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ZINC LEACHING FROM SMITHSONITE ORE IN LACTIC ACID SOLUTION: STUDIES ON PARAMETRIC OPTIMIZATION, KINETIC AND MECHANISM

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ABSTRACT. The solubility of low-grade zinc ores with a selective leaching environmentally friendly reagent has become a focus of great interest since zinc and its compounds have found wide application. For this purpose, lactic acid was used to investigate the selective leaching kinetics of smithsonite ore obtained from Kayseri region. The effects of particle size (137.5-725 µm), acid concentration (0.5-5 M), solid/liquid ratio (0.5/250-3/250 g mL^{-1}), stirring speed (500-800 rpm) and temperature (40-70 °C) parameters on the smithsonite dissolution rate were experimentally studied. The results obtained show that leaching of about 99.8% of zinc is achieved using 425 µm particle size at a reaction temperature of 70 °C for 45 min reaction time with 2 M lactic acid, the solid/liquid ratio of 1/250 g mL^{-1} and stirring speed of 600 rpm. The statistical analysis of the experimental data obtained from the parameters revealed that smithsonite dissolution was the surface reaction-controlled with an apparent activation energy of 53.62 kJ.moL^{-1}. The kinetic model describing the process was found as $1-(1-X)^{\frac{1}{3}} = 2.5\times10^{5}e^{\frac{-53.62}{RT}}t$.

KEY WORDS: Smithsonite, Dissolution kinetics, Lactic acid, Zinc lactate

INTRODUCTION

In the globalizing world, the consumption rate is increasing day by day. Meeting the increasing needs of limited resources is possible with the optimum utilization of the resources. Ores that fall into the limited resource category can be processed according to needs and become ready for use.

Various methods are used to separate the desired mineral from ores. The cost of the process is the most important factor in the selection of methods to apply. Ore leaching with an appropriate solvent is the most cost-effective one [1-3]. It is well known that inorganic acids are often used as the leaching reactant in most of the hydrometallurgical processes.

Dhawan *et al*. have investigated the dissolution kinetics of smithsonite ore in hydrochloric acid solution. The activation energy of the process was calculated to be 59.58 kJ mol^{-1}. The dissolution rate was found to be controlled by surface-chemical reaction. The rate of the reaction based on shrinking core model can be expressed by a semi-empirical equation as $1-(1-x)^{1/3}=k_o[HCl]^{0\cdot70}(S/L)^{-0\cdot76}r_0^{-0\cdot95}\exp(-59\cdot58/RT)t$ [4]. Ilyas *et al.* examined the dissolution kinetics of the pretreated waste printed circuit board by using aqueous nitric acid solutions. The determined activation energy of copper (Ea (Cu), 26.2 kJ mol^{-1}), nickel (Ea (Ni), 16.2 kJ mol^{-1}), and zinc (Ea(Zn), 19.7 kJ mol^{-1}) exhibited to follow the solid-liquid mass transfer shifts from the surface chemical reactions at low temperature to the diffusion-controlled at higher temperature [5].

However, the undesired impurities can be appreciably dissolved in these processes. On the other hand, organic acids have advantages such as low corrosion effect and selective dissolution, which have been widely preferred in recent years [6].

Hursit *et al.* studied the dissolution kinetics of smithsonite ore in aqueous gluconic acid solutions. They found that the dissolution kinetics follow a shrinking core model with the surface chemical reaction as the rate-controlling step. The activation energy of the process is determined to be 47.92 kJ mol^{-1} [6]. Wu *et al.* investigated the dissolution kinetics of smithsonite ore by using

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sulfamic acid from organic acids as the leaching reagent. The dissolution rate can be controlled by the shrinking core model for surface chemical reactions. The activation energy of the dissolution process was determined to be 42.86 kJ mol^{-1} [7]. Feng *et al.* proposed that the methane sulfonic acid as efficient leaching agent to extract zinc from smithsonite examined the dissolution kinetics of smithsonite ore. The apparent activation energy of this process was determined to be 32.66 kJ mol^{-1}. The dissolution kinetics was found to be controlled by both interfacial transfer and diffusion across the product layer [8].

