

## STUDY ON INDIUM LEACHING FROM MECHANICALLY ACTIVATED HARD ZINC RESIDUE

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### Abstract

*In this study, changes in physicochemical properties and leachability of indium from mechanically activated hard zinc residue by planetary mill were investigated. The results showed that mechanical activation increased specific surface area, reaction activity of hard zinc residue, and decreased its particle size, which had a positive effect on indium extraction from hard zinc residue in hydrochloric acid solution. Kinetics of indium leaching from unmilled and activated hard zinc residue were also investigated, respectively. It was found that temperature had an obvious effect on indium leaching rate. Two different kinetic models corresponding to reactions which are diffusion controlled,  $[1-(1-x)^{1/3}]^2=kt$  and  $(1-2x/3)-(1-x)^{2/3}=kt$  were used to describe the kinetics of indium leaching from unmilled sample and activated sample, respectively. Their activation energies were determined to be 17.89 kJ/mol (unmilled) and 11.65 kJ/mol (activated) within the temperature range of 30 °C to 90 °C, which is characteristic for a diffusion controlled process. The values of activation energy demonstrated that the leaching reaction of indium became less sensitive to temperature after hard zinc residue mechanically activated by planetary mill.*

*Keywords: Indium; Leaching; Mechanical activation; Kinetics; Planetary mill*

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### 1. Introduction

Indium is a versatile metal with several

important applications due to its unique physical and chemical properties [1]. The most prominent use of indium is in making

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Indium Tin Oxide (ITO) used as transparent conducting electrodes in many opto-electronic and electro-optic devices such as solar cells and flat panel displays [2-4]. Like iron ore resources, Indium resources are also in shortage [5]. Indium is found in trace amount in many minerals, particularly in sphalerite and in association with sulfides of copper, iron and tin [6]. It is produced mainly from residues generated during zinc ore processing [7]. However, the leaching procedure presents the character of long leaching cycle and low leaching rate in the whole recovery process of indium. One is the improvement of the leaching rate of valuable metals in ores or residues from ore processing via outfield intensifying, such as pressure leaching of copper sulfide concentrates and nickel sulfide concentrates [8], dissolving of metal zinc in sulphuric acid by introducing copper cathode [9], and in this regard, mechanical activation is considered to be the most common method. The utilization of mechanical activation in leaching process of minerals can lead to the decrease of reaction temperature, the reduction of the leaching agent consumption, and the promotion of the recovery of valuable components [10-13].

The studies on the extraction of valuable metals from raw materials as well as the determination of the kinetic parameters of these dissolution processes with the aim of choice of the optimal technological conditions are the most important directions of physico-chemical investigations in hydrometallurgy [14]. The purpose of this

study is to investigate the changes in physicochemical properties and the kinetic behaviors of indium leaching from mechanically activated hard zinc residue in hydrochloric acid solution.

## 2. Experimental

### 2.1. Materials

The hard zinc residue used in this study was kindly supplied by a zinc producer in Guangxi province, China. Hard zinc residue was obtained from vacuum distillation for hard zinc. The chemical composition of the initial sample is given in Table 1. X-ray diffraction (XRD, Rigaku model D/max-2500) analysis showed the hard zinc residue was mainly composed of ZnO, ZnO<sub>2</sub>, SiO<sub>2</sub>, Pb<sub>5</sub>O<sub>8</sub>, InSb, FeZn<sub>10.98</sub>, and InAlO<sub>3</sub>(ZnO)<sub>19</sub>, as shown in Fig. 1. Different particle size fractions were obtained by wet sieving. The indium content of hard zinc residue with different particle size distribution was done by polarographic analysis (Model JP-303)

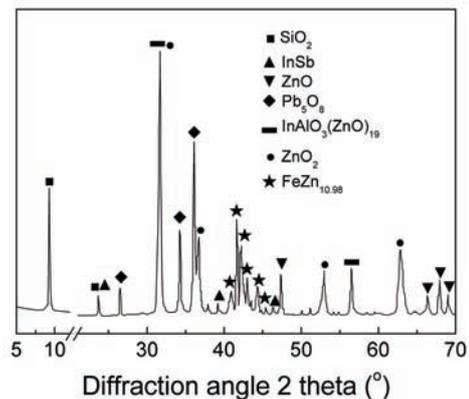


Fig. 1. X-ray diffraction pattern of hard zinc residue.

