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Dissolution kinetics of sphalerite with hydrogen peroxide in sulphuric acid medium

S. Aydogan [*]

Department of Mining Engineering, Selcuk University, Konya, Turkey

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Abstract

The kinetics of dissolution of sphalerite with hydrogen peroxide in sulphuric acid solution was investigated. The influence of stirring speed (0–600 rpm), dissolution temperature (10–60 °C), sulphuric acid concentration (0.5–6.0 M), hydrogen peroxide concentration (0.1–6 M), and particle size were studied. The dissolution kinetics was found to follow a shrinking-core model, with the surface chemical reaction as the rate-determining step. This finding is in concordance with the activation energy of 43 kJ/mol and a linear relationship between the rate constant and the reciprocal of particle size. Increasing concentrations of sulphuric acid and hydrogen peroxide have a positive effect on the dissolution of sphalerite, and orders of reaction of 0.35 and 0.48 were established with respect to sulphuric acid and hydrogen peroxide concentrations, respectively. Stirring speed had no effect on the rate of sphalerite dissolution.

Keywords: Sphalerite; Hydrogen peroxide; Dissolution; Kinetic model

1. Introduction

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

The conventional process of zinc recovery from sphalerite concentrates involves roasting the concentrate to zinc oxide or sulphate, leaching the resultant calcine with dilute sulphuric acid, and electrodepositing the zinc from the purified leach solution (roast-leach-electrowinning) [1]. The roasting step produces SO_2 gas, however, and the environmental restrictions imposed on sulphide smelters have stimulated the development of alternative methods, especially hydrometallurgical routes that avoid SO_2 production.

The elimination of the roasting step is an important advantage, and the high zinc extraction also turned the focus to 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 oxidating agents such as ferric ions [14–20].

Hydrogen peroxide is a good oxidizing agent, as depicted by the redox potential of 1.77 V in acid medium. In addition, hydrogen peroxide is an environmentally safe reagent. It is reported that with hydrogen peroxide, no reaction products apart from water are generated during oxidation of sulphide minerals [21]. The oxidation action of hydrogen peroxide in acidic medium is based on its reduction according to the equation [22]:

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O \qquad E_0 = 1.77\,V \tag{1}$$

However, hydrogen peroxide can also act as a reducing agent in accordance with the following equation:

$$H_2O_2 = O_2 + 2H^+ + 2e^- \tag{2}$$

This potential value (1.77 V) is adequate to oxidise almost all the metal sulphides. Hydrogen peroxide has been used as a

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[*] Tel.: +90 332 2232060; fax: +90 332 2410635.
E-mail address: saydogan@selcuk.edu.tr.

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Table 1
Chemical analysis of zinc concentrate (wt.%)

Particle size (μm)	Zn (%)	Fe (%)	S (%)	Acid insolubles (%)
−106 + 75	59.97	0.16	30.15	8.86
−75 + 53	61.65	0.11	30.93	6.10
−53 + 45	61.73	0.08	30.91	6.13
−45 + 38	57.70	0.81	29.23	1.06

leaching agent for various mineral raw materials, such as uranium ores [23,24], and its use has been studied with a zinc–lead bulk sulphide concentrate [25] and silver ore [26,27] and with a concentrate of pyrite [28–32] and sphalerite [33].

In the present study, the reaction kinetic of dissolution of sphalerite in sulphuric acid solution with hydrogen peroxide was determined. For this purpose, the effects of variables such as stirring speed, temperature, acid and hydrogen peroxide concentration, and particle size on the reaction rate were investigated.

2. Material and methods

2.1. Material

In this study, samples of the sphalerite concentrate were taken from the 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 −106 + 75, −75 + 53, −53 + 45, and −45 + 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 a temperature-controlled water bath, closed by a rubber cover. The 10–60 °C temperature of the leach solution in the reactor was provided by a thermostatically controlled water bath with ±0.2 °C sensitivity. Stirring was carried out by a Heidolph RZR 2021 model mechanic stirrer equipped with a propeller. During the experimental setup, the solid content of the solution and the particle size were held constant at 0.2% (1 g/500 mL w/v) and −45+38 μm, respectively. Stirring speed was changed in the range of 0 (no stirrer) to 600 rpm; temperature was varied in the range of 10–60 °C; sulphuric acid and hydrogen peroxide concentrations were in the range of 0.5–6.0 and 0.1–6 M, respectively; particle size range was −106 + 75, −75 + 53, −53 + 45, and −45 + 38 μm. Zn in leaching solution was determined using a Unicam 929 model AAS. Distilled water and reagent grade chemicals were used to make up all required solutions.

