ELSEVIER

Chemical Engineering Journal 141 (2008) 233–241

Chemical Engineering Journal

www.elsevier.com/locate/cej

Determination of semi empirical kinetic model for dissolution of bauxite ore with sulfuric acid: Parametric cumulative effect on the Arrhenius parameters

Zafar Iqbal Zafar*

Department of Chemistry, Bahauddin Zakariya University, Multan 60800, Pakistan

Received 14 June 2007; received in revised form 9 December 2007; accepted 28 December 2007

Abstract

Sulfuric acid was used to investigate the dissolution of bauxite ore. It was found that the dissolution rate increased with an increase in the acid concentration, liquid/solid ratio, stirring speed and temperature along with a decrease in the particle size of the sample. The dissolution curves were evaluated in order to test the validity of kinetic models for liquid/solid systems. The results were analyzed by graphical and statistical methods and it was found that the dissolution of the bauxite ore was controlled by shrinking core model, i.e., $[1-(1-\alpha)^{1/3}]^2 = 7.6495 \times 10^2 D^{-1.0114} C^{0.9105} (L/S)^{0.5969} \mathrm{SS}^{0.3032} \mathrm{e}^{-65.0436/\mathrm{RT}}{}_t$. The apparent activation energy of the process was found to be 65043.61367 $\mathrm{J\,mol^{-1}}$ over the reaction temperature range from 358 to 398 K. The cumulative effect of parameters on the dissolution process was investigated. The results indicated that the parametric cumulative effect (PCE) on the Arrhenius parameters was controlled by an exponential relation, i.e. $A_\mathrm{o} = f(E_\mathrm{a}) = A\mathrm{e}^{Z_\mathrm{iz} E_\mathrm{o}}$, where A (=$9.65595 \times 10^{-42}\,\mathrm{min^{-1}}$) is pre-exponential factor and Z_iz (=$1.5582\,\mathrm{mol\,kJ^{-1}\,min^{-1}}$) is energy sensitivity coefficient of the parameters.

Keywords: Dissolution model; Bauxite ore; Sulfuric acid; Parametric cumulative effect

1. Introduction

Bauxite ores can be used for the production of alum depending on the type and nature of impurities such as silica, iron oxide, titania, calcareous and dolomitic impurities. For the production of aluminium metal, most of the bauxite ore is consumed in the metallurgical industrial sector in the world [1]. The ores can also be mined for direct use in high alumina refractories as well as for the production of alum in various commercial forms and technical grades depending on the type and nature of impurities. For the dissolution of low-grade bauxite ore, Hulbert and Huff [2] used mineral acid and the results indicated that the rate of calcined bauxite dissolution was fastest with hydrochloric acid, slower with sulfuric acid, and slowest with nitric acid. In the case of sulfuric acid, the results also showed that the rate-controlling step was the diffusion of hydronium ions to the phase boundary. Paspalliaris and Tsolakis [3] used hydrochloric acid to dissolve the bauxite ore and the results showed that the rate of dissolution of iron followed the shrinking core model along with variation in the activation energy of 80.3, 73.6, 64.0 and 63.6 $\mathrm{kJ\,mol^{-1}}$ for the average particle size of 426.5, 256, 161.5 and 74.5 μm, respectively.

Patermarakis and Paspaliaris [4] investigated the leaching of iron from the low-grade bauxite ore using hydrochloric acid and the data fitted the shrinking core model. The results also suggested that the leaching of bauxite specimens was controlled by diffusion of the acid through the pores formed by dissolution of hematite and γ-AlOOH along with the estimated activation energy of 19.6 $\mathrm{kJ\,mol^{-1}}$. Zivkovic and Strbac [5] carried out the dissolution of low-grade bauxite ore with hydrochloric acid and the results showed that the rate of leaching of hematite was controlled by the first order kinetics fitting the progressive conversion model, while the rate of dissolution of kaolinite was found to be a chemically controlled process. The amount of activation energies was found to be 106 and 68 $\mathrm{kJ\,mol^{-1}}$ for hematite and kaolinite, respectively. In another similar work, Reddy et al. [6] claimed that the rate of dissolution of iron from gibbsitic bauxite ore followed the first order kinetics fitting the progres-

---

* Tel.: +92 61 9210075x2405; fax: +92 61 9210068.
E-mail address: drzafarbzu@hotmail.com.