Table 1 Chemical composition of initial hard zinc residue (mass fraction/%).

| element | Zn   | Pb   | Fe | In   | Si | Se  | Sb   | As   | Ca   | Cu   | Bi   |
|---------|------|------|----|------|----|-----|------|------|------|------|------|
| content | 31.2 | 28.9 | 14 | 11.2 | 1  | 0.5 | 0.15 | 0.05 | 0.03 | 0.02 | 0.02 |

[15] and listed in Table 2. For the present study, the hard zinc residue with particle size distribution of 0.175–0.370 mm was used. Hydrochloric acid used as the reagent. Deionized water and analytical grade chemicals were used in all the experiments.

Table 2 Indium contents in the different size fractions of hard zinc residue.

| Number | Particle size fraction (mm) | Indium contents (%) |
|--------|-----------------------------|---------------------|
| 1      | >0.833                      | 10.72               |
| 2      | 0.370~0.833                 | 11.90               |
| 3      | 0.175~0.370                 | 11.24               |
| 4      | 0.121~0.175                 | 10.63               |
| 5      | <0.074                      | 8.83                |

## 2.2. Mechanical activation

The unmilled residue (0.175–0.370 mm) was dried at 70 °C for 5 h and then reserved. The mechanical activation of the residue was performed in a planetary mill (Model QM-ISP2004, made by Nanjing university, China), 40 g residue and 600 ml the activation medium of Corundum spheres ( $\Phi$  4–5 mm) were added into a stainless steel chamber with effective volume of 1000 ml. Then the samples were subjected to dry milling in ambient atmosphere. The mill was run at 500 rpm for different milling time (1 h and 2 h). After milling for a designed time, the grinding chamber and activation medium were thoroughly cleaned and dried for the next milling experiment. The activation samples were sealed for the following leaching experiments.

## 2.3. Leaching experiment

Leaching tests of the unmilled and milled

samples were carried out in a 1000 ml three-necked flask, heated by a constant temperature water bath (Model LB801) and furnished with an agitator, a thermometer to maintain the desired temperature in the reactor, and a reflux condenser. For each leaching reaction, a total of 500 ml of hydrochloric acid known concentration was put in the flask and heated up to the pre-set temperature under continuous stirring (700 rpm). Then 5.0 g of sample was added to the flask. At required time intervals, 2 ml of the solution was withdrawn. The content of the dissolved indium was analyzed by the polarographic method.

The influences of particle size and temperature on the leaching process were studied while keeping all other factors constant.

## 3. Results and discussion

### 3.1. Effect of particle size on indium extraction

The influence of particle size on the indium leaching rate was investigated using three different particle size distributions of 0.370–0.833 mm, 0.175–0.370 mm, and 0.121–0.175 mm. For the series of tests, the initial hydrochloric acid concentration, reaction temperature and stirring speed were kept constant at 1 mol/L, 60 °C, and 700 rpm, respectively. The results are shown in Fig. 2, from where it can be seen that indium leaching rate increased with decreasing of particle size. After 20 min leaching time, indium leaching rate reached 12%, 48% and 57% for 0.370–0.833 mm, 0.175–0.370 mm, and 0.121–0.175 mm particle sizes, respectively. In addition, the results showed

that about 79% of indium presented in the fine fraction (0.175–0.370 mm) of samples was extracted after 100 min. Smaller particle provides a larger contact area between hard zinc residue and the leaching reagent. To investigate the other leaching parameters, a particle size fraction of 0.175–0.370 mm was chosen in the study.