Each experiment was repeated at least three times and the arithmetic average of the results is used in the discussion of experimental results. One millilitre of solution was withdrawn from the reactor at various time intervals and diluted with distilled water to 100 mL in a volumetric flask. For calculation of the fraction of zinc leached, an equation developed by Papangelakis and Demopolous [34] was used which includes correction factors to account for volume losses during sampling.

3. Results and discussion

3.1. Effect of stirring speed

The effect of stirring speed on the dissolution of sphalerite was investigated at various stirring speeds (0 (no stirring), 100, 300, and 600 min^{-1}) at 40 °C in solutions containing 1.0 M hydrogen peroxide and 2.0 M sulphuric acid. The duration of each experiment was 150 min. Results are given in Fig. 1, which shows that the rate of sphalerite oxidation is independent of the stirring speed.

Antonijević et al. [21] found similar results for chalcopyrite oxidation by hydrogen peroxide in sulphuric acid, and they reported that this situation clearly demonstrated that the reaction is not controlled by film diffusion. However, Adebayo et al. [35] reported that the chalcopyrite oxidation decreased with increased stirrer speed because the decomposition of hydrogen peroxide takes place faster, accompanied by evolution of molecular oxygen that adsorbs onto the particle surface, thus hindering particle/peroxide contact. Similar results were obtained for pyrite oxidation by hydrogen peroxide in sulphuric acid [31]; stirring had a negative influence on the oxidation of pyrite, and the authors concluded that this influence was not caused by peroxide decomposition at higher stirring speeds but probably by better contact between pyrite particles and peroxide in the absence of stirring.

In the current study, during the sphalerite oxidation by hydrogen peroxide, the generation of bubbles by the reaction

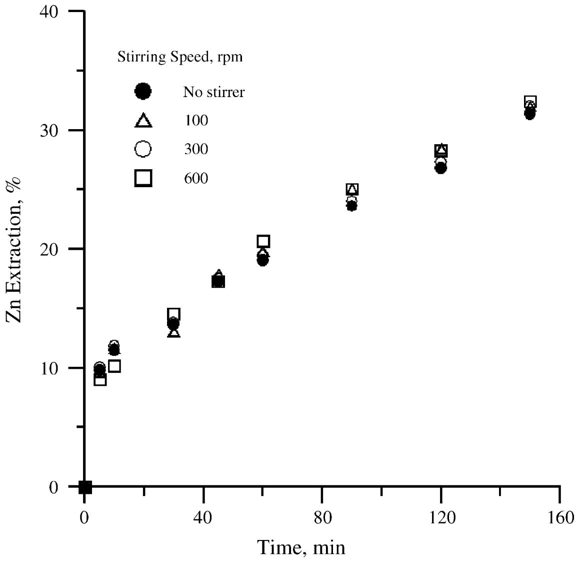

Fig. 1. Effect of stirring speed on the sphalerite dissolution.

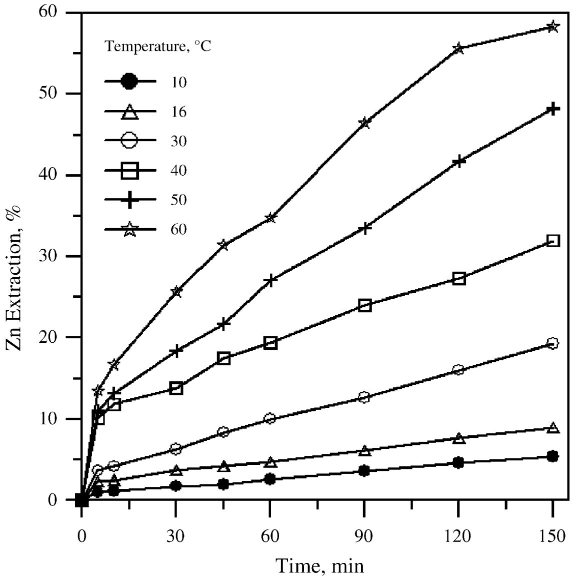

Fig. 2. Effect of temperature on the sphalerite dissolution.

