

Reductive leaching of indium from the residue of neutral leaching by using oxalic acid in sulfuric acid solution

F. Maddah, M. Alitabar, and H. Yoozbashizadeh

Department of Materials Science and Engineering, Sharif University of Technology, Azadi Ave, P.O.Box 11155-9466, Tehran, Iran

Corresponding Author: yoozbashi@sharif.edu

Abstract

The present study sought to assess the reductive leaching of indium from indium-bearing zinc ferrite by using oxalic acid as reducer in sulfuric acid solution. The effect of more main factors affecting the procedure on process rate, including the ratio of oxalic acid to sulfuric acid, stirring rate, grain size, temperature and the initial concentration of synergic acid was precisely evaluated. The results confirmed the acceptable efficiency of dissolving indium in the presence of oxalic acid, representing that shrinking-core model with chemical reaction controlling step can describe the kinetics of indium dissolution correctly. Based on the apparent activation energy of 44.55 KJ/mole and reaction order with respect to the acid concentration of 1.14, it was found that the presence of oxalic acid reduces sensitivity to temperature changes and increases the effect of changes in acid concentration. Finally, the equation of kinetic model based on the factors under study was presented.

1. Introduction

Indium, as a versatile novel metal, is considered as one of the scattered metals. The neutral leaching residue (NLR), as one of by-products in the hydrometallurgical processes of zinc production, is regarded as the most important primary source for producing indium due to the high concentration of indium in NLR.[1, 2]

Indium occupies the crystal lattice of iron in zinc ferrite, the main component of NLR, owing to the similarity between the behavior of indium and iron. Indium-bearing zinc ferrite (IBZF) of general formula ($ZnFe_{2-x}In_xO_4$) is regarded as a stable and indissoluble oxidic compound.[3, 4]

Several techniques were used to dissolve indium from indium-bearing oxidic compounds such as zinc ferrite including oxidative pressure leaching method [5], microwave heating instead of conventional heating [6, 7], mechanical activation [8-11] and ultrasonic technique [12]. Although these techniques are successful in leaching indium-bearing compounds, they face some problems like the consumption of high acid value, great working temperature, similarity of dissolution behavior of indium with zinc and especially with iron when changing the effective leaching parameters and the presence of Fe (III) ion in the solution produced by leaching, leading to the reduction of the efficiency related to the next steps of the indium production process.[13, 14]

Regarding reductive leaching by using reducers such as sphalerite and marmatite [15-18], some disadvantages are observed for instance increasing impurities, enhancing acid consumption and existing sulfur as an unwanted element in dissolution process although there are some advantages such as the reduction of iron to Fe (II) and the synchronous dissolution of zinc ferrite and indium-bearing sphalerite or marmatite.

Considering the significant properties of oxalic acid like biocompatibility, less contamination, reducing power and the power of complex formation, it has attracted the attention of many researchers for dissolving stable oxidic compounds. [19-21]

The most important weakness of oxalic acid compared to conventional inorganic acids is regarded as lower acidic strength. Hence, oxalic acid is used along with hydrochloric acid and sulfuric acid to dissolve iron [22], manganese [23, 24] and titanium [25-27], respectively. Represents developing the synergic effect of the reducing power and complex formation of oxalic acid and the acidic strength of sulfuric acid, as well as improving dissolution process.

The ability of oxalic acid for dissolving indium existing in the scraps of liquid crystal display panels was assessed. According to the previous researches [28, 29], enhancing in the temperature and the presence of ultrasonic waves yield to increasing the transfer of hydrogen ion from the liquid phase to the surface of the solid phase. In addition, the existence of oxalate ion can facilitate with lower costs the next step of the process, which involves filtering indium from impurity ions.

As a novel work of science, the present study used the synergic combination of sulfuric acid and oxalic acid for leaching zinc ferrite and extracting indium and assessed the kinetics of indium dissolution. This is the first time that oxalic acid is used to dissolve zinc ferrite for obtaining indium.

2. Experimental procedures

2.1. Materials

Primary material was the residue produced by leaching roasted zinc concentrate from the Bama Company in Isfahan, the center of Iran.

Regarding the preparation of primary material, the zinc concentrate was heated at 850 °C for 90 min. Thereafter, to eliminate soluble compounds such as zinc oxide and zinc sulfate in NLR, the obtained substance was washed in 1 M hydrochloric acid at 45 °C for 30 min, so that the concentrate can be enriched with indium. Finally, the residue obtained by filtrating was dried and assessed after grading in desired sizes.

ICP method was used for the elemental analysis of NLR and the results were provided in Table 1 which indicates the presence of iron and zinc as main elements, as well as 210 ppm of indium in NRL composition.

Table 1: Chemical compositions of NLR (wt%)

Zn	Fe	In	S	SiO ₂
33.04	37.56	0.021	1.81	6.21

X-ray diffraction pattern (XRD, Rigaku model D/max-2500) analysis shown in Fig.1, illustrated the existence of zinc ferrite (ZnFe₂O₄) and zinc silicate (ZnSiO₃) as the main compositions of NLR.

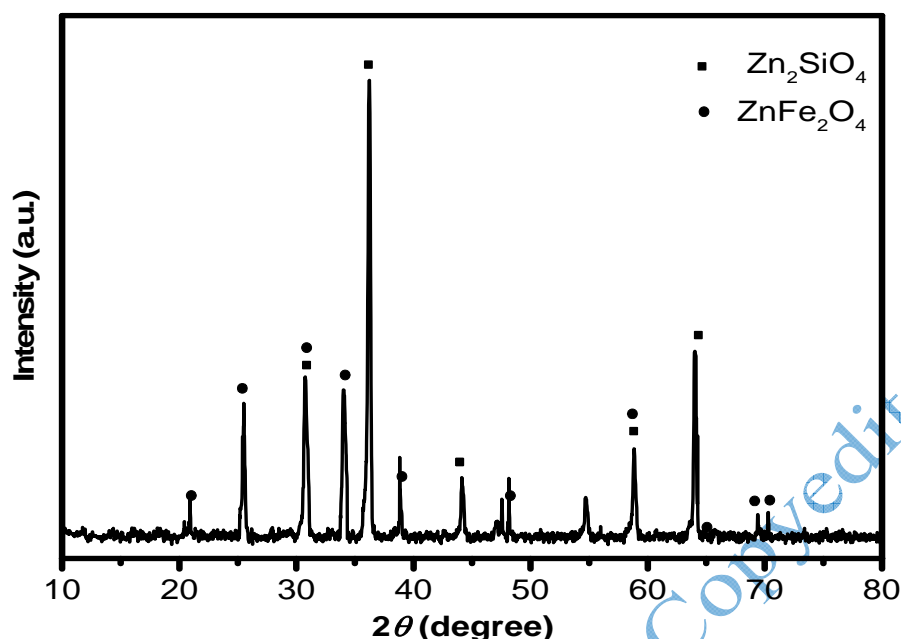


Figure 1. XRD pattern of NLR.