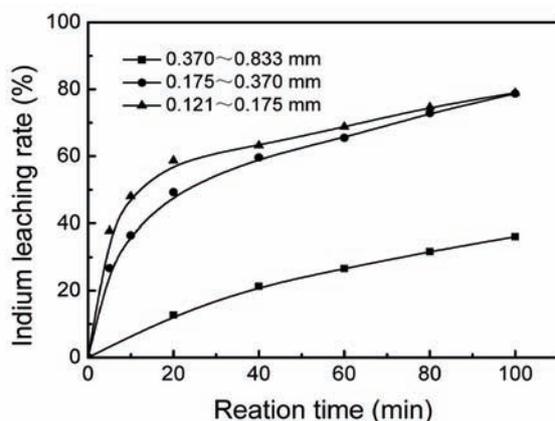


Fig. 2. Effect of different particle size distributions of unmilled sample on indium extraction.

### 3.2. Effect of mechanical activation on physicochemical properties

Particle size distributions of the unmilled sample and the activated samples were measured by Laser Diffraction Particle Size Analyzer (Mastersizer 2000) in liquid mode with deionized water as a dispersing agent, and the results are depicted in Fig. 3. The specific surface area was measured by specific surface area analyzer (DBT-127). The values of specific surface area ( $S_A$ ) and particle size are listed in table 3. The unmilled sample is composed of the particles with a  $d_{50}$  around 399.6  $\mu\text{m}$ . After activating for 1 h and 2 h by planetary mill, the  $d_{50}$  decreased from 399.6  $\mu\text{m}$  to 373.2  $\mu\text{m}$  and 362.7  $\mu\text{m}$ ,

respectively. It is obvious that the decrease of particle size was an important aspect of mechanical activation, and longer activating time essentially had a minor effect on the particle size. The specific surface area increased from 0.3150  $\text{m}^2\text{g}^{-1}$  to 0.6734  $\text{m}^2\text{g}^{-1}$  and 0.9676  $\text{m}^2\text{g}^{-1}$  when samples were activated for 1 h and 2 h by the planetary mill, respectively.

The changes of particle size and specific surface area lead to the increase of contact area between leaching reagent and hard zinc residue and the decrease in thickness of product layer, which contributes to the increase of indium extraction from hard zinc residue.

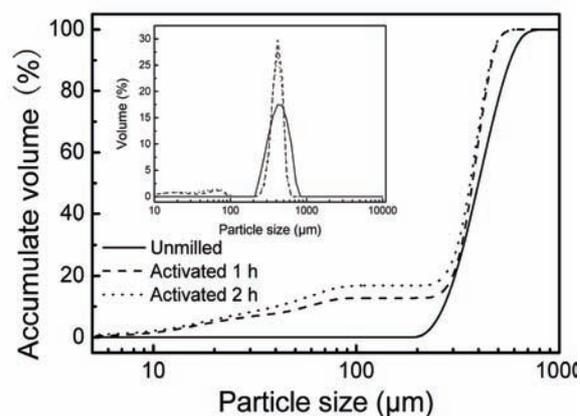


Fig. 3. Particle size distributions of unmilled sample and samples activated for 1 h and 2 h by planetary mill.

Both the unmilled sample and activated sample were subjected to differential scanning calorimetry (DSC) analysis using DSC6200 Differential Scanning Calorimetry Instrument (Seiko Instruments Inc, Japan). The results are illustrated in Fig. 4. The DSC patterns of the activated sample as well as the unactivated one had two endothermic peaks between 0  $^{\circ}\text{C}$  and 600  $^{\circ}\text{C}$ . However,

Table 3 The particle size and specific surface area of unmilled sample and samples activated for different time by planetary mill.