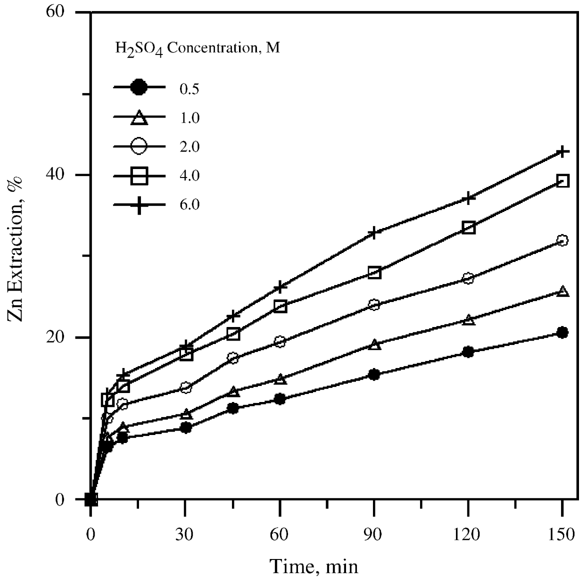

Fig. 3. Effect of sulphuric acid concentration on the sphalerite dissolution.

was visible to the naked eye; this process mixed the sphalerite particles through "self mixing" a phenomenon caused by bubbles rapidly moving upwards. For this reason, all subsequent experiments were carried out without stirring, which was used only to homogenize the solution prior to sampling.

3.2. *Effect of temperature*

The effect of temperature on the zinc extraction of sphalerite was carried out in the 10–60 °C temperature range in solution containing 2.0 M sulphuric acid and 1.0 M hydrogen peroxide. The results are given in Fig. 2, which shows that zinc extraction increases with increasing temperature. While the zinc extraction after 10 min was 1.09% and 15.16% at 10 and 60 °C, respectively, the extraction after 150 min reached 5.39% and 58.31%, respectively, at those temperatures.

3.3. *Effect of H_2SO_4 concentration*

The effect of sulphuric acid concentration on sphalerite extraction was carried out by varying concentrations in the 0.5–6.0 M sulphuric acid range at 40 °C in solution containing 1.0 M hydrogen peroxide. The results are given in Fig. 3, which shows that the zinc extraction of sphalerite increased with increasing sulphuric acid concentration. The zinc extractions after 150 min leaching at 0.5 and 6.0 M sulphuric acid were found to be 20.56% and 42.95%, respectively. This result suggests that sulphuric acid significantly affects sulphide concentration in order to release the zinc ion. The effect of the acid was the result of the increase in the redox potential of the oxidant [31]; the hydrogen ion concentration increases the redox potential of hydrogen peroxide, which consequently increases the rate of the reaction.

3.4. *Effect of H_2O_2 concentration*

The experiments were carried out by varying the initial hydrogen peroxide concentration in the 0.1–6.0 M range at 40 °C in solutions containing 0.5 M sulphuric acid. The obtained results are given in Fig. 4, which shows that increasing the hydrogen peroxide concentration considerably accelerated sphalerite oxidation. The zinc extractions after 150 min leaching for 0.1 and 6.0 M hydrogen peroxide were found to be 7.45% and 56.35%, respectively.