The intended solvent was prepared by diluting the calculated values of sulfuric acid (Merck) and oxalic acid (Merck) by using deionized water.

2.2. Method

Leaching tests were conducted by using a 1000 cc three-necked flask equipped by reflux condenser, a thermometer, and mechanical stirrer and placed into a water bath with controlled temperature. The parameters of the ratio of oxalic acid to sulfuric acid in the composition of the acidic solvent, stirring rate, grain size, temperature, and acid concentration were evaluated. The experiments were designed based on the univariate method and other variants were assumed constant during assessing the effect of changes in each variant.

Regarding all experiments, the ratio of solid to liquid was fixed at 1 to 20. All experiments were conducted at different times of 5, 15, 30, 60 and 90 min to evaluate the rate of the leaching process.

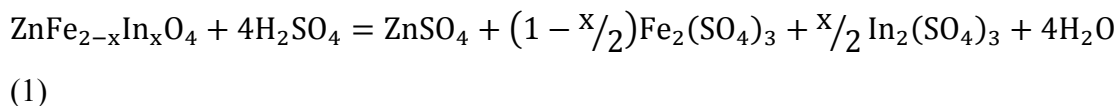
In addition, 200 cc solvent was added into the flask and heated up to intended temperature. Then, 10 gr of the sample was added into the flask.

After passing the intended time for each test, 5 cc of the solution was taken by using pipettes. The obtained samples were cooled, filtered and identified by using the ICP method in order to determine their indium value.

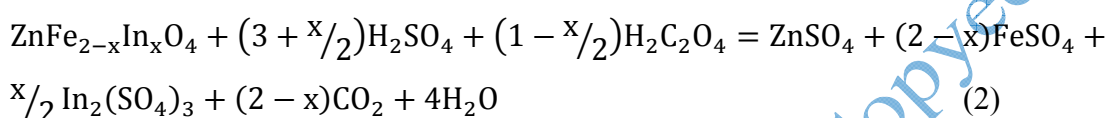
3. Results and Discussion

3.1. Chemical Reactions

IBZF is regarded as the main composition of NLR as shown in Fig.1 Equation 1 indicates the reaction of IBZF leaching in sulfuric acid solution in the absence of reducer.



Based on Le Chatelier's principle, the progress of recent reaction leads to increasing Fe (III) ion concentration and decreasing dissolution rate. Regarding the presence of oxalic acid in sulfuric acid solution, Fe (III) ion reduces to Fe (II) and the chemical reaction of IBZF leaching is written as equation 2.



Accordingly, the presence of oxalic acid in the solvent composition could thermodynamically progress dissolution process.

3.2. Effect of Parameters

3.2.1. the effect of the ratio of oxalic acid to sulfuric acid

Fig.2 displays the effect of percentage changes of the oxalic acid existing in solvent composition (0-100%) on indium dissolution (stirring rate 600 rpm; grain size 45-53 μm ; temperature 55 °C; acid concentration 1.5 M; time 90 min).

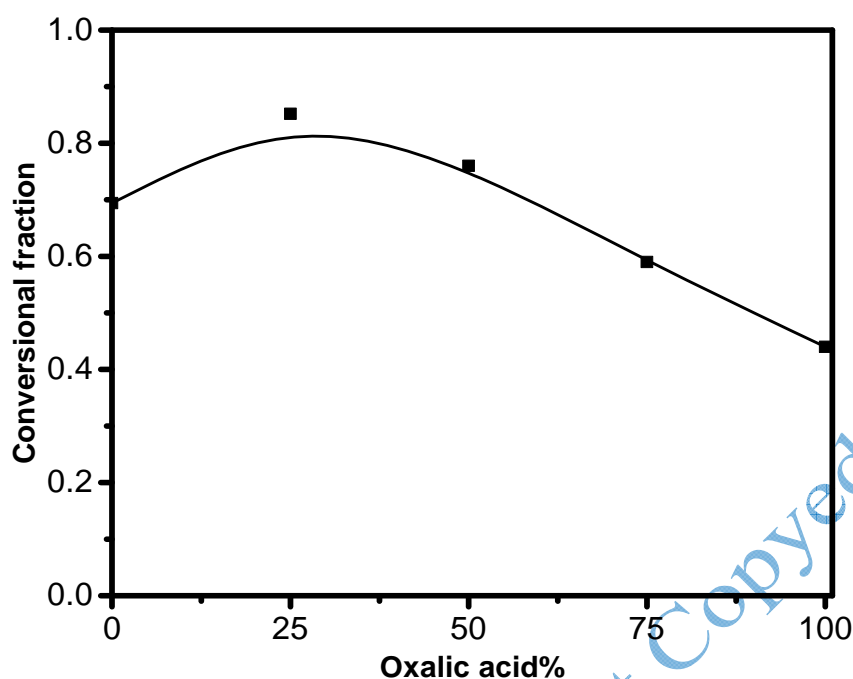


Figure2. Effect of Oxalic acid percent on indium dissolution.