| Milling time h | d <sub>10</sub> μm | d <sub>50</sub> μm | d <sub>90</sub> μm | Specific surface area, m <sup>2</sup> g <sup>-1</sup> |
|----------------|--------------------|--------------------|--------------------|---|
| 0              | 270                | 399.6              | 574                | 0.315   |
| 1              | 56.7               | 373.2              | 466                | 0.6734  |
| 2              | 39.6               | 362.7              | 460.5              | 0.9676  |

compared with the two endothermic peaks of unactivated sample, the ones of sample mechanically activated 1 h by planetary mill shifted to lower temperature. The onset temperature of the first endothermic peak in the curves of heat flow against temperature moved from 219 °C to 203 °C. The onset temperature of the second endothermic peak moved from 420 °C to 417 °C. Barriga et al. [16], Wen et al. [17], Shaw et al. [18] Huang et al. [19] Cao et al. [20] all found similar phenomenon on the endothermic peak shifting to lower temperature after mechanical activation. This implies that the thermodynamic stability of the sample was reduced and the reaction activity was increased after mechanical activation, which

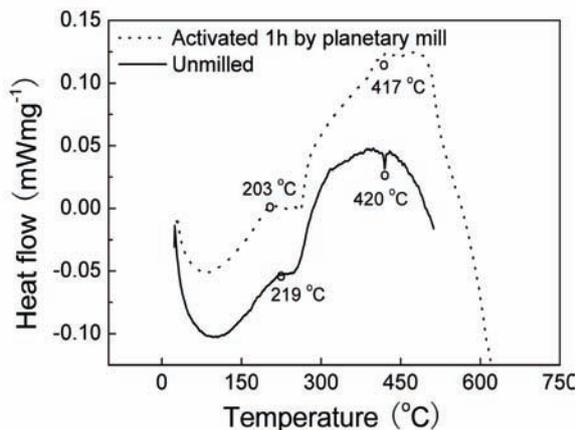


Fig. 4. DSC patterns of unmilled sample and sample activated 1 h by planetary mill.

facilitate chemical reaction occurring at lower temperature.

### 3.3. Effect of mechanical activation on indium extraction

To validate the strengthening effect of mechanical activation on indium extraction from hard zinc residue, the extractions of unmilled sample and those activated for 1 h and 2 h by planetary mill were studied at 30 °C in 1 mol/L HCl. The indium leaching rate of various samples is shown in Fig. 5. The results indicated that indium leaching rate was improved obviously when hard zinc residue was mechanically activated for 1 h; while a very slight increase of indium leaching rate appeared when the activation time was prolonged to 2 h. The leaching rate reaches 54% and 61.4% after leaching for 20 min when hard zinc residue was mechanically activated for 1 h and 2 h, respectively. However, the leaching rate was only 34% when the sample was not activated. In addition, mechanical activation shortened the leaching time significantly. It took the sample activated for 1 h by planetary mill 36 min to reach 60% but 100 min for the unmilled sample. The strengthening effect of mechanical activation was ascribed to the change of physicochemical properties. During mechanical activation the disintegration by high-energy is accompanied by the increase of the number of particles and by the generation of fresh, previously unexposed surface [11]. Generally, small particle tend to dissolve more rapidly compared with large particles due to large

specific surface areas. Moreover, during mechanical activation the crystal structure of a mineral is usually disordered and generation of defects or other metastable forms can be registered [13, 21]. Lattice defect also accelerates the dissolution of hard zinc residue. Thus reaction activity of hard zinc residue increases after mechanically activated for different time by planetary mill, which results in the increase of indium leaching rate.

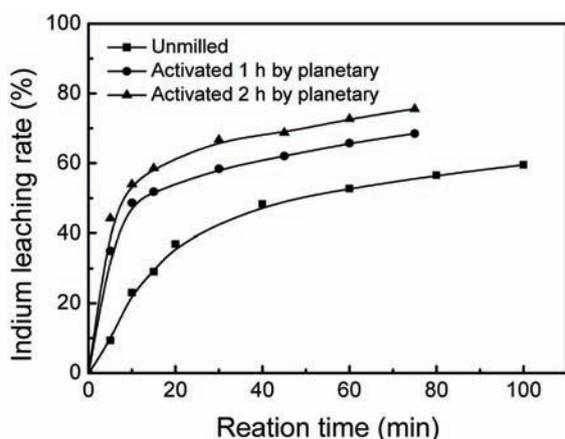


Fig. 5. Effect of mechanical activation on Indium extraction.

