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Dissolution kinetics of sphalerite in acidic ferric chloride leaching

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Abstract

This paper presents a study for leaching kinetics of sphalerite concentrate in $FeCl_3$–HCl solution. The shrinking core model was applied to the results of experiments investigating the effects of stirrer speed of 200–600 rpm, ferric ion concentration in range of 0–1 M, solid/liquid ratio in range of 1/100–1/5, leaching temperature range of 40–80 °C and particle size on zinc dissolution rate. The activation energy for the leaching process was found to be 45.30 kJ/mol and the Arrhenius constant was calculated to be 5.454 s^{-1}. The order of reaction for ferric ion concentration, solid/liquid ratio and particle size were also obtained. The rate of the reaction based on reaction-controlled process can be expressed as,

$$[1-(1-\alpha)^{1/3}] = k_0(\mathrm{Fe}^{3+})^{0.36}(\rho_{\mathrm{S/L}})^{-0.33}r_0^{-0.97}\exp^{(-45300/RT)}t.$$

The dissolution of sphalerite with acidic ferric chloride solution was found to be controlled by reaction-controlled process.

Keywords: Sphalerite; Ferric chloride; Leaching; Kinetic model; Reaction-controlled process

1. Introduction

Sphalerite (ZnS), which associates mainly with other metal sulphide minerals, such as chalcopyrite ($CuFeS_2$), galena (PbS) and pyrite (FeS_2) in the nature, is the principal source from which zinc is produced commercially. In mineral processing engineering, they are collected in separate concentrates through selective conventional froth flotation applied to separate each other. Sphalerite concentrates usually contain more than 50% Zn.

Conventional zinc recovery process from sphalerite concentrates involves roasting the concentrate to zinc oxide or sulphate, leaching the resultant calcine with dilute sulphuric acid and electrodepositing of zinc from purified leach solution (roasting–leaching–electrowinning, RLE) [1]. The need to utilize small and complex deposits and the environmental restrictions imposed on sulphide smelters stimulated the development of alternative methods, especially hydrometallurgical routes that avoid the production of SO_2 as a pollutant.

The elimination of roasting step is an important advantage and high zinc extraction increases the importance of hydrometallurgical treatment processes. For this purpose, various leaching studies have been performed by many researchers in basic medium using ammonia solution [2–7] or in acidic medium using nitric acid [8], hydrochloric acid [9–11], sulphuric acid [12,13] and also oxidating agents, such as ferric ions [14–20].

Ferric ion, which is one of the most important oxidative agents in leaching process, is mostly used from the source of ferric chloride ($FeCl_3$) and ferric sulphate ($Fe_2(SO_4)_3$). Ferric chloride is well recognized as a leaching agent and it was reported that ferric chloride has more advantage than ferric sulphate [14,15]. Many investigations indicate that sphalerite can be dissolved readily under certain conditions. Nevertheless, few kinetic studies for the sphalerite dissolution have been reported.

Sphalerite leaching with acidic ferric chloride solutions products, including zinc chloride and other zinc chloride complexes, elemental sulphur, ferrous chloride, Fe^{2+} and Fe^{3+} complexes and sulphides (H_2S, HS^-, S^{2-}), mainly depending on the solution pH. The dissolution reaction of sphalerite in acidic ferric chloride solutions, which was a simple oxidation–reduction reaction, was expressed as follows [21]:

$$\mathrm{ZnS} + 2\mathrm{Fe}^{3+} \rightarrow \mathrm{Zn}^{2+} + 2\mathrm{Fe}^{2+} + \mathrm{S}^0 \qquad (1)$$

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Sphalerite reactivity depends on its iron content, i.e., the more iron in the solution, the easier the sphalerite lattice can be opened [22,23].