The results indicated that increase in oxalic acid value results in going up the dissolution percentage of indium, and then it decreases. The dissolution percentage of indium in the absence of oxalic acid was obtained 69.4% after 90 min. The dissolution percentage of indium upsurges to the maximum value of 82.5% by adding oxalic acid into solvent composition and reaching the ratio of oxalic acid to sulfuric acid of 1 to 3 due to the decreasing power of oxalic acid which leads to an rise in Fe (III) ion to Fe (II) ion and increase in zinc ferrite leaching rate. Regarding the ratio over than 1 to 3, the uptrend of the dissolution percentage of indium stops and then it decreases. The steps of dissolution mechanism related to oxidic compounds by using oxalic acid include the decomposition of acid, adsorption of hydrogen ion on surface site, formation of zinc surface complex and complex dissolution.[30-32] Furthermore, the addition of oxalic acid results in reducing sulfuric acid and decreasing acidic strength, which justifies the reducing in the extraction percentage of indium by the excessive increase of oxalic acid.

3.2.2. the effect of stirring rate

The effect of stirring rate in the range of 250-900 *rpm* on indium dissolution is depicted in Fig. 3 (the ratio of oxalic acid to sulfuric acid 1 to 3; grain size 45-53 μm ; temperature 55 °C; acid concentration 1.5 *M*; time 90 min).

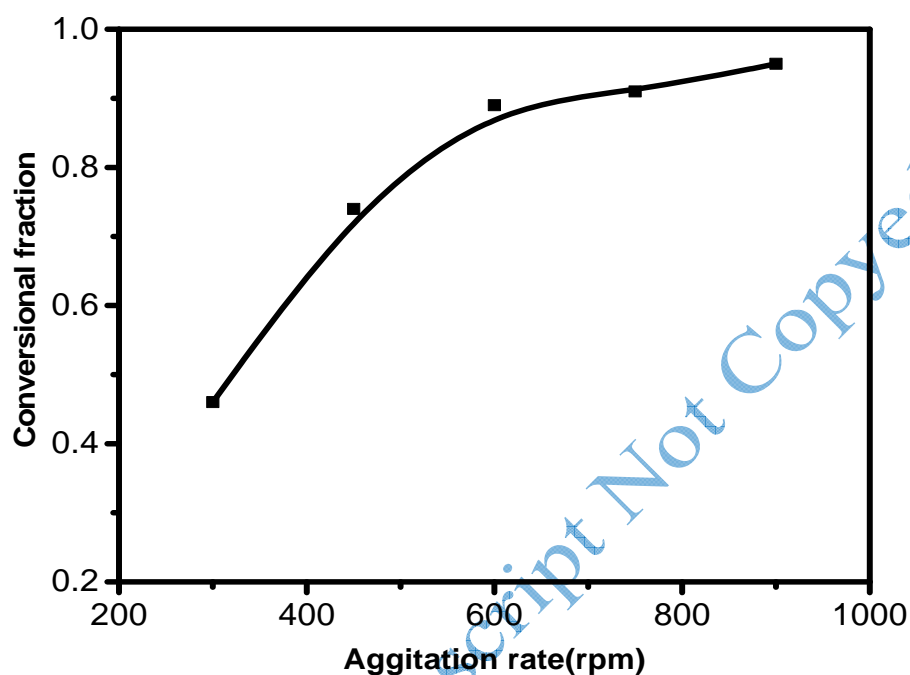


Figure 3. Effect of Agitation rate on indium dissolution.

According to the results of Fig. 3, the indium dissolution rate rises by adding the stirring rate, while increase in stirring rate fails to affect indium dissolution rate in leaching rate over 600 *rpm*. Thus, the stirring rate of 600 *rpm* was considered proper for the next experiments.

3.2.3. the effect of grain size

Fig. 4 demonstrates the effect of NLR grain size (45-150 μm) on indium dissolution (the ratio of oxalic acid to sulfuric acid 1 to 3; stirring rate 600 *rpm*; temperature 55 °C; acid concentration 1.5 *M*).

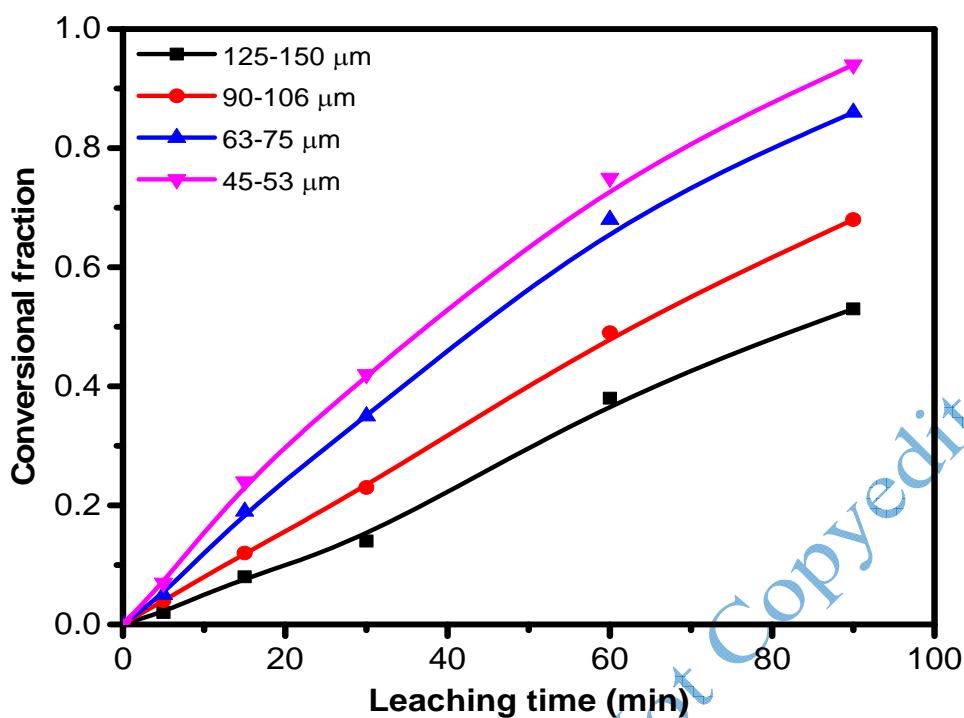


Figure4. Effect of Grain size on indium dissolution.

Based on the results in Fig. 4, grain size influenced significantly and inversely on NLR leaching rate. Thus, NLR grain size was determined 45-53 μm to study the kinetic of indium leaching better in the next experiments.