3.5. *Effect of particle size*

The effect of particle size was studied in the range of −106 + 75 to −45 + 38 μm at 40 °C in solution containing 0.5 M

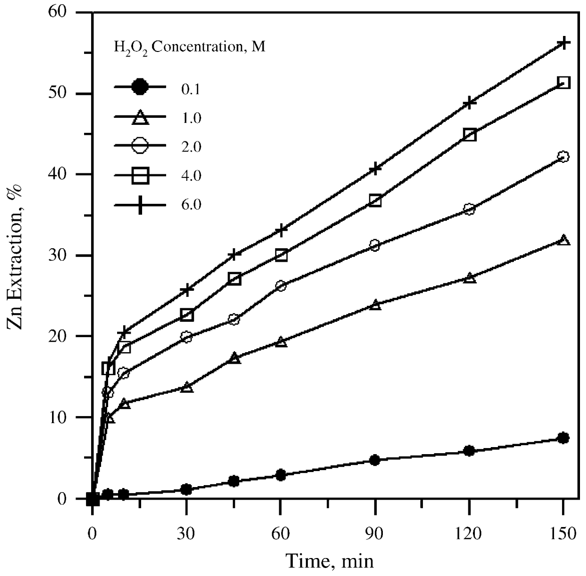

Fig. 4. Effect of hydrogen peroxide concentration on the sphalerite dissolution.

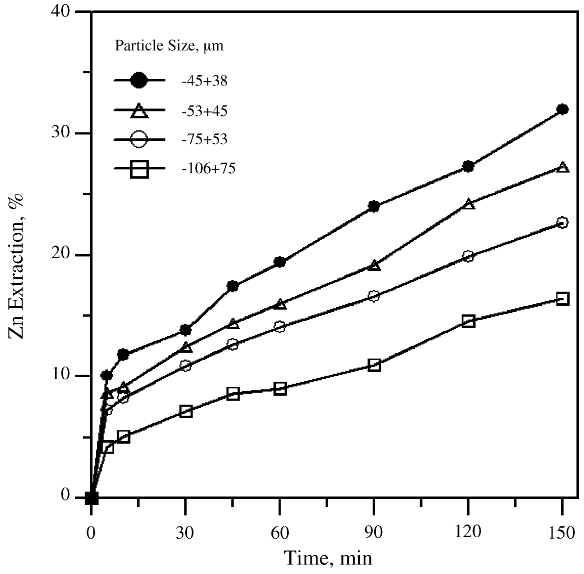

Fig. 5. Effect of particle size on the sphalerite dissolution.

sulphuric acid and 1.0 M hydrogen peroxide. Results are given in Fig. 5, which shows that zinc extraction increases with decreasing particle size. In other words, smaller particles have a faster rate of dissolution than larger particles. The zinc extraction reached 16.44% and 31.97% after 150 min leaching for −106 + 75 and −45 + 38 μm particle sizes, respectively.

3.6. Kinetic analysis

The dissolution of sphalerite depending on proceeding reaction can be explained by the shrinking core model [36]. The dissolution reaction can be expressed as follows:

$$\mathrm{aA_{fluid}} + \mathrm{bB_{particle}} \rightarrow \text{ product} \tag{3}$$

If the reaction rate is controlled by diffusion through the product layer, it will be an integrated rate equation, as follows [37]:

$$1-\frac{2}{3}X-(1-X)^{2/3}=\frac{2M_{\mathrm{B}}DC_{\mathrm{A}}}{\rho_{\mathrm{B}}ar_0^2}t=k_dt \tag{4}$$

If the reaction is controlled by the surface reaction, Eq. (4) transforms to following equation [38]:

$$1-(1-X)^{1/3}=\frac{k_cM_{\mathrm{B}}C_{\mathrm{A}}}{\rho_{\mathrm{B}}ar_0}t=k_rt \tag{5}$$

In Eq. (5), X is the fraction reacted, k_c the kinetic constant, M_{B} the molecular weight of the solid; C_{A} the concentration of the dissolved gas 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 is the reaction time, D the diffusion coefficient in the porous product layer, ρ_{B} is the density of the solid and k_d and k_r are the rate constants which are calculated from Eqs. (4) and (5), respectively.

Eq. (4) reveals that if diffusion through the product layer controls the leaching rate, there must be a linear relation between the left side of the equation and time. The slope of the line is the rate constant k_d, and 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. (5) and time must be linear. The slope of this line is called the apparent rate constant k_r and must be directly proportional to $1/r_0$.