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.12.025

Nomenclature

A_o	pre-exponential factor (min^{-1})
C	acid concentration (M)
D	average diameter of particle (mm)
E_a	activation energy ($J mol^{-1}$)
EDX	energy dispersive X-ray analysis
ER	relative mean square of errors
k	reaction rate constant (min^{-1})
k_s	surface reaction rate constant ($m\,min^{-1}$)
L/S	liquid/solid ratio ($cm^3\,g^{-1}$)
N	number of experimental data
SS	stirring speed (min^{-1})
t	reaction time (min)
T	reaction temperature (K)
Z_{iz}	energy sensitivity coefficient ($mol\,kJ^{-1}\,min^{-1}$)
Greek symbols	
α_{cal}	predicted fraction of Al^{+++} (–)
α_{cxp}	dissolved fraction of Al^{+++} (–)

sive conversion model along with apparent activation energy of 81.0 kJ mol^{-1}. The literature survey reveals that the variation in activation energy and fitting of the experimental data may vary from ore to ore and deposit to deposit depending on the type and nature of impurities as well as the parametric process conditions.

The composition of bauxite ores varies from source to source. Therefore, these ores from different deposits may be expected to behave differently in dissolution processes. A number of physicochemical techniques such as magnetic separation and reduction roasting are available to remove the impurities from low-grade bauxite ores, but these techniques could only meet with marginal fruitful results [7]. Magnetic or other physical separation techniques may be used to remove iron impurities from the bauxite ores. However, when the iron impurities present in the bauxite ore are too weakly magnetic and/or too finely divided, they cannot be removed appreciably by magnetic separation used either alone or in concert with other physical up-gradation methods [8]. Dissolving bauxite or clays with sulfuric acid, alum may be produced depending on the impurities present in the bauxite ores. However, the role of type and nature of impurities may not be ignored as the presence of these impurities is expected to influence the choice of process technology as well as the economy of the process.

Using sulfuric acid for the dissolution of low-grade bauxite ores, after calcination at higher temperatures, a number of studies [9–11] have been carried out. A number of low-grade bauxite deposits are available in Pakistan. These sources also contain high aluminous clays in salt range and Kalachatta range of Khushab and Attock areas of the country [12–15]. However, Pakistan has to import a considerable amount of $Al(OH)_3$ and Al_2O_3 to produce aluminium sulfate (commercially known as Filter Aalum) to meet its requirements for paper, water and sewage treatments, pharmaceutical and various other allied chemical industries. Without prior calcinations of bauxite ore, alum can be produced from low-grade bauxite ore [16]. However, no guidelines are available for the dissolution kinetics of indigenous calcined bauxite ore. Therefore, in the present work, the low-grade calcined bauxite ore has been treated with sulfuric acid to study the kinetics of the dissolution process.

2. Dissolution of bauxite ore

In the dissolution of bauxite ore with sulfuric acid the following reactions may occur:

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O \quad (1)$$

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O \quad (2)$$

$$TiO_2 + H_2SO_4 \rightarrow TiOSO_4 + H_2O \quad (3)$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \quad (4)$$

The kinetic study of reaction (1) is the main interest of the present work. The degree of dissolution of bauxite ore in reaction (1) will depend on the type and nature of material as well as the reaction parameter conditions. For selective dissolution at specific reaction conditions, the reaction (1) should compete with the other three reactions (2–4) towards its completion or equilibrium depending on the solubility product (K_{sp}) of $Al_2(SO_4)_3$ as well as the degree of ionization of the leaching agent. The reaction mechanism may involve a number of elementary steps regarding the ionization of sulfuric acid, dissolution of the ore and formation of the product. However, a simplified reaction mechanism for reaction (1) may be given:

$$H_2SO_4 + H_2O \Leftrightarrow HSO_4{}^{-1} + H_3O^{+1} \quad (1.1)$$

$$HSO_4{}^{-1} + H_2O \Leftrightarrow SO_4{}^{-2} + H_3O^{+1} \quad (1.2)$$

$$Al_2O_3 + 3SO_4{}^{-2} \Leftrightarrow Al_2(SO_4)_3 + 3O^{-2} \quad (1.3)$$

$$2H_3O^{+1} + O^{-2} \Leftrightarrow 3H_2O \quad (1.4)$$

The rate of dissolution would be controlled by the slowest of these sequential steps. According to the elementary steps, it would be expected that the solubility of $Al_2(SO_4)_3$ and the diffusion of hydronium ions may control the overall kinetics of the leaching process depending on the reaction conditions.