3.2.4. the effect of temperature

The effect of temperature changes (25-70 $^{\circ}\text{C}$) on indium dissolution rate is shown in Fig. 5 (the ratio of oxalic acid to sulfuric acid 1 to 3; stirring rate 600 rpm; grain size 45-53 μm ; acid concentration 1.5 M).

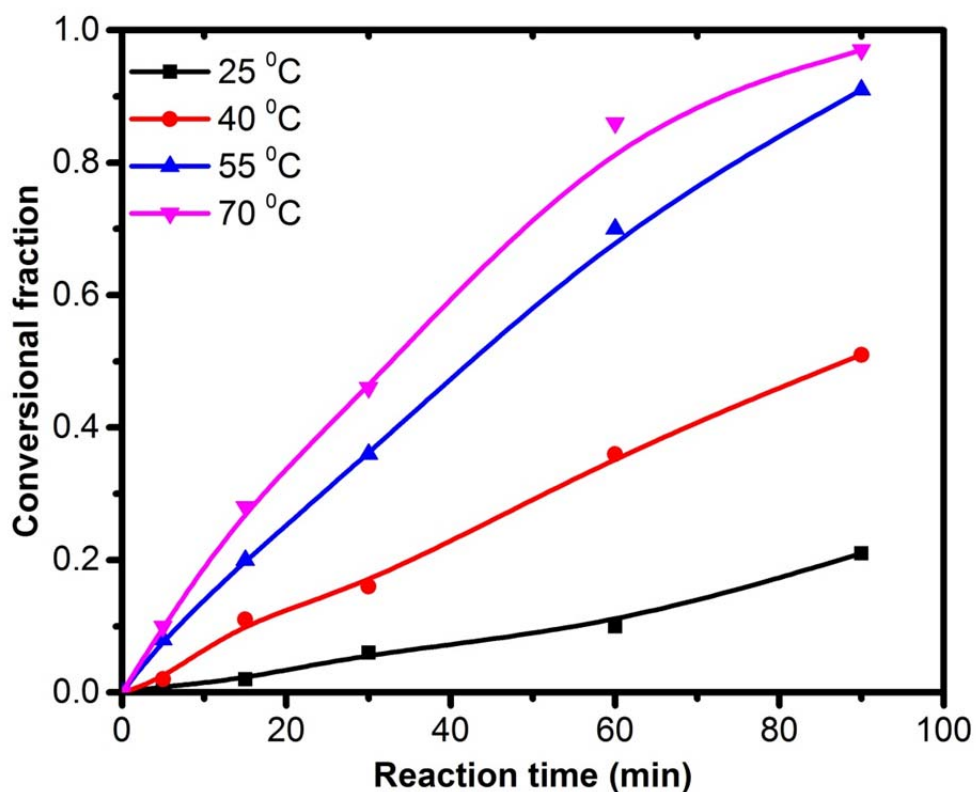


Figure 5. Effect of Temperature on indium dissolution.

As illustrated in Fig. 5, the addition of temperature increased indium dissolution rate so that indium dissolution was obtained 21% and 97% at 25 °C and 70 °C after 90 min, respectively. The presence of sulfuric acid along with oxalic acid leads to growing the uptrend of the indium dissolution rate significantly by adding temperature over 55 °C.

3.2.5. the effect of acid concentration

Fig. 6 indicates the effect of acid concentration (0.5-2M) on indium dissolution rate (the ratio of oxalic acid to sulfuric acid 1 to 3; stirring rate 600 rpm; grain size 45-53 μm ; temperature 55 °C).

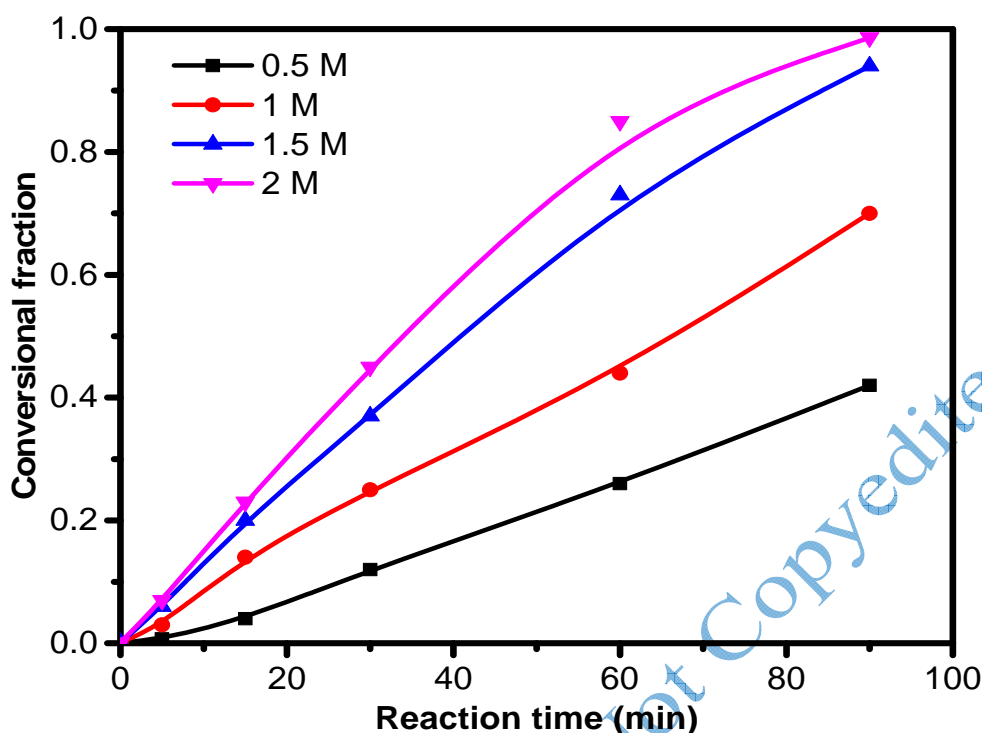


Figure 6: Effect of Acid concentration on indium dissolution.

According to the results of Fig. 6, indium dissolution rate was enhanced by adding the primary concentration of acid. The value of indium dissolution was achieved 42% and 98% in the acid concentration of 0.5 and 2 M, respectively, after passing 90 min from the leaching process. Further, upturn in acid concentration led to a decrease in the gradient of the increase in the indium dissolution rate. Due to the trend of climbing the curves while increasing the concentration of acid, the amount of 1.5M, as optimal concentration, is selected for other tests.

