. It was determined that the dissolution rate fitted to a semi-empirical model in the following form

$$-\ln(1 - X) = k \cdot t^m \quad (11)$$

To show the effect of the parameters in the kinetic model, the following empirical model was developed by multiple regression.

$$-\ln(1 - x) = k_0 \cdot [(c)^a \cdot \exp(-E/RT)] \cdot t^m \quad (12)$$

where  $k_0 = 4412.71$ ;  $a = 1.25$ ;  $m = 0.74$  and  $E = 48.15 \text{ kJ} \cdot \text{mol}^{-1}$

Thus Equation 12 can be written as follows:

$$-\ln(1 - X) = 4412.71 [(c)^{1.25} \cdot \exp(-48150/T)] \cdot t^{0.74} \quad (13)$$

To verify the agreement between the experimental conversion values and the calculated values from the empirical equation, a plot of  $X_{\text{Exp.}}$  versus  $X_{\text{Prd.}}$  is given in Figure 5. The experimental and calculated values were found to compare very well.

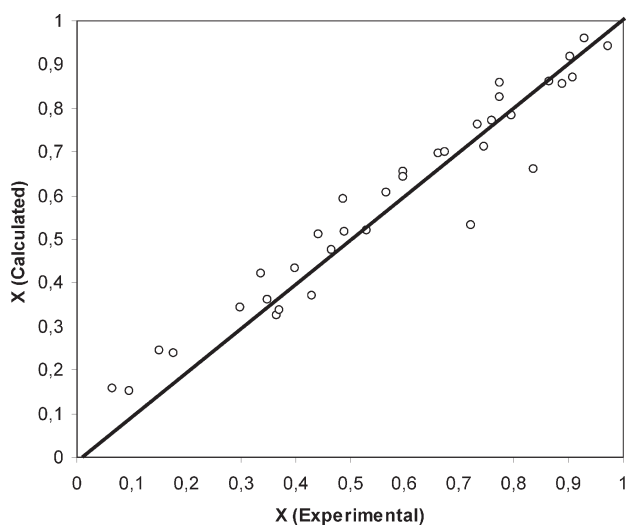


Fig. 5 – The agreement between experimental values and calculated values from semi-empiric expression

## Conclusions

The dissolution of zinc sulphide concentrate in nitric acid solutions was investigated in a batch reactor. It was observed that the dissolution rate increased by increasing temperature and acid concentration, but it was not affected by stirring speed. The activation energy of the process was calculated to be  $48.15 \text{ kJ} \cdot \text{mol}^{-1}$ . A semi empirical mathematical model, which expresses the process very well, was developed. The empirical model is applicable for the experimental condition ranges and the reactor geometry of the present study.

It is believed that these experimental results can be beneficial to produce metallic Cu and Zn from ZnS concentrate containing  $\text{CuFeS}_2$  and  $\text{FeS}_2$

## Nomenclature

$X$  – Fractional conversion  
 $x$  – Dissolution amount fraction,  $n_{d,Zn}/n_{t,Zn}$   
 $t$  – Reaction time, min

$k_0$  – A constant in Eq. (12)  
 $a$  – A constant in Eq. (12)  
 $m$  – A constant in Eq. (12)  
 $E$  – Molar activation energy,  $\text{kJ} \cdot \text{mol}^{-1}$   
 $T$  – Temperature, K

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