### 3.4. Effect of reaction temperature

The effects of reaction temperature on indium leaching rate of unmilled sample and sample activated for 1 h by planetary mill at different reaction time were investigated in temperature range of 30 °C to 90 °C and hydrochloric acid concentration of 1 mol/L. The results are presented in Fig. 6. As we can see in Fig. 6, the indium leaching rate was significantly dependent on the temperature, especially for the one of unmilled samples. At 30 °C, 52.5% and 72.1% of indium was extracted from the unmilled and activated samples at

60 min, increasing to 72.6% and 88% at 90 °C, respectively. It was obvious that a relatively weaker temperature effect for the leaching of the activated sample was observed. This indicated that the leaching process became less sensitive to temperature after mechanical activation.

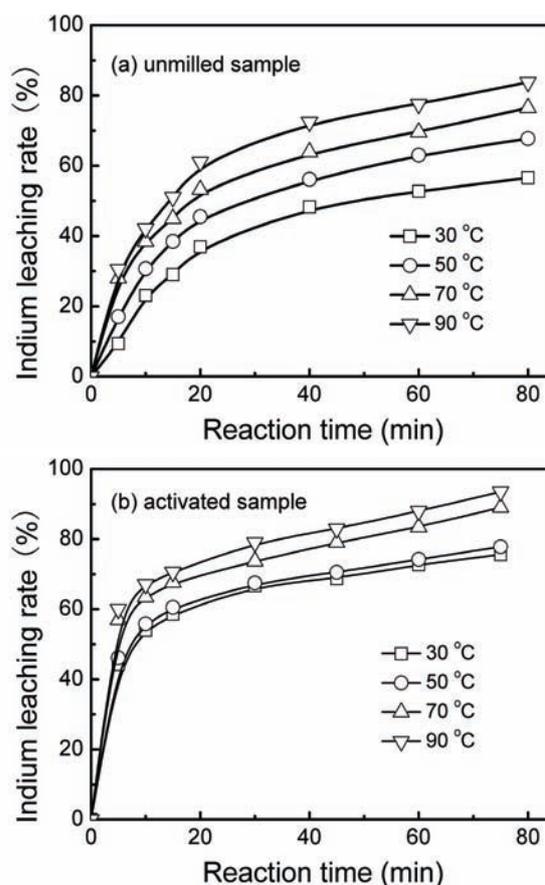


Fig. 6. Effect of reaction temperature on Indium extraction ((a) unmilled sample, (b) activated sample).

### 3.5. Kinetics analysis

The selection of the kinetic model for the linearization of the experimental results (Fig. 6a and Fig. 6b) was done using the method of reduced half time of reaction defined by Sharp [22]. In this method, nine equations

corresponding to reactions which are diffusion controlled, or are reaction-rate controlled, or obey first order kinetics, or follow the equations of Avrami and Erofe'ev were proposed. These equations can be expressed in the form  $F(x)=A(t/t_{0.5})$ , where  $x$  is the extent of reaction,  $t$  is reaction time,  $t_{0.5}$  is the time for 50% reaction,  $t/t_{0.5}$  is reduced half time of reaction,  $A$  is a calculable constant depending on the form of  $F(x)$  and  $k$  is the rate constant. The criteria for accepting a model as the best for linearization of the experimental data is the least deviation of experimental curve  $(t/t_{0.5})$  in comparison with curves presenting kinetic equations proposed by Sharp, Fig. 7. This method for selection of kinetic equation for optimal fit of experimental data points was used earlier [23-26]. From Fig. 7 it was obvious that the values of the reduced half time of reaction for unmilled data and activated data were approximated to values that represent the kinetic functions  $[1-(1-x)^{1/3}]^2=kt$  and  $(1-2x/3)-(1-x)^{2/3}=kt$ , respectively, which means that the function  $[1-(1-x)^{1/3}]^2=kt$  should be