3.3. Kinetic Analysis

3.3.1. Kinetic modeling

NLR leaching reaction in acidic solutions was considered as a heterogeneous reaction. Hence, assuming that NLR particles are spherical with constant size and acid concentration is fixed, the kinetic model of shrinking-core can be used to describe process mechanism.[33]

Based on this model, the relationship between reacted fraction and time is defined by equations 3, 4 and 5 for chemical reaction-controlled, diffusion-controlled and combined-controlled processes, respectively.

$$1 - (1 - x)^{1/3} = k_c t \quad (3)$$

$$1 - \frac{2}{3}x - (1 - x)^{2/3} = k_d \quad (4)$$

$$\left[1 - (1 - x)^{1/3}\right] + B \left[1 - \frac{2}{3}x - (1 - x)^{2/3}\right] = k_m t \quad (5)$$

Where x indicates reacted fraction, t is time, k_c , k_d and k_m represent apparent rate constant for chemical reaction-controlled, diffusion-controlled and combined-controlled processes, respectively. Furthermore, B corresponds to the ratio of the apparent rate constant of chemical reaction-controlled to that of diffusion-controlled processes.

The correlation coefficients (R^2) obtained by matching equations 3, 4 and 5 with experiments data at different temperature are summarized in Table 2.

Table 2: Fitting results of the kinetic equation at different temperatures

$T/^\circ\text{C}$	Correlation coefficients			Apparent rate constant/ 10^3 min^{-1}
	Chemical model	Diffusion model	Mixed Model	
25	0.951	0.754	0.859	0.747
40	0.993	0.887	0.955	2.306
55	0.988	0.886	0.946	5.825
70	0.993	0.933	0.971	7.640

The comparison of correlation coefficients indicates that chemical-controlled model is better matched with experimental data compared to diffusion and combined models. Thus, the dissolution process of indium from NLR by using the synergic combination of oxalic acid-sulfuric acid is regarded as chemical reaction-controlled.

3.3.2. The relationship between rate and grain size

Fig. 7 indicates the curve of $1 - (1 - x)^{1/3}$ against time in different grain sizes.

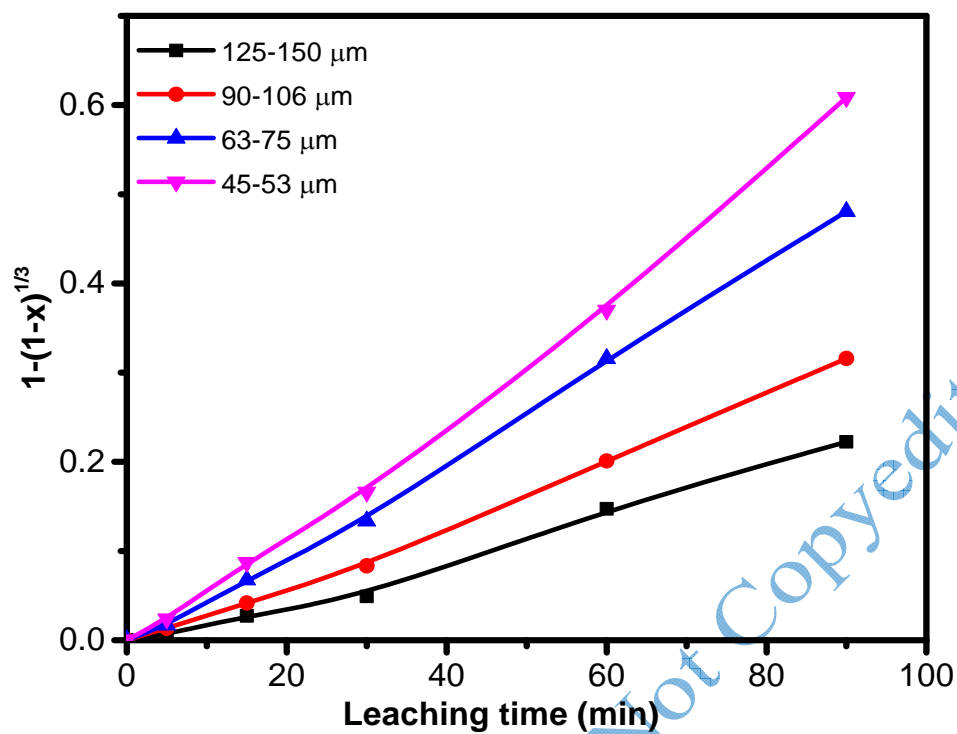


Figure 7: Plot of $1 - (1 - x)^{1/3}$ versus t at different grain sizes.

The curve of the apparent rate constant versus the inverse of grain size is presented in Fig. 8 by using the gradient values of the lines matched with the data in Fig. 7.

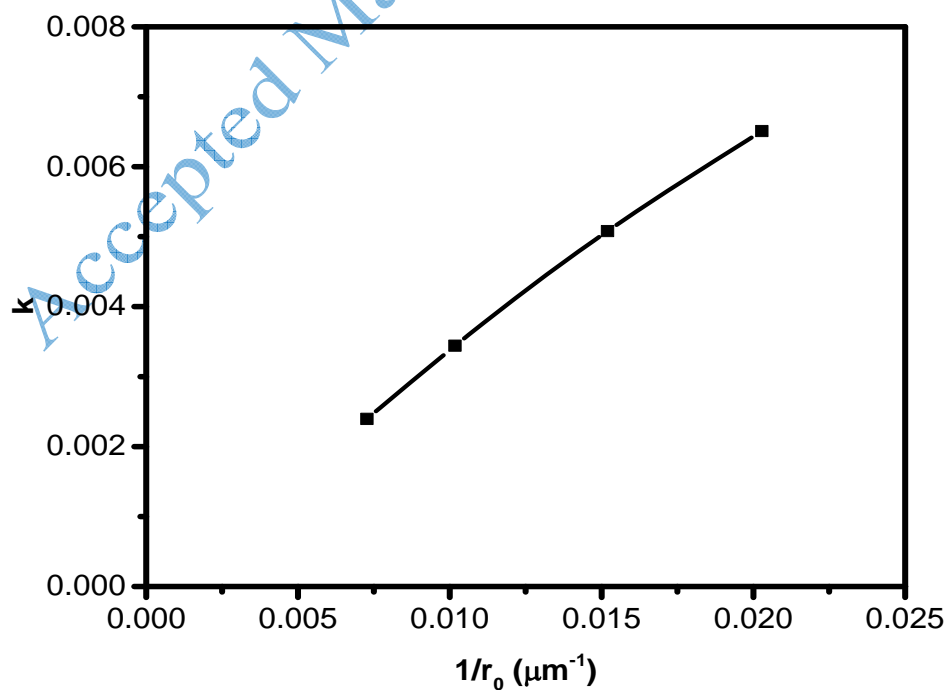


Figure 8: Relationship between k and $1/r_0$.