Zinc ores are divided into two categories in nature as sulfide (sphalerite (ZnS) and marmatite ($Zn_xFe_{1-x}S$)) and oxide (smithsonite ($ZnCO_3$), hydrozinsite ($2ZnCO_3{\cdot}3Zn(OH)_2$), hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$), zincite (ZnO) and willemite (Zn_2SiO_4)) minerals [7]. Zinc minerals have large reserves especially in Australia (69 million metric tons), China (44 million metric tons) and Russia (22 million metric tons) [9]. Sphalerite (ZnS) is one of the most common sulfide ores in the world. However, the emission of sulfur during the processing limits the use of sulfurous zinc compounds. Therefore, new sources are being sought for the production of zinc and its compounds as an alternative to sulfide ores [10, 11]. One of these alternative sources is smithsonite ore and it has important reserves in China and Turkey [12].

Zinc, the third most used metal after non-ferrous metals, is widely used in many fields such as cosmetics, ceramics, food, pharmaceutical, photography to storage batteries, metallic coatings for corrosion protection [13, 14].

Lactic acid is a weak organic acid that can be produced by fermentation or chemical synthesis and is widely used in industrial and biotechnological applications worldwide. It is actively used in industry, agricultural activities, animal husbandry, drug production, the food industry and many areas related to human life [15, 16].

When smithsonite reacts with lactic acid, it forms zinc lactate, carbon dioxide and water. The obtained zinc lactate is mainly used in dental care products such as toothpaste and mouthwash due to its antimicrobial properties and its ability to reduce or prevent the formation of dental plaque and tartar. Aside from this, there are many industrial applications such as food, cosmetics, pharmacology, medical raw materials [17-19].

The aim of this study is to determine a kinetic model to account for smithsonite dissolution with lactic acid contributing to improving the production of zinc lactate. Therefore, the effects of parameters such as solid/liquid ratio, acid concentration, reaction time, temperature, mixing speed and particle size on smithsonite solubility with lactic acid have been investigated. Using the experimental data obtained, a kinetic model that represents the dissolution process was determined by non-linear regression analysis.

EXPERIMENTAL

Chemicals and reagents

In this study, smithsonite ore obtained from Kayseri region was used. First, the ore was crushed in a jaw crusher and ground in the ball mill and then sieved into fractions of 725, 425, 200 and 137.5 µm using ASTM standard sieves. Chemical composition (% (w/w)) of smithsonite ore obtained by standard volumetric and gravimetric analysis methods; ZnO: 59.1, Al_2O_3: 1.5, SiO_2: 1.8, CaO: 0.9, Fe_2O_3: 1.6, Loss on ignition: 33.9 and others: 1.2. Lactic acid was supplied by Sigma-Aldrich. Other chemicals used in the experiments were of analytical purity.

Experimental procedure

For each experiment, 250 mL of lactic acid solution (0.5-5 M) was poured into the glass reactor, and the stirring was started. The solution was heated to the desired temperature. The speed of the mechanical stirring was fixed. Then, the desired amounts of smithsonite (0.5/250-3/250 $g.mL^{-1}$) ore were added to the solution.

At different time intervals, 2 mL of sample were withdrawn from the reactor and immediately filtered. Thereafter, the content of Zn^{+2} in the filtrate was analyzed using the volumetric method [20].

RESULTS AND DISCUSSION

Dissolution reactions

The reactions occurring in the overall smithsonite dissolution process in the aqueous medium with lactic acid are.

$$2C_3H_6O_{3\,(aq)} + 2H_2O_{(l)} \leftrightarrow 2H_3O^+_{(aq)} + 2C_3H_5O_3{}^{-1}{}_{(aq)} \quad (1)$$

$$ZnCO_{3\,(s)} + 2H_3O^+_{(aq)} \leftrightarrow Zn^{+2}{}_{(aq)} + CO_{2(g)} + 3H_2O_{(l)} \quad (2)$$

$$ZnCO_{3(s)} + 2C_3H_6O_{3(l)} \rightarrow Zn^{+2}{}_{(aq)} + 2C_3H_5O_3{}^{-1}{}_{(aq)} + H_2O_{(l)} + CO_{2(g)} \quad (3)$$

XRD of the smithsonite ore sample

The X-ray diffraction pattern of the smithsonite ore (Figure 1) was obtained using a Bruker-AXS D8 ADVANCE model XRD instrument coupled with monochromatic CuKα radiation (λ = 0.1542 Å). Smithsonite is the only phase identified.