It has been known that dissolution rate during the leaching decreases with time and it is directly dependent on the activation energy. Habashi [24] stated that if the rate of reaction in the bulk of the solution was fast, the process would be governed by the rate of diffusion of the ions from the surface of the solid through the boundary layer. On the other hand, if the rate of reaction is slow, it will control the overall process and the process will be chemically controlled, thus, diffusion through the boundary layer will not play any critical role.

Wadsworth [25] stated that leaching reactions are heterogeneous processes. Therefore, most of the models used to describe these processes are similar to those used for non-catalytic heterogeneous processes, such as the shrinking core model. It has been stated that a diffusion-controlled heterogeneous process was characterised by being slightly dependent on temperature, while the chemically controlled process was strongly dependent on temperature [26]. The reason for this phenomenon can be attributed to linear dependency of diffusion coefficients and exponential dependency of chemical velocity constants on temperature. Thus, the activation energy of the diffusion-controlled process is characterised as being 4–12 kJ/mol, while it is usually >40 kJ/mol for a chemically controlled process.

Hence, the objectives of this study were to investigate the main factors involved in the leaching of sphalerite by acidic ferric chloride solution, such as ferric ion concentration, solid/liquid ratio, particle size, temperature and stirring speed, and also to determine what process controls the rate of the dissolution of sphalerite or what kinetic model can be applied.

2. Material and methods

2.1. Material

In this study, samples of the sphalerite concentrate were taken from Menka Flotation Plant (Sivas, Turkey) where $CuFeS_2$–PbS–ZnS complex ore is enriched. The concentrate used in the test was wet sieved to obtain 212 × 106, 106 × 75, 75 × 45, 45 × 38 and −38 μm particle size fractions. Chemical analysis of each size fraction is listed in Table 1.

2.2. Experimental procedure

A pyrex beaker of 1 L was used as a leaching reactor and put in temperature-controlled water bath. It was closed by a rubber cover. The temperature of 20–80 °C of the leach solution in the reactor was provided by a thermostatically controlled water bath with ±0.2 °C sensitivity. Stirring process was carried out by Heidolph mark RZR 2021 model mechanic stirrer equipped with propeller. During the set-up of the experiments, solid content of the solution, particle size and HCl concentration were held constant at 2.0% (w/v), 75 × 45 μm and 0.1 M, respectively. Stirring speed was changed in the range of 200–600 rpm; temperature was varied in the range of 40–80 °C; Fe^{3+} concentration was in the range of 0–1.0 M; particle size was ranged as 212 × 106, 106 × 75, 75 × 45, 45 × 38 and −38 μm. Liquid volume was kept constant and the amount of solid was changed to obtain the desired ratio during the experiments carried out at various solid/liquid ratios. Zn in leaching solution was determined by Vista AX CCD model ICP-AES. Distilled water and reagent-grade chemicals were used to make up all required solutions.

Table 1
Chemical analysis of zinc concentrate (wt%)

Particle size (μm)	Zn (%)	Fe (%)	S (%)	Acid insolubles (%)
−212 + 106	57.87	0.98	29.32	10.83
−106 + 75	59.97	0.16	30.15	8.86
−75 + 45	61.73	0.09	30.93	6.12
−45 + 38	57.70	0.81	29.23	1.06
−38	39.53	2.36	22.35	7.35

3. Results and discussion

3.1. Effect of stirrer speed

Fig. 1 shows the effect of stirring speed applied in the range of 200–600 rpm on the dissolution of sphalerite. As seen from Fig. 1, the dissolution of Zn was not changed when 200–400 rpm stirring speed was applied, while this reached to 17.24% at the end of 4 h leaching time with increasing stirring speed up to 600 rpm. Therefore, 600 rpm was selected as a stirring speed for investigation of the effect of other parameters.