Accordingly, equation 6 represents the effect of grain size on the indium dissolution rate.

$$k_c = 3.32 \times 10^{-1} r_0^{-1} \quad (6)$$

3.3.3. The relationship between rate and temperature (the calculation of activation energy)

The curve of $1 - (1 - x)^{1/3}$ against time at different temperatures is shown in Fig. 9, by offering that indium matching enhances by increasing the temperature.

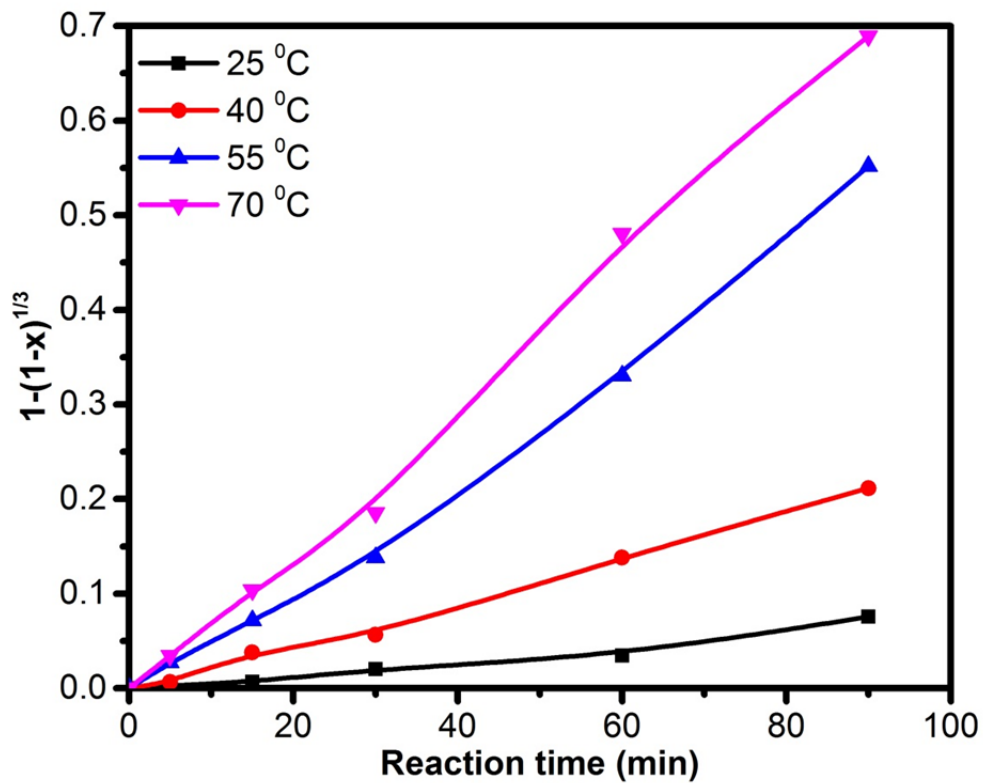


Figure 9 : Plot of $1 - (1 - x)^{1/3}$ versus t at different temperatures.

The logarithm of the apparent rate constant versus temperature inverse curve is presented in Fig. 10 by using the gradient values of the lines matched with data derived from Fig. 9.

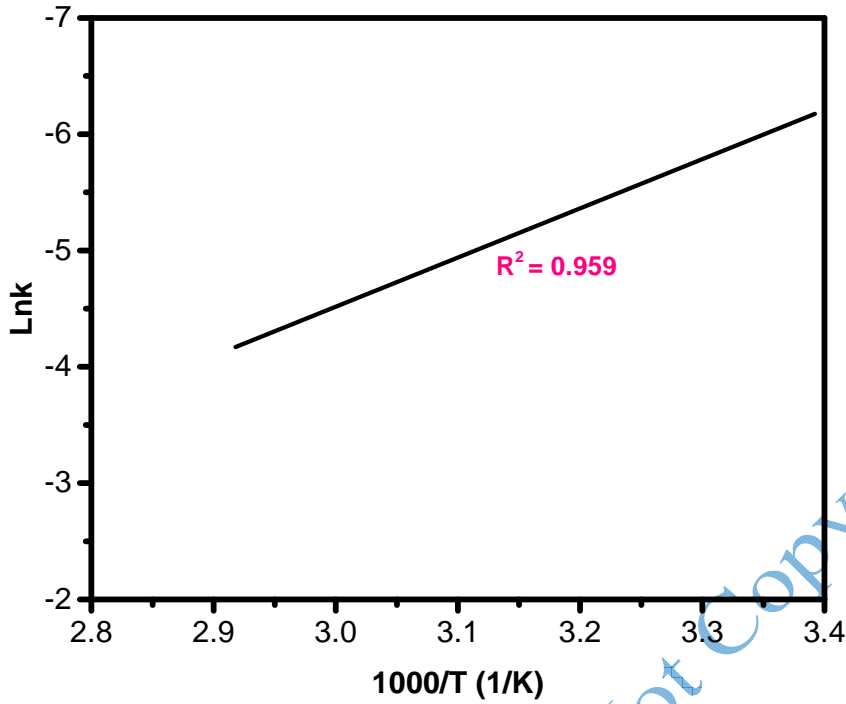


Figure 10: Relationship between $\ln k$ and T^{-1}

Therefore, the effect of temperature on indium dissolution rate is expressed with equation 7.