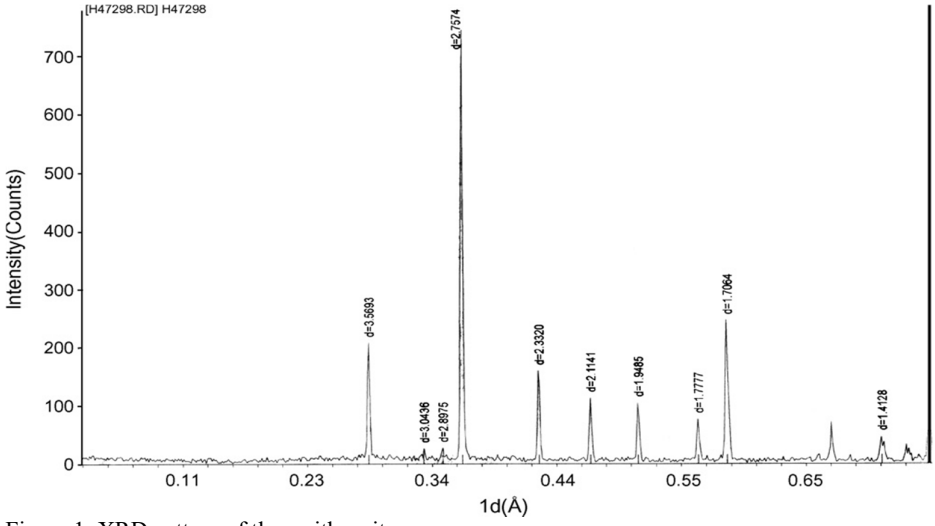

Figure 1. XRD pattern of the smithsonite ore.

The effects of parameters

The effects of particle size (μm, 137.5, 200, 425, 725), acid concentration (M, 0.5, 1, 2, 3, 4, 5), solid/liquid ratio ($g.mL^{-1}$, 0.5/250, 1/250, 2/250, 3/250), stirring speed (rpm, 500, 600, 700, 800), temperature (°C, 40, 50, 60, 70) and reaction time (min, 5, 10, 20, 30, 45, 60, 90, 120) on the dissolution rate of smithsonite were examined. Variation in fraction conversion (X %), calculated using Eq. (4), was plotted as a function of time (Figures 3–7).

$$X_{Zn} = \frac{\text{Zn amount in the solution (g)}}{\text{Zn amount in the original sample (g)}} \quad (4)$$

Effect of particle size

The effect of particle size on the dissolution rate of smithsonite ore with lactic acid was examined in experiments containing different particle sizes (725, 425, 200, 137.5 µm). The other parameters (reaction temperature 50 °C, acid concentration 2 M, solid/liquid ratio 1/250 g.mL^{-1} and stirring speed 600 rpm) were constant. Results are plotted in Figure 2, where the conversion rate increases with decreasing particle size. This result is due to an increase in surface area with decreasing particle size leading to an efficient diffusion of solvent-leaching reagent into the ore.

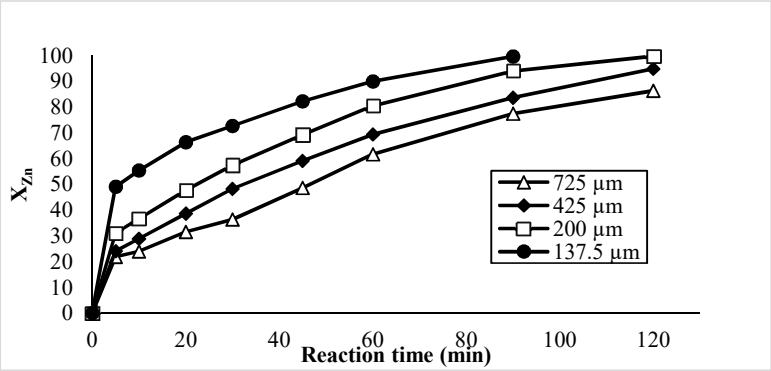

Figure 2. Variation in 137.5-725 µm as a function of time to study the effect of particle size on the leaching of smithsonite.