3.2. Effect of Fe^{3+} concentration

The study for the effect of ferric ion concentration on sphalerite dissolution is given in Fig. 2. As shown from Fig. 2, the sphalerite dissolution increases gradually with leaching time and with increasing ferric ion concentration. At the end of 4 h

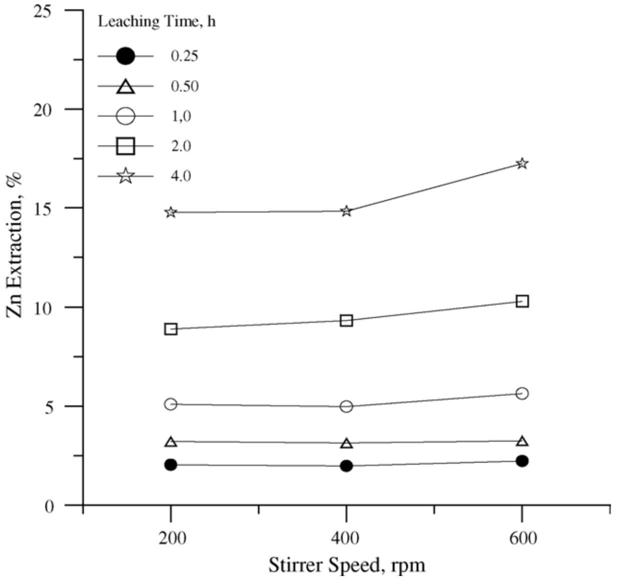

Fig. 1. Effect of stirring speed on the recovery of zinc from the sphalerite ([Fe^{3+}]: 0.25 M; temperature: 50 °C; solid/liquid ratio: 20 g/L; particle size: 75 × 45 μm).

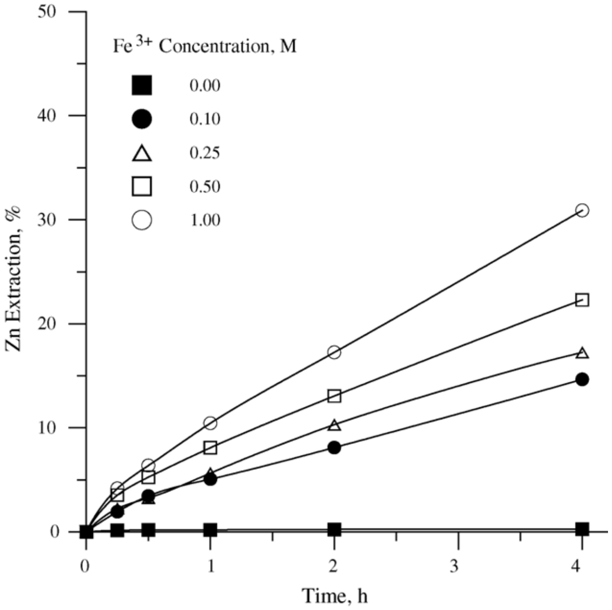

Fig. 2. Effect of leaching time on the recovery of zinc from the sphalerite for various ferric ion concentrations (temperature: 50 °C; solid/liquid ratio: 20 g/L; stirrer speed: 600 rpm; particle size: 75 × 45 μm).

leaching, 0.26 and 14.66% zinc extraction were achieved with 0 M $FeCl_3$ and 0.1 M Fe^{3+}, respectively. These results show that ferric ions are the only oxidation agent that has direct effects on sphalerite dissolution.

3.3. *Effect of temperature*

The effect of temperature on the sphalerite dissolution is shown in Fig. 3. As seen in Fig. 3, zinc recovery increases with leaching time and with increasing temperature in the range of 40–80 °C. While the zinc recovery after 15 min was 2.05 and 13.17%, the recovery after 4 h reached to 14.20 and 82.01% for 40 and 80 °C, respectively.