The reaction (2) is also expected to proceed during the dissolution of bauxite depending on the concentration of the leaching agent. Reactions (3) and (4) may occur under the conditions given but, due to the low $CaCO_3$ and TiO_2 contents in the bauxite are not discussed. Here it is worth mentioning that any strong acid cannot be expected to appreciably react with calcareous material [17,18] due to the large polarity of the acid O–H bond. Therefore, at relatively high concentration of the acid, the degree of dissolution of calcareous impurities may not be significant in the present case. On the other hand, the dissolution of anatase may be expected at relatively high concentrations of the acid. Liang et al. [19] used sulfuric acid to produce $TiOSO_4$ and the results indicated that the acid concentration of 15.4 M could achieve the appreciable degree of dissolution of the ilmenite ore. The results showed that the leaching kinetics could be described by shrinking core model along with estimated activation energy

Table 1
Analysis of the ore samples

Sample(mesh)	Size (mm)	Al_2O_3%	SiO_2%	Fe_2O_3%	TiO_2%	CaO%	LOI%
−80 + 100	−0.175 + 0.147	64.3	13.6	2.2	3.2	3.7	12.2
−100 + 115	−0.147 + 0.125	64.7	13.5	2.7	3.7	2.8	12.1
−115 + 150	−0.125 + 0.104	64.5	13.3	2.8	3.4	2.6	12.9
−150 + 170	−0.104 + 0.089	64.8	13.7	2.3	3.6	2.7	12.3
−170 + 200	−0.089 + 0.074	64.4	13.9	2.1	3.3	2.6	12.5

of 72.6 kJ mol^{-1}. The leaching of hematite during the course of dissolution was also observed depending on the concentration of the acid and, at higher concentration of the acid, the dissolution of iron was found to be relatively low than the aluminum [19]. Ata et al. [20] studied the leaching of malachite ore with sulfuric acid and the results showed that the dissolution of Cu was about 99.9%, while the dissolution of Fe in the acid was only up to 40%. However, in the present case of dissolution the total amount of iron sulfate formation was not significant due to the lower content of iron present in the bauxite ore. The alum with relatively high content of iron may not be used to produce alumina by the Bayer process or for the production of anhydrous aluminum chloride. However, the alumino ferric type of filter alum may be used for water and sewage treatment purposes as well as for paper industry depending on the quality of the paper and paper products.

3. Methods and material

3.1. Sample preparation and analysis

The present work is aimed to study the dissolution kinetics of low-grade bauxite ore from Khushab (Pakistan). The bauxite sample was crushed and sieved using US. Tyler standard sieves to collect the different size fraction for analysis. The sieved sample was dried in an electric oven at about 105 °C, cooled to room temperature and stored in closed desiccators. The sample was analyzed for the main conditions, namely, Al_2O_3, SiO_2, Fe_2O_3, TiO_2, CaO and loss on ignition (LOI) contents as shown in Table 1. Atomic Absorption Spectrophotometer (AAS) and conventional [21,22] methods were used for analysis. Energy dispersive X-ray (EDX) analysis technique was also used for the analysis of the bauxite ore. The EDX spectrum indicates the elemental composition of the raw bauxite particles as shown in Fig. 1. It shows the presence of inorganic elements, which basically consists of boehmite, hematite, kaolinite and anatase. The profile indicates that the bauxite ore has a high percentage of aluminium and oxygen along with the presence of different impurities in the ore matrix.

3.2. Experimental procedure

For reaction kinetic study, different size fractions were used in a well-mixed spherical batch reactor (500 mL) heated by a constant temperature bath and equipped with a mechanical stirrer. A thermostat was used to control the temperature of the reactor content. A cooler was also attached to the reactor to avoid the loss of reactor content by evaporation as shown in Fig. 2. A specific amount of sulfuric acid was slowly added into the reactor vessel containing a known amount of the sample for each run. The reaction vessel was immediately placed in an ice bath to stop the reaction at the end of each experimental run. The leach slurry was separated by filtration before weighing and analysis. The rate of change in pH value may be exploited to study the reaction kinetics and mechanism for liquid/solid dissolution systems [23–25]. However, in the present case, atomic absorption spectrophotometer and conventional methods were used for analysis as mentioned before. The conversion of Al^{3+} content in the leach solution was determined by using Eq. (5). In the analysis, the dissolution fraction of Al^{+3} was calculated by Eq. (5):

$$\alpha_{\mathrm{exp}} = \frac{\text{Amount of } Al^{3+} \text{ in the solution}}{\text{Total amount of } Al^{3+} \text{ in original sample}} \quad (5)$$