Effect of temperature

To study the effect of temperature on the smithsonite dissolution rate, the experimental temperature was 40 °C, 50 °C, 60 °C and 70 °C, keeping constant the grain size (200 µm), the lactic acid concentration (2 M), the solid/liquid ratio (1/250 g mL^{-1}) and the stirring speed (600 rpm) during the experiments. It is observed that the fraction conversion and its rate increase with temperature, yielding a 99.8% Zn conversion in 45 min at 70 °C (Figure 3). An increase in temperature enhances the collision speed per unit of time due to the increase in the kinetic energy of the particles, increasing the dissolution rate significantly. The high dissolution rate obtained by increasing temperature suggests that the dissolution process is surface reaction controlled.

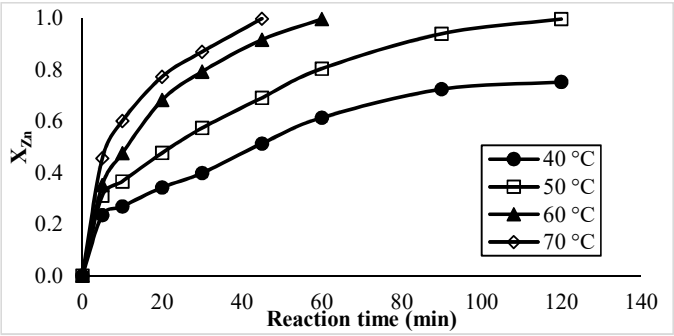

Figure 3. Variation in 40-70 °C as a function of time to study the effect of temperature on the smithsonite leaching.

Effect of stirring speed

To determine the effect of the stirring speed on the dissolution rate of smithsonite the stirring speed used was 500, 600, 700 and 800 rpm keeping the other parameters constant (fraction size = 200 µm, lactic acid concentration = 2 M, solid/liquid ratio = 1/250 g mL^{-1} and T = 50 °C). Figure 4 shows that the effect of stirring speed on conversion fraction is negligible, indicating that the dissolution process is not diffusion controlled. A homogenous suspension was obtained at a stirring speed of 600 rpm. Hence, the stirring speed rate of 600 rpm was selected as a constant value in all experiments.

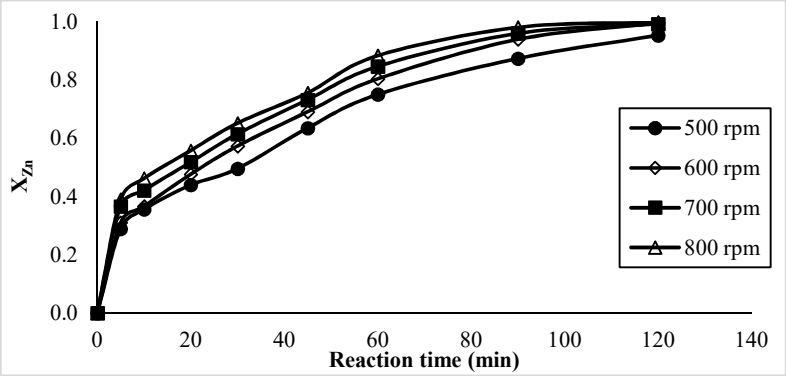

Figure 4. Variation in 500-800 rpm as a function of time to study the effect of stirring speed on the leaching of smithsonite.

Effects of acid concentration

To investigate the effect of lactic acid concentration on the smithsonite dissolution rate, the acid concentration was changed between 0.5 and 5 M. The grain size (200 µm), reaction temperature (50 °C), stirring speed (600 rpm) and solid/liquid ratio (1/250 g mL^{-1}) were constant Figure 5a shows a dissolution rate increase with an acid concentration up to 2 M. By contrast, Figure 5b shows that X_{Zn} decreases as the acid lactic concentration is above 2 M.