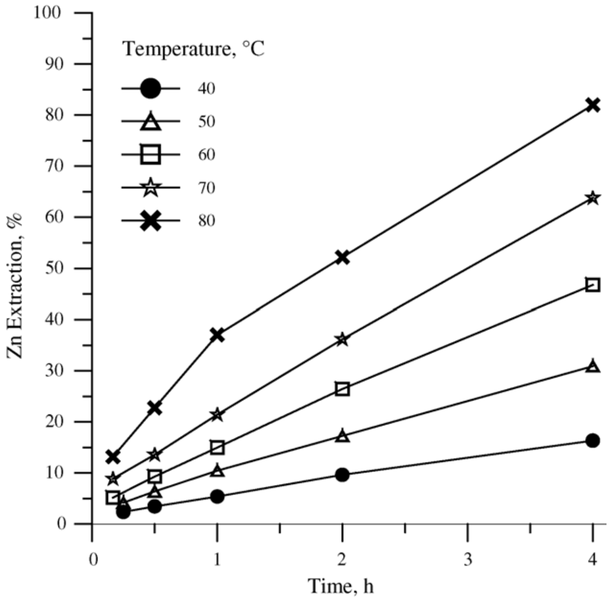

Fig. 3. Effect of leaching time on the recovery of zinc from the sphalerite for various temperatures ([Fe^{3+}]: 1.0 M; solid/liquid ratio: 20 g/L; stirrer speed: 600 rpm; particle size: 75 × 45 μm).

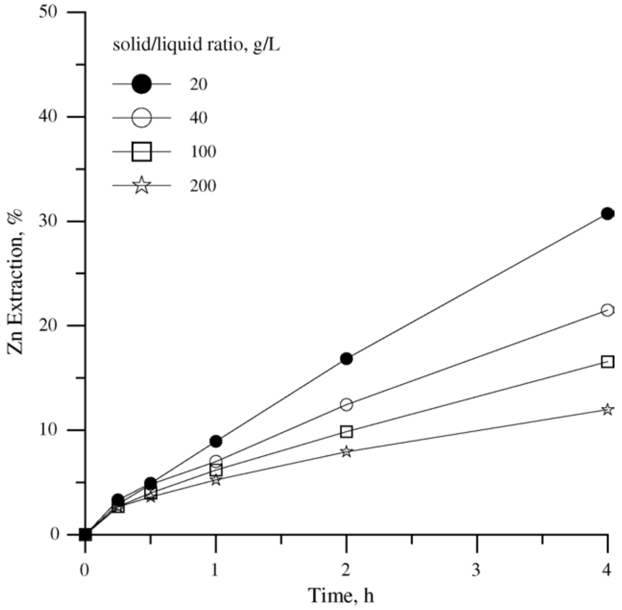

Fig. 4. Effect of leaching time on the recovery of zinc from the sphalerite for various solid/liquid ratios ([Fe^{3+}]: 1.0 M; temperature: 50 °C; stirrer speed: 600 rpm; particle size: 75 × 45 μm).

3.4. *Effect of solid/liquid ratio*

The effect of solid/liquid ratio on the dissolution of sphalerite was investigated in the range of 1/5–1/50. The results are presented in Fig. 4. The zinc recovery increased with decrease in the amount of solid. While the zinc recovery after 4 h leaching reached to 11.96 and 30.91% at ratios 100/500 (1/5) and 10/500 (1/50), respectively.

3.5. *Effect of particle size*

Leaching was also investigated by various particle size of sphalerite concentrate. Fig. 5 shows that the zinc dissolution increases with leaching time and with decreasing particle size. The zinc recovery reached 40.94 and 96.14% after 4 h leaching for −212 + 106 and −38 μm particles size, respectively.