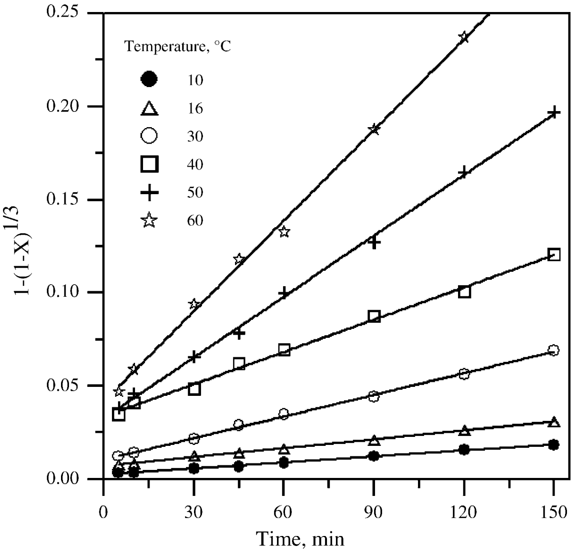

Fig. 6. The variation in $1-(1-X)^{1/3}$ with time at various temperatures.

Eqs. (4) and (5) were applied for results obtained from each temperature value. The plot of Eq. (5) gave a straight line (Fig. 6). The apparent rate constants (k_r) were calculated as slopes of the straight lines. Using the apparent rate constants obtained by application of Eq. (5), the Arrhenius plot was obtained (Fig. 7). The activation energy was calculated as 43 kJ/mol. This value clearly confirms that this process was controlled by a chemical reaction at the sphalerite surface and that this reaction was the rate-determining step in the dissolution of sphalerite by hydrogen peroxide in sulphuric acid [39]. A similar value of activation energy was found for the sphalerite oxidation by ferric ions [20]. On the other hand, Antonijević et al. [21] and Adebayo et al. [35] identified the activation energy for chalcopyrite dissolu-

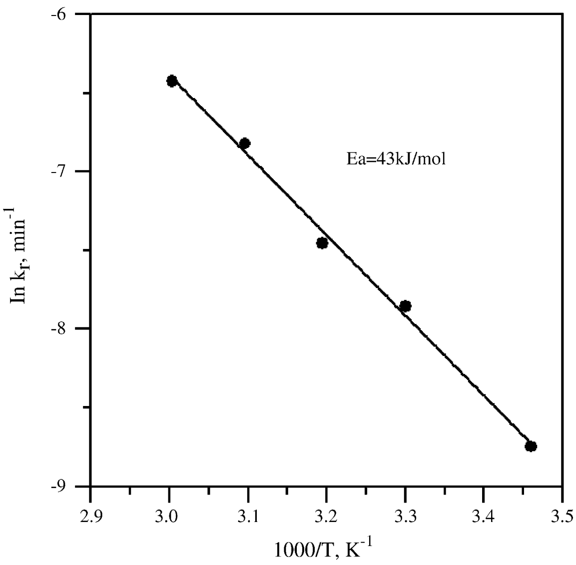

Fig. 7. Arrhenius plot of reaction rate against reciprocal temperature.

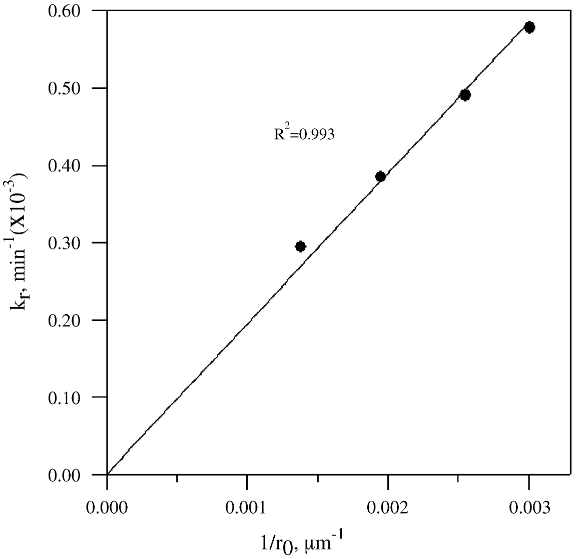

Fig. 8. Plot of k_r vs. $1/r_0$.