The explanation of this observation is that as the acid concentration increases, the conversion rate of the product increases, and the product formed covers the reacting particle, forming a less soluble product film layer. Hence, the dissolution rate reduces [21]. Moreover, an increase in acid concentration results in a decrease in the amount of water present as a solvent in the solution, negatively affecting the solubility.

Effect of solid/liquid ratio

To investigate the effect of the solid/liquid ratio on the smithsonite dissolution rate, the solid/liquid ratio varied was changed between 0.5/250 and 3/250 g.mL^{-1} in the experiments. The grain size, acid concentration, stirring speed and temperature were maintained constant (200 µm, 2 M, 600 rpm, 50 °C).

Figure 6 shows that an increase in the solid/liquid ratio from 0.5/250 to 3/250 g mL^{-1} results in a decrease in the conversion from 0.98 to 0.64 after 60 min. This can be attributed to a decrease in the number of smithsonite particles per solution.

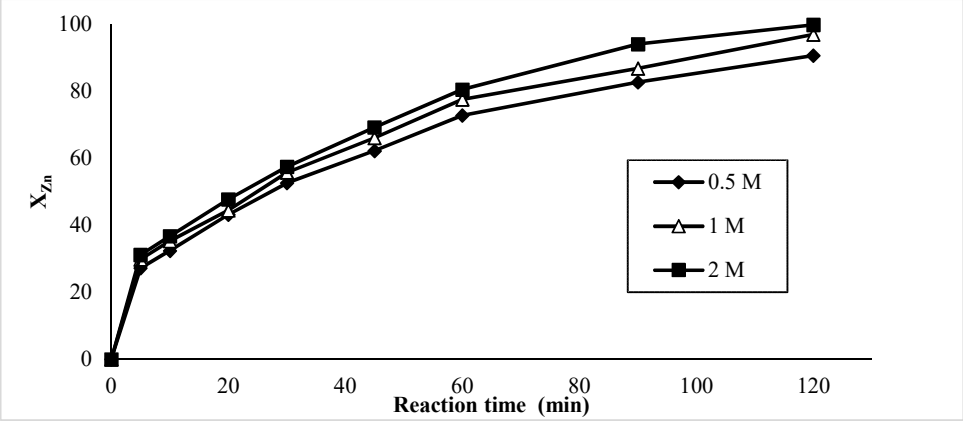

Figure 5a. Variation in 0.5-2 M as a function of time to study the effect of acid concentration on the leaching of smithsonite.

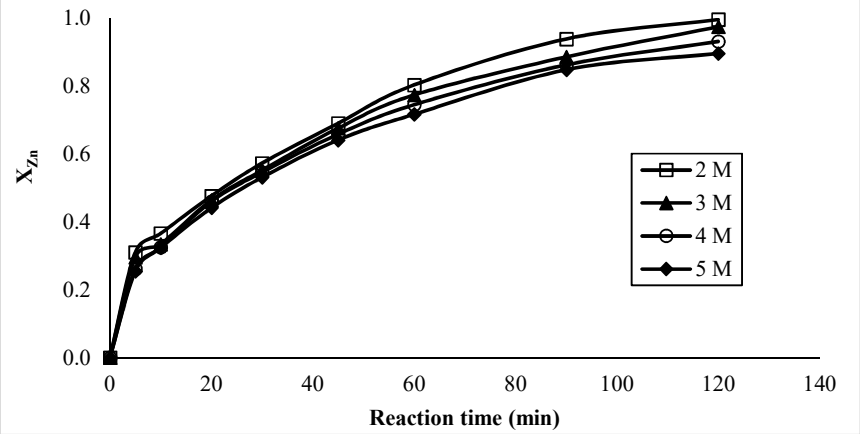

Figure 5b. Variation in 2-5 M as a function of time to study the effect of acid concentration on the leaching of smithsonite.

Kinetic analysis

In a heterogeneous reaction, the reaction takes place at the particle surface. With the reaction progress, the unreacted core shrinks and the product layer grows. A heterogeneous reaction model comprises three steps:(1) diffusion of fluid reactant through the fluid film surrounding the surface particle, (2) diffusion of fluid reactant through the product film to the unreacted core surface and (3) fluid-solid chemical reaction on the reaction surface.