3.6. *Kinetic analysis*

The shrinking core model considers that the leaching process is controlled either by the diffusion of reactant through the solution boundary layer, or through a solid product layer, or by rate of the surface chemical reaction. The simplified equations of the shrinking core model when either diffusion or the surface chemical reactions are the slowest step can be expressed as follows, respectively [27]:

$$\left[1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}\right]=\frac{2M_{\mathrm{B}}DC_{\mathrm{A}}}{\rho_{\mathrm{B}}ar_0^2}t=k_{\mathrm{d}}t \qquad (2)$$

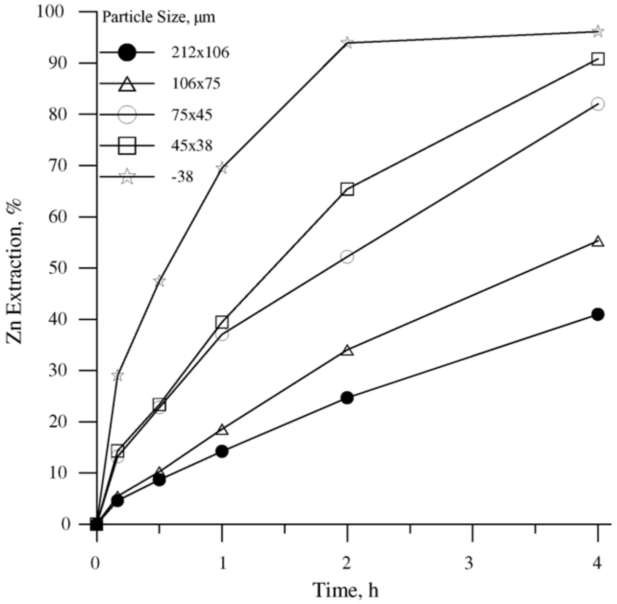

Fig. 5. Effect of leaching time on the zinc recovery from the sphalerite for various particle sizes ([Fe^{3+}]: 1.0 M; temperature: 80 °C; solid/liquid ratio: 20 g/L; stirrer speed: 600 rpm).

$$[1-(1-\alpha)^{1/3}]=\frac{k_cM_BC_A}{\rho_Bar_0}t=k_rt \tag{3}$$

where α is the fraction reacted, k_c the kinetic constant, M_B the molecular weight of the solid, C_A the concentration of the dissolved lixiviant A in the bulk of the solution, a the stoichiometric coefficient of the reagent in the leaching reaction, r_0 the initial radius of the solid particle, t the reaction time, D the diffusion coefficient in the porous product layer and k_d and k_r are the rate constants, respectively, which are calculated from Eqs. (2) and (3), respectively.

Eq. (2) reveals that if the diffusion through the product layer controls the leaching rate, there must be a linear relation between the left side of equation and time. The slope of the line is the rate constant k_d, it must be directly proportional to $1/r_0^2$. If the surface reaction controls the rate, the relation between the left side of Eq. (3) and time must be linear. The slope of this line is called the apparent rate constant k_r and must be directly proportional to $1/r_0$.

The rate constants values, k_d and k_r calculated from Eqs. (2) and (3), respectively, and their correlation coefficients for each temperature are given in Table 2. These results indicate that the dissolution rate of sphalerite is controlled by surface chemical reactions and not by the diffusion of the ferric ion. The apparent rate constants for zinc dissolution increased with increase in temperature up to 80 °C. The application of surface chemical reactions kinetic model is shown in Fig. 6. Arrhenius plot considering the apparent rate constants was obtained by applying Eq. (3) to leaching experimental data (Fig. 7). The calculated activation energy was 45.30 kJ/mol that clearly suggests chemical reaction control for the process [26]. Various investigators reported this activation energy value as 58 kJ/mol [28,29], 46.9 kJ/mol [16], 41.8 kJ/mol [15], 46.0 kJ/mol [30] and 40.30 kJ/mol [31].