$$\ln(k_c) = 10.98 - 5.359 \times 10^3 T^{-1} \quad (7)$$

Considering the leaching process depends on temperature based on the Arrhenius equation, the relationship between the logarithm of the apparent rate constant and temperature inverse is rewritten in equation 8.

$$\ln(k_c) = \ln A - \frac{Q}{R} T^{-1} \quad (8)$$

Where A indicates the coefficient of constant to temperature, Q represents activation energy, and R and T show universal gas constant and absolute temperature, respectively. Comparing the equations of 7 and 8, the activation energy of indium dissolution was determined 44.55 KJ/mole, confirming that indium dissolution process is considered as chemical reaction-controlled. Based on the comparison of this value with 68.8 KJ/mole [34] and 53.55 KJ/mole [6], adding oxalic acid into sulfuric acid in solvent composition leads to decreasing the dependency of indium dissolution rate on temperature changes.

3.3.4. The relationship between rate and acid concentration (the calculation of reaction order)

Fig. 11 represents the curve of $1 - (1 - x)^{1/3}$ against time in different concentrations of acid.

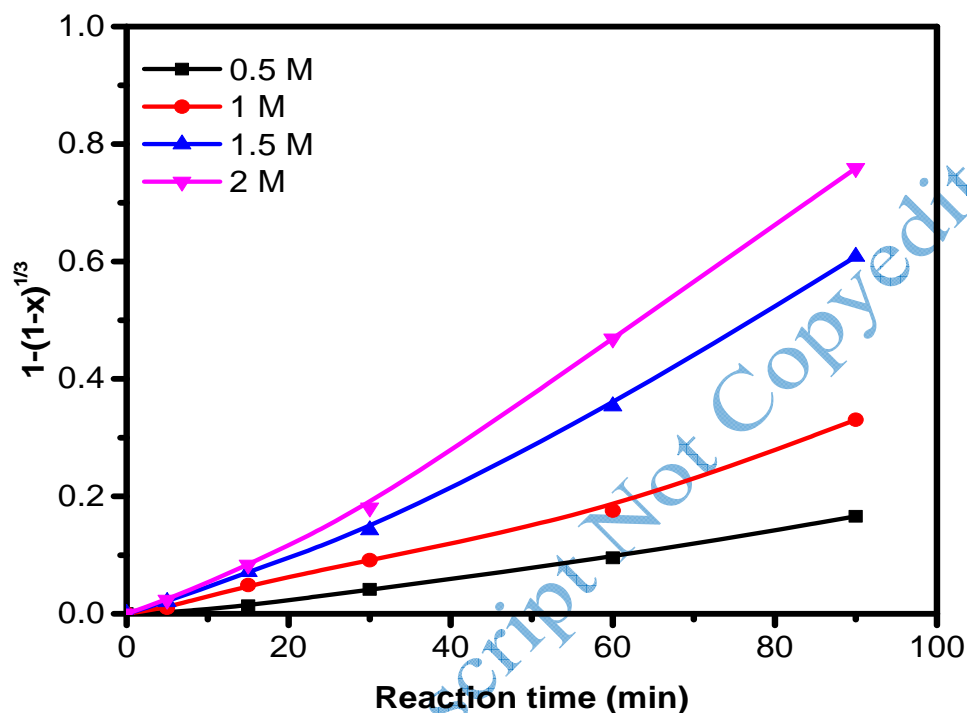


Figure 11: Plot of $1 - (1 - x)^{1/3}$ versus t at different acid concentrations

The curve related to the logarithm of the apparent rate constant versus the logarithm of the concentration changes of acid is presented in Fig. 12 by using the gradient values of the lines matched with data derived from Fig. 11.

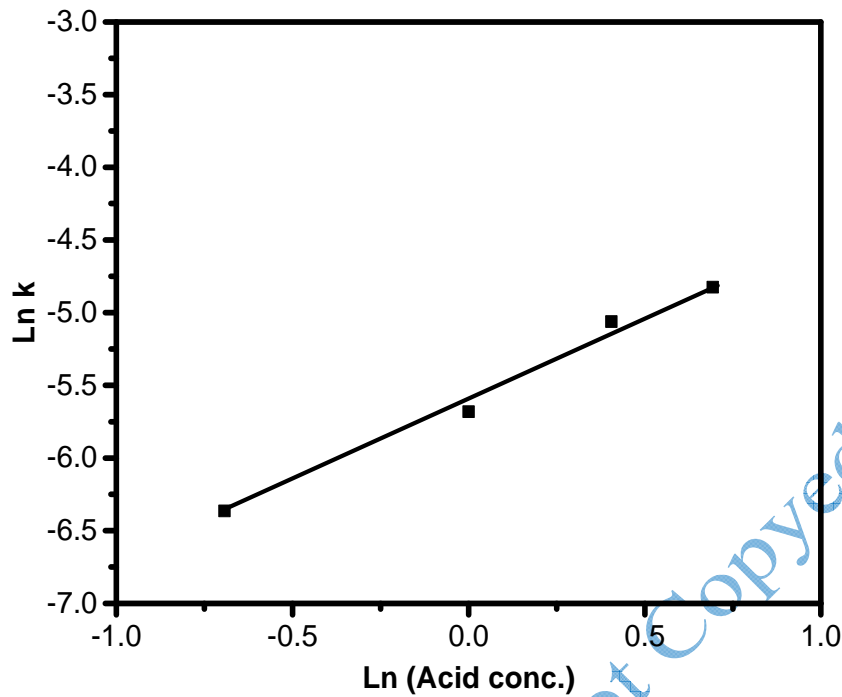


Figure 12: Relationship between $\ln k$ and $\ln C$

Accordingly, equation 9 indicates the effect of acid concentration on indium dissolution rate.

$$\ln(k_c) = -5.598 + 1.142 \times \ln C \quad (9)$$

According to the law of mass action, the relationship between the logarithm of the apparent rate constant and the logarithm of acid concentration is rewritten in equation 10.

$$\ln(k_c) = \ln A' + n \ln C \quad (10)$$

In this equation, A' corresponds to the coefficient of constant to the changes of acid concentration, n indicates the reaction order in leaching with respect to acid concentration and C refers to acid concentration. The comparison of equations 9 and 10 represents that the reaction order in leaching with respect to acid concentration is determined 1.14. Comparing this value with 0.69 [9, 34] and 0.75 [35], the addition of oxalic acid into sulfuric acid in solvent composition results in increasing the dependency of indium dissolution rate to the concentration changes of acid.