Here, the model that determines the reaction rate is the model that depends on the highest reaction resistance. To determine the rate of the control step, the equations given in Table 1 were analysed by using multiple regression analysis and graphical methods [22]. The highest R^2 value was obtained from the chemically controlled model (Eq. 7).

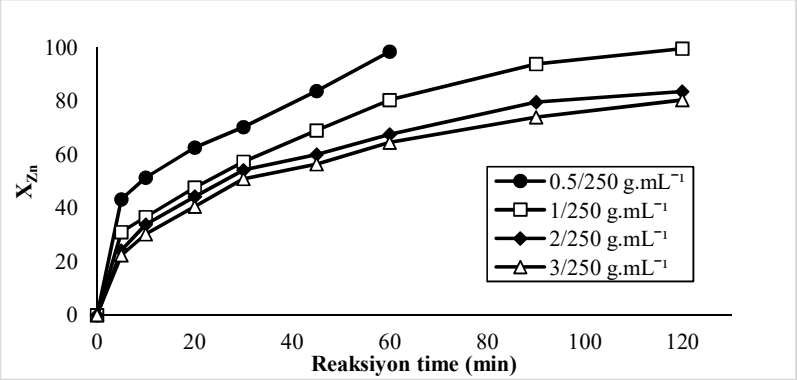

Figure 6. Variation in 0.5/250-3/250 g.mL^{-1} as a function of time to study the effect of solid/liquid ratio on the leaching of smithsonite.

Table 1. Integrated rate equations for the unreacted core and the other models, and regression analyses.

Rate controlling	Step rate equation	R^2	Equation Number
kt = X	Film diffusion	0.9365	(5)
kt =1-3(1-X)$^{2/3}$+ 2(1-X)	Diffusion through product	0.9790	(6)
kt = 1-(1-X)$^{1/3}$	Surface-reaction	0.9962	(7)
kt = 1-(1-X)$^{1/2}$	Film diffusion (large grain)	0.9864	(8)
kt = 1-(1-X)$^{2/3}$	Film diffusion (small grain)	0.9791	(9)
kt = -ln(1-X)	First-order pseudo homogeneous model	0.9020	(10)
kt = X/1-X	Second-order pseudo homogeneous model	0.6933	(11)

Another analysis used to determine the step that controls the reaction rate is the graph of different particle sizes (R_k) versus the time required for complete conversion (t*). In this graph, if t* versus R_k is directly proportional, the dissolution process is controlled by a chemical reaction [22]. If the t* values are plotted versus R_k, the obtained curve is a straight line and this verifies that the reaction is surface reaction-controlled (Figure 7).

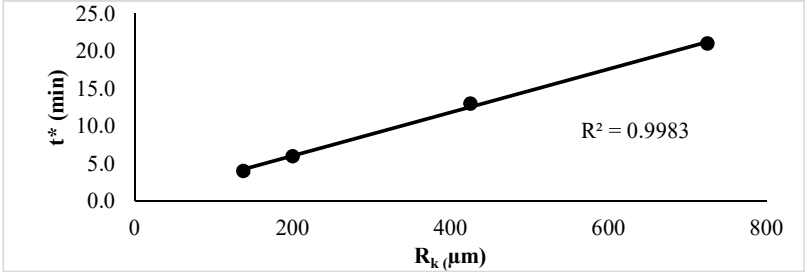

Figure 7. Agreement between t* and R_k.

In this model, the fractional conversion (X) is given as a function of time. The variation in $[1-(1-X)^{1/3}]$ with time is plotted for different smithsonite temperatures in Figure 8. It is seen that the regression lines for all samples display correlation coefficients that range between 0.9367 and 0.9888.