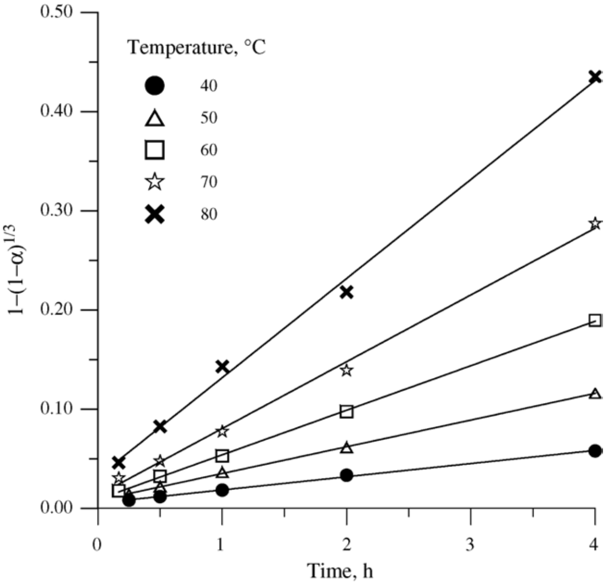

Fig. 6. Plot of $1-(1-\alpha)^{1/3}$ vs. t for different temperatures ([Fe^{3+}]: 1.0 M; solid/liquid ratio: 20 g/L; stirrer speed: 600 rpm; particle size: 75 × 45 µm).

The results on the effect of ferric ion concentration were applied to this kinetic model and k_r values and correlation coefficients for each Fe^{3+} concentration are given in Table 3. From the k_r and ferric ion concentration values, plot of $\ln k_r$ versus $\ln C_{[Fe^{3+}]}$ was obtained (Fig. 8). As seen in Fig. 8, the order of reaction with respect to ferric ion was proportional to 0.36 power of ferric ion concentration ($[Fe^{3+}]^{0.36}$) with a correlation coefficient of 0.954.

From the effects of solid/liquid ratios and particle sizes on zinc dissolution given in Figs. 4 and 5, the apparent rate constants can be determined. The orders of reaction with respect to solid/liquid ratio and initial particle size (r_0) were determined

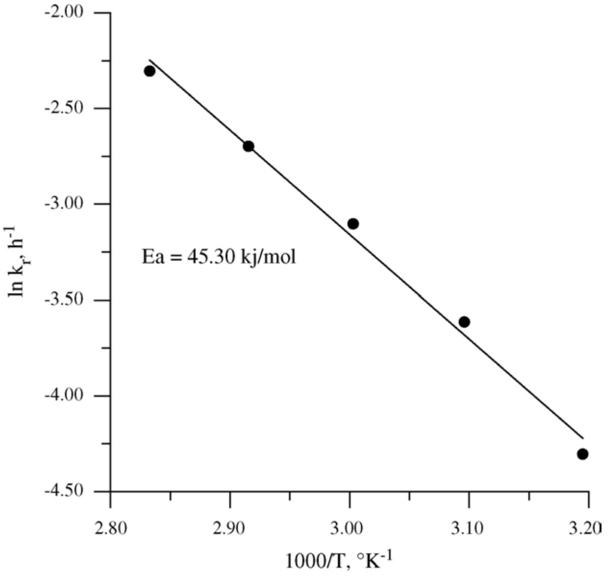

Fig. 7. Arrhenius plot of reaction rate against reciprocal temperature ([Fe^{3+}]: 1.0 M; solid/liquid ratio: 20 g/L; stirrer speed: 600 rpm; particle size: 75 × 45 µm).

Table 2
The k_r, k_d and correlation coefficients values for different temperatures

Temperature (°C)	Apparent rate constants (10^{-3} h^{-1})		Correlation coefficient (R^2)	
	k_r	k_d	k_r	k_d
40	13.506	0.6370	0.998	0.976
50	26.946	3.329	0.999	0.963
60	44.913	8.256	0.999	0.955
70	67.364	17.453	0.998	0.946
80	99.910	34.816	0.996	0.963

[Fe^{3+}], 1.0 M; solid/liquid ratio, 20 g/L; stirrer speed, 600 rpm; particle size, 75 × 45 μm.