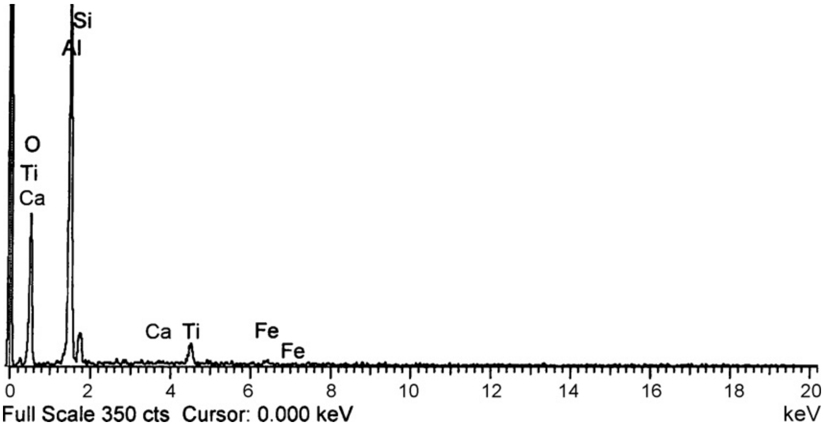

Fig. 1. EDX profile of the sample.

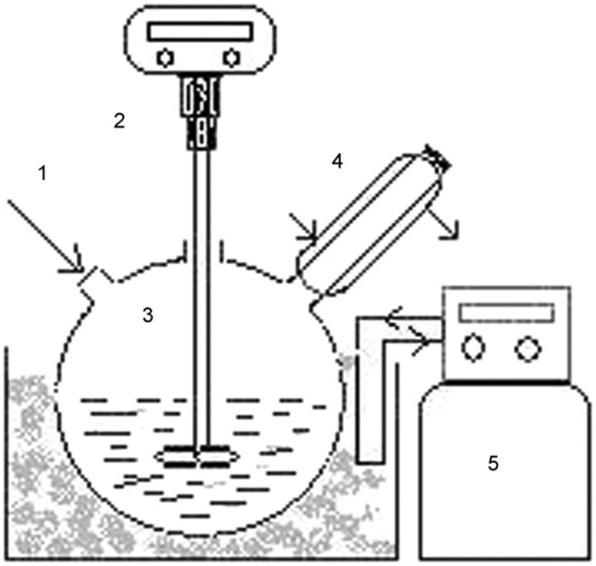

Fig. 2. Schematic view of experimental set up. (1) leaching agent inlet, (2) mechanical stirrer, (3) reactor, (4) condenser, (5) thermostat.

4. Results and discussion

4.1. Effect of reaction parameters

A number of experiments were carried out to see the effect of reaction time on the leaching of bauxite ore at different acid concentration, liquid/solid ratio, particle size, stirring speed and reaction temperature as shown in Figs. 3–7 respectively. The experimental results indicate that the dissolution rate of bauxite ore increases with increasing the acid concentration and liquid solid ratio depending on the dissolution conditions as shown in Figs. 3 and 4 respectively. Fig. 3 shows that the concentration has a significant effect on the rate of dissolution of the bauxite ore. In the present case, increasing the acid concentration can increase the efficiency of the leaching process. The pH depends on the leaching agent concentration and its degree of ionization. The pH decreases as the concentration of the acid increases. However, higher concentration, after a specific concentration of the leaching agent, may cause an increase in the dissolved fraction of silica in the process. The higher concentration of the acid resulted in the decrease of dissolution rate of calcareous

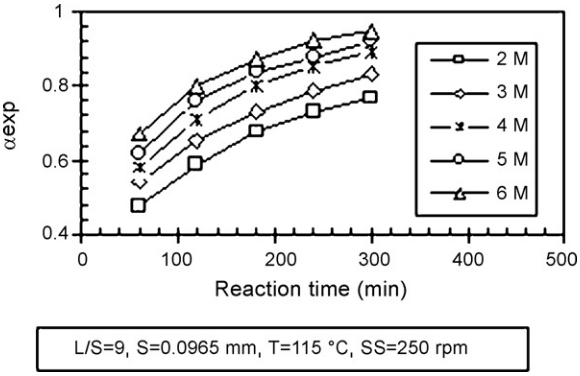

Fig. 3. Effect of reaction time on the conversion at different acid concentrations.

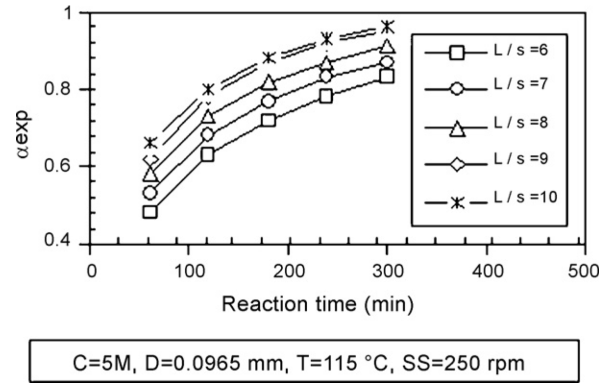

Fig. 4. Effect of reaction time on the conversion at various liquid/solid ratios.