3.3.5. The rate equation of indium dissolution

Apparent rate constant for the chemical reaction-controlled process is related to the parameters affecting process based on equation 11.

$$k_c = \frac{k_r C^n}{r_0 \rho} \quad (11)$$

Where k_r indicates the rate constant of chemical reaction, C represents acid concentration, n refers to reaction order with respect to acid, and r_0 and ρ correspond to the size of primary particles and the density of solid particles, respectively. According to equation 12, k_r is assigned to temperature through the Arrhenius equation, similar to k_c .

$$k_r = A_0 \exp\left(-\frac{Q}{RT}\right) \quad (12)$$

By combining equations 3, 11 and 12, the rate equation of indium dissolution based on variable parameters is written as equation 13.

$$1 - (1 - x)^{1/3} = \frac{A_0}{\rho} \times \frac{C^n}{r_0} \exp\left(-\frac{Q}{RT}\right) t \quad (13)$$

The curve of $1 - (1 - x)^{1/3}$ against $\frac{C^{1.14}}{r_0} \exp\left(-\frac{44550}{8.314T}\right) t$ is drawn for different experimental data in Fig. 13.

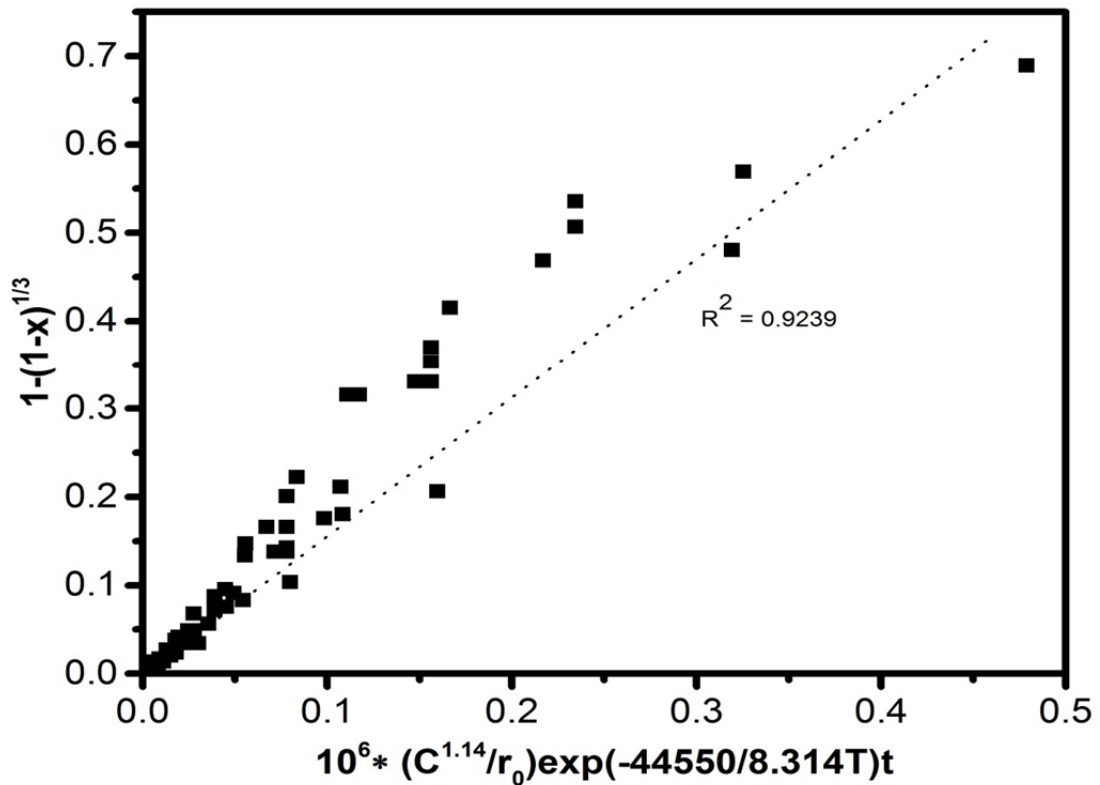


Figure 13: Plot of $1 - (1 - x)^{1/3}$ versus $[10^6 (C^{1.14}/r_0) \exp(-44550/8.314T) t]$

The $\frac{A_0}{\rho}$ coefficient was calculated 1.869×10^6 by measuring the gradient of the straight line passing among the points of the curve.

By the placement of the obtained values related to the activation energy, reaction order and $\frac{A_0}{\rho}$ coefficient in equation 13, the final rate equation is written as equation 14.

$$1 - (1 - x)^{1/3} = 1.869 \times 10^6 \times \frac{C^{1.14}}{r_0} \exp\left(-\frac{44550}{8.314T}\right) t \quad (14)$$

Where x is the dissolution rate of indium (%), C is the acid concentration (M), r_0 is the average grain size (μm), T is the leaching temperature (K), and t is time (min).

4. Conclusions

The present study assessed the effect of the ratio of oxalic acid to sulfuric acid, stirring rate, temperature, grain size and acid concentration on the extraction kinetics of indium from the residue of zinc concentrate leaching.

The results indicated that reductive leaching method can be appropriately used to leach the oxidic compound of zinc ferrite with low dissolution power. Oxalic acid as a reducer was successfully used compared to other reducers due to its reducing power, the ability to form complex, less contamination and hydrogen ion production. Based on the kinetic model of shrinking-core, indium dissolution rate is regarded as chemical reaction-controlled under mentioned conditions. In addition, the comparison of the activation energy of 44.55 KJ/mole and the reaction order with respect to acid concentration of 1.14 which were obtained in the present study with those in other studies indicates that the presence of oxalic acid in solvent composition leads to the lower dependency of indium dissolution to temperature changes and its relatively higher dependency to concentration changes.

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