Table 3
The k_r values and correlation coefficients for each Fe^{3+} concentration

Fe^{3+} concentration (M)	Correlation coefficient (R^2)	Apparent rate constant, k_r (10^{-3} h^{-1})
0.10	0.998	11.669
0.25	0.996	14.408
0.50	0.999	18.137
1.00	0.999	26.942

Temperature, 50 °C; solid/liquid ratio, 20 g/L; stirrer speed, 600 rpm; particle size, 75 × 45 μm.

to be inversely proportional to 0.33 power ($[\mathrm{S/L}]^{-0.33}$) and 0.97 power ($r_0^{-0.97}$), respectively.

Furthermore, activation energy and the order of reaction values with respect to ferric ion, solid/liquid ratio and particle size also confirm to the shrinking core model for a reaction-controlled process. So, the leaching of sphalerite can be clearly controlled by surface chemical reactions as described by Eq. (4).

$$[1-(1-\alpha)^{1/3}] = k_0(\mathrm{Fe}^{3+})^{0.36}(\rho_{\mathrm{S/L}})^{-0.33} r_0^{-0.97} \times \exp^{(-45300/RT)}\, t \tag{4}$$

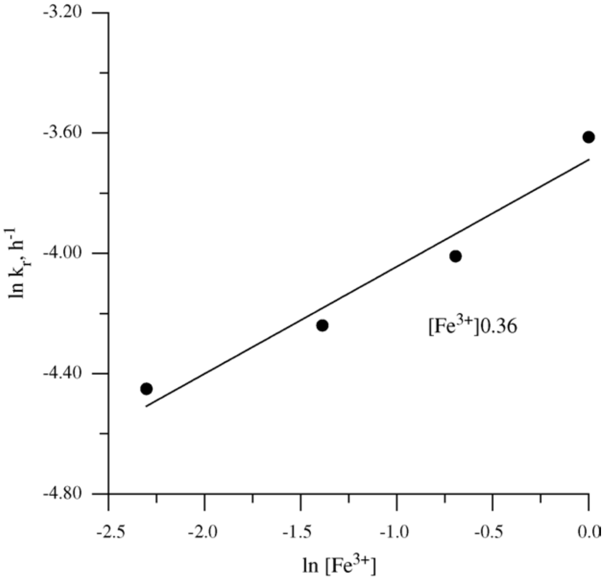

Fig. 8. Plot of $\ln k_r$ vs. $\ln C_{[\mathrm{Fe}^{3+}]}$ (temperature: 50 °C; solid/liquid ratio: 20 g/L; stirrer speed: 600 rpm; particle size: 75 × 45 μm).

where k_0 is a reaction constant, which can be determined from the function of the fraction reacted, α, from Eq. (4) and α found experimentally. This value is found $3.37 \pm 0.9 \times 10^6$.

4. Conclusions

In the present study, the dissolution kinetics of sphalerite in acidic ferric chloride solution was studied. It was found that the reaction rate increases with increase in ferric ion concentration, reaction temperature, stirring speed and with decrease in solid to liquid ratio and particle size.

A shrinking core model can be used to describe the dissolution kinetics of sphalerite concentrate in acidic ferric chloride solution. The dissolution of sphalerite with acidic ferric chloride solution was found to be controlled by the shrinking core model for reaction-controlled process. Dissolution rate can be expressed by Eq. (4), which is a semi-empirical mathematical model representing the process properly.

Acknowledgement

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Appendix A

A	stoichiometric coefficient of the reagent in leaching solution
C_A	concentration of the dissolved reagent A in the bulk of the liquid (mol L^{-3})
D	diffusion coefficient in the porous layer (L^2 t^{-1})
E_a	activation energy of the leaching reaction (M L^2 t^2)
k_c	kinetic constant (M L^{-1})
k_d	apparent rate constant defined in Eq. (2) (t^{-1})
k_r	apparent rate constant defined in Eq. (3) (t^{-1})
M_B	molecular weight of the solid (M mol^{-1})
r_0	initial radius of the solid particles
t	reaction time (h)
T	reaction temperature (K)
α	fraction extracted
ρ_B	density of the solid

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