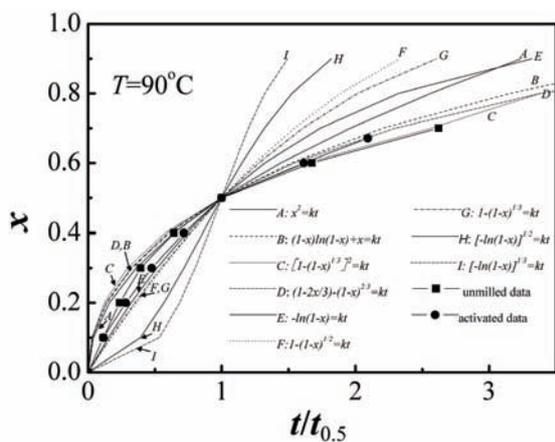


Fig. 7. Selection of kinetic model for linearization of the experimental results using the method of reduced half time of reaction defined by Sharp.

used for fine linearization of experimental results of unmilled sample (Fig. 6a) and the function  $(1-2x/3)-(1-x)^{2/3}=kt$  should be used for fine linearization of experimental results of activated sample (Fig. 6b). In addition, both kinetic models are diffusion control, which indicates that the process of leaching indium from hard zinc residue at temperatures of 30–90 °C is solely controlled by diffusion.

Using equation  $[1-(1-x)^{1/3}]^2=kt$ , linearization of experimental data for unmilled sample was performed, as shown in Fig. 8. The quality of the linear fitting is quite good. From the slopes of linearized isotherms, rate constant  $k$  was determined. Rate constant  $k$  changes with temperature according to the Arrhenius equation:  $k=k_0\exp(-E_a/RT)$ , where  $k_0$  is pre-exponential factor,  $E_a$  is activation energy,  $R$  is the gas constant, and  $T$  is temperature in Kelvin. The results were illustrated as Arrhenius diagram in Fig. 9.

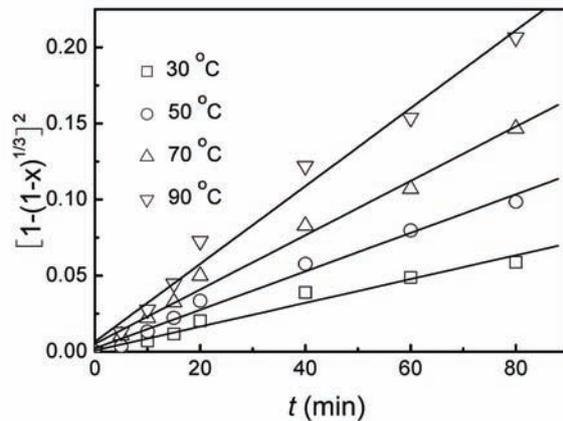


Fig. 8. Plot of  $[1-(1-x)^{1/3}]^2$  versus  $t$  for indium leaching from unmilled sample at different reaction temperatures.

According to the Arrhenius diagram, activation energy of the process was calculated and its value is 17.89 kJ/mol.

Similarly, according to the experimental data of activated sample presented in Fig.7b, the variation in  $(1-2x/3)-(1-x)^{2/3}=kt$  with  $t$  at different temperatures is shown in Fig. 10. From the slopes of linearized isotherms in Fig. 10, the activation energy of 11.65 kJ/mol was calculated using Arrhenius equation (Fig. 11).

The values of activation energy for unmilled sample and activated sample also illustrated the leaching rate were diffusion control. Similar values of activation energy were determined using diffusion kinetic

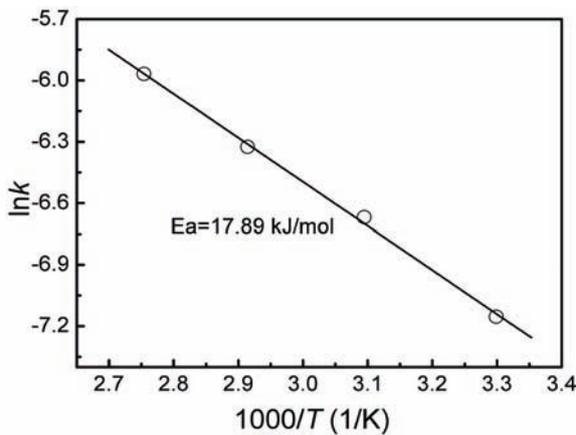


Fig. 9. Arrhenius plot for the indium leaching from unmilled sample.