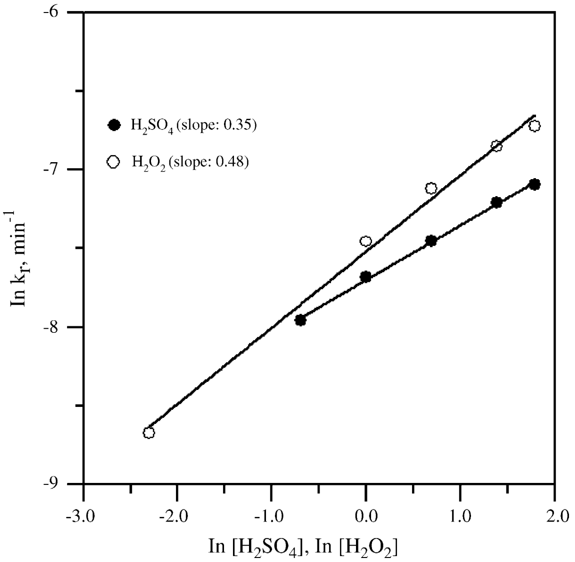

Fig. 9. Determination of reaction order with respect to ln[H_2SO_4], ln[H_2O_2].

tion in hydrogen peroxide and sulphuric acid solution to be 60 and 39 kJ/mol, respectively. In addition, the kinetic curves for particle size results were linearised by means of Eq. (5), and the apparent rate constant (k_r) was drawn as a function of the inverse of the particle radius (Fig. 8). A linear relationship between k_r versus $1/r_0$ confirms the chemical reaction on the sphalerite surface as the rate-controlling step.

We detected no solid products using XRD and microscope analyses of the solid residue after sphalerite oxidation at 40 °C temperature in a solution containing 0.5 M sulphuric acid and 1.0 M hydrogen peroxide during which a sphalerite conversion of 31.97% was attained. However, hydrogen sulphide was detected using the lead acetate method. This observation suggests that sulphate ion and hydrogen sulphide are the products of sulphide-sulphur oxidation.

This result implies that the dissolution reaction is as follows:

$$2ZnS + 4H_2O_2 + 2H^+ \rightarrow 2Zn^{2+} + {SO_4}^{2-} + H_2S + 4H_2O \qquad (6)$$

The results for the effect of sulphuric acid concentration were applied to this kinetic model, and k_r values for each sulphuric acid concentration were determined. From the k_r and sulphuric acid concentration values, a plot of $\ln k_r$ versus ln [H_2SO_4] was obtained (Fig. 9). As seen in Fig. 9, the order of reaction with respect to sulphuric acid was proportional to a 0.35 power ($[H_2SO_4]^{0.35}$) with a correlation coefficient of 0.998. Similarly, the results for the effect of hydrogen peroxide concentration was applied to this kinetic model, and k_r values and correlation coefficients for each hydrogen peroxide concentration was determined (Fig. 9). The orders of reaction with respect to hydrogen peroxide was proportional to 0.48 power of hydrogen peroxide concentration ($[H_2O_2]^{0.48}$) with a correlation coefficient of 0.994.

4. Conclusions

This study has focused on the kinetic model of sphalerite leaching in acidified hydrogen peroxide solution, assessing the effect of sulphuric acid and hydrogen peroxide concentration, reaction temperature, and particle size. It was determined that the leaching rate increased with increasing sulphuric acid and hydrogen peroxide concentrations and increasing temperature and decreased with particle size. The activation energy was calculated as 43 kJ/mol for studied sphalerite concentrate in the temperature range of 10–60 °C. The empirical orders of reaction with respect to sulphuric acid and hydrogen peroxide concentration are 0.38 and 0.48, respectively. The kinetic studies demonstrated the leaching of sphalerite by a shrinking core model and the leaching rate controlled by surface reaction under the studied conditions.

Acknowledgement

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Appendix A

A	stoichiometric coefficient of the reagent in leaching solution
C_A	concentration of the dissolved gas 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 (4) (T^{-1})
k_r	apparent rate constant defined in Eq. (5) (T^{-1})
M_B	molecular weight of the solid (M mol^{-1})
r_0	initial radius of the solid particles

t	reaction time (minute)
T	reaction temperature (K)
X	fraction extracted
a	stoichiometric coefficient of the reagent in the leaching reaction
ρ_B	density of the solid

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