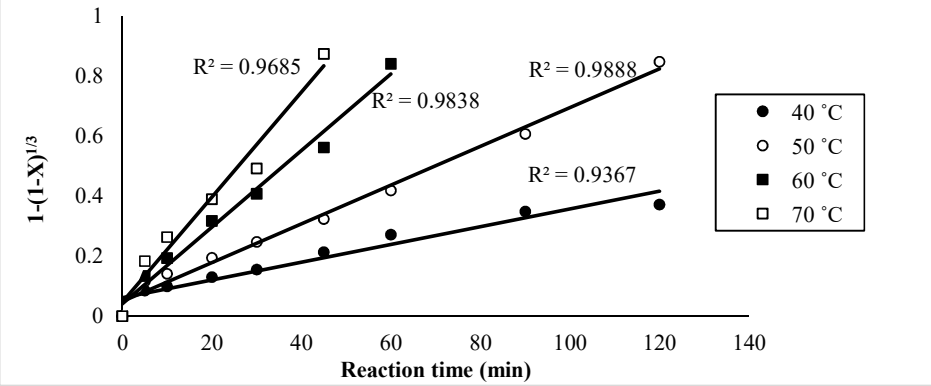

Figure 8. Variation in 40-70 °C as a function of the model with time for different temperatures.

The apparent rate constant k is obtained from the slopes of the regression lines in Figure 9. From the Arrhenius expression, the k term is obtained as

$$\ln k = \ln k_o - (E/R_gT) \quad (12)$$

A plot of lnk versus 1/T is a straight line with a slope of $-E/R_g$ and an intercept $\ln k_o$ (Figure 9). The derived apparent activation energy and pre-exponential factor were calculated as 53.62 kJ.mol^{-1} and 2.5 x10^5 s^{-1}, respectively, yielding.

Thus, the kinetic expression of this process could be given as (Eq. 13)

$$1-(1-X)^{\frac{1}{3}} = 2.5\times10^5 e^{\frac{-53.62}{RT}}t \quad (13)$$

The activation energy of diffusion-controlled processes ranges between 4.18 and 12.55 kJ mol^{-1}, whereas for a surface-reaction controlled processes it is usually greater than 41.84 kJ mol^{-1} [23]. Therefore, the apparent activation energy obtained in this study indicates that the dissolution reaction is surface-action controlled.

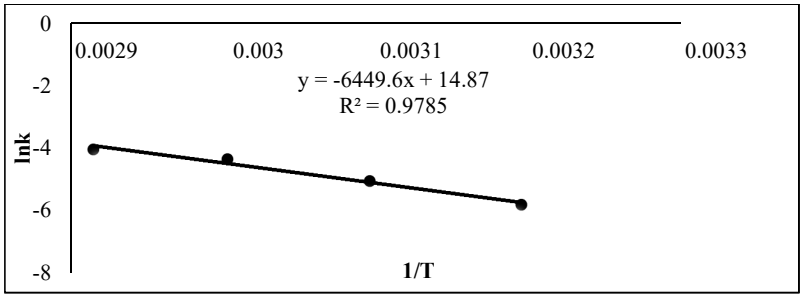

Figure 9. Arrhenius plot: lnk versus 1/T.

CONCLUSIONS

An experimental study was conducted to propose a dissolution kinetic model that improves the current knowledge of the production of zinc lactate. The conclusions obtained from the experimental study are as follows: (1) As the particle size decreases, the dissolution rate of smithsonite ore in lactic acid solution increases due to the increase in surface area. The negligible effect of stirring speed on the smithsonite dissolution rate indicates that the dissolution process is not diffusion-controlled from the product film. (2) The conversion of Zn increased by increasing the acid concentrations up to 2 M (99.65% in 120 min.). By contrast, it decreases by increasing the acid concentrations above 2 M. (3) The significant increase in the dissolution rate with the increase in temperature indicates that the dissolution process is surface-reaction controlled. (4) As the solid/liquid ratio increased, the amount of solid per unit solvent increased, leading to a decrease in the dissolution rate. (5) A surface reaction-controlled model was determined to be suitable to match the experimental data by statistical analysis (R^2 = 0.9962). Moreover, as the t^*-R_k change is directly proportional (R^2=0.9785) and the apparent activation energy is > 40 kJ mol^{-1} (53.62 kJ mol^{-1}) also supports this result. (6) In the context of metal recovery from ores using acid leaching, the results of this study may improve the production of zinc lactate.

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