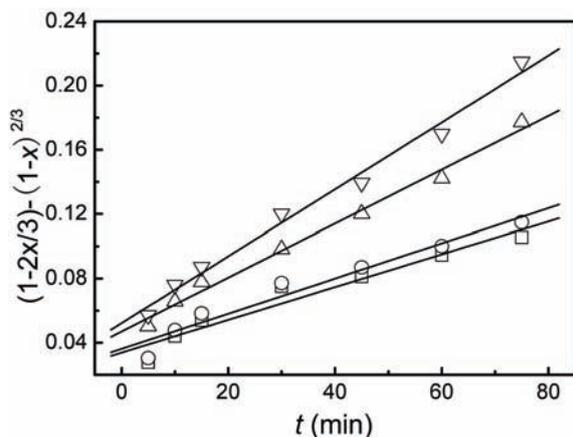


Fig. 10. Plot of  $(1-2x/3)-(1-x)^{2/3}$  versus  $t$  for indium leaching from activated sample at different reaction temperatures.

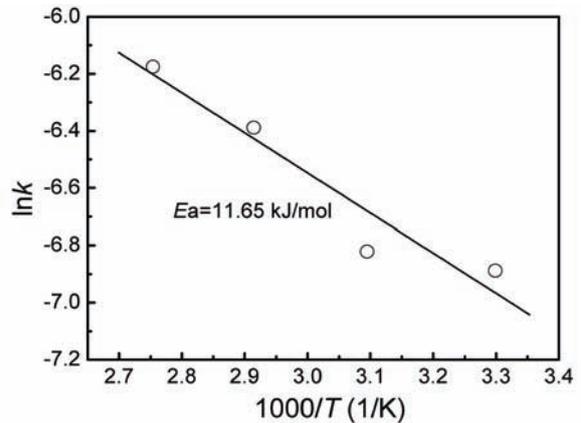


Fig. 11. Arrhenius plot for the indium leaching from activated sample.

model for antimony leaching from mechanically activated berthierite, boulangerite and franckeite [27], for the leaching of low grade zinc oxide ore in  $\text{NH}_3\text{-NH}_4\text{Cl-H}_2\text{O}$  system [28], for silver leaching from a manganese-silver associated ore in sulfuric acid solution in the presence of  $\text{H}_2\text{O}_2$  [29], for antimony leaching from oxidizing-converting Slag of Pb-Sb alloy [30], and for cobalt leaching from spent catalys [31].

Moreover, the activation energy decreased obviously after sample mechanically activated by planetary mill, which demonstrated that mechanical activation accelerated the indium leaching from hard zinc residue and leaching reaction become less sensitive to temperature.

#### 4. Conclusions

The study on indium leaching from mechanically activated hard zinc residue by planetary mill in hydrochloric acid was performed. Mechanical activation of hard zinc residue resulted in the decrease of particle size and thermostability, the increase

of specific surface area and structural disorder, and the improvement of leachability of indium. Indium leaching rate was evidently accelerated. Indium leaching from unmilled and activated for 1 h hard zinc residue was found to be diffusion-controlled and followed the kinetic models:  $[1-(1-x)^{1/3}]^2=kt$  and  $(1-2x/3)-(1-x)^{2/3}=kt$ , respectively. Their respective activation energies were determined to be 17.89 kJ/mol and 11.65 kJ/mol within the temperature range of 30 °C to 90 °C, which provided further evidence that the reactions of indium leaching from unmilled and activated hard zinc residue were all controlled by diffusion. The values of activation energy indicated that the leaching reaction of indium become less sensitive to temperature after mechanical activation.

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