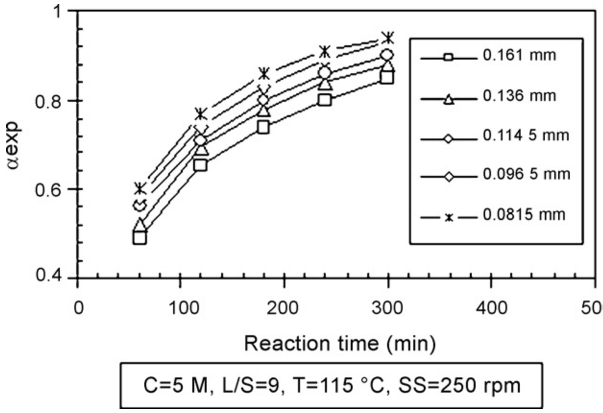

Fig. 5. Effect of reaction time on the conversion at varying particle size.

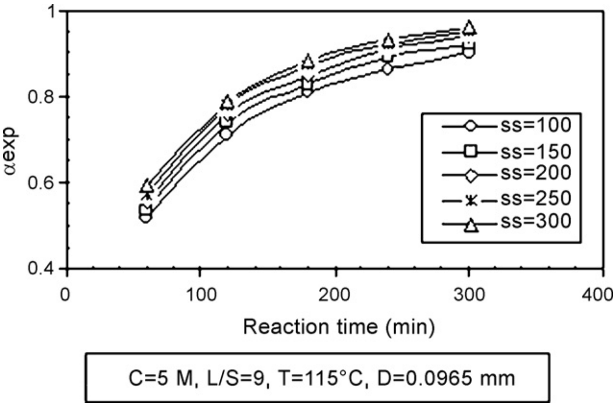

Fig. 6. Effect of reaction time on the conversion at different stirring speed.

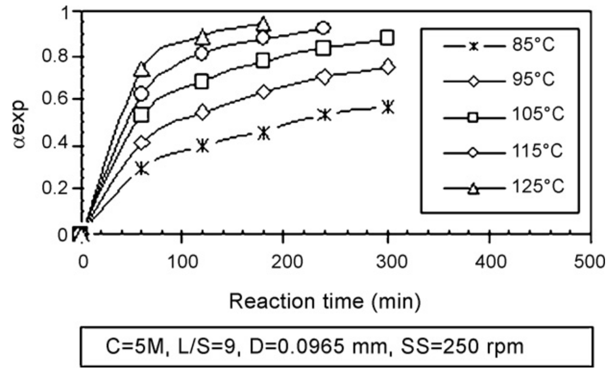

Fig. 7. Effect of reaction time on the conversion at various temperatures.

material in the rock, a situation that could be attributed to the increase in the polarity of the acid O–H bond decreasing the number of hydrogen ions and proton activity due to the decrease in water amount more and more in the medium [18]. In the present case, at higher concentration of the acid, a small fraction of unreacted acid has been observed. Therefore, the leach slurry may be recycled back into the process to consume the traces of unreacted acid or aluminium hydroxide may be used to appreciably increase the yield of the required product. On the other hand, at lower concentration of the acid the rate of dissolution of calcareous impurities may increase along with the dissolution of the required material. Fig. 4 shows that the rate of dissolution increases with an increase in the liquid solid ratio. The results indicate that the liquid solid ratio also appears to have a significant effect on the rate of dissolution of the bauxite ore.

Experiments were also performed to see the effect of dissolution time on the leaching of bauxite ore at varying particle size and stirring speed at the known parameter conditions as shown in Figs. 5 and 6, respectively. The bauxite leaching rate curves show that the rate of dissolution of the ore increases by decreasing the particle size of the ore, which can be attributed to the fact that the overall surface area per unit weight of sample increases due to an increase in the degree of size reduction of the ore. The efficiency of the dissolution process may be increased by further reduction in particle size of the bauxite ore. On the other hand, the effect of stirring speed on the dissolution rate of bauxite ore is relatively low as shown in Fig. 6. For the specific parameter conditions, Fig. 7 shows the effect of leaching time on the dissolution of low-grade bauxite ore at different temperatures. The bauxite leaching rate curves show that the rate of dissolution of the ore increases by increasing the reaction temperature. The results indicate that the temperature effect on the dissolution rate is much higher as compared to the acid concentration as well as liquid solid ratio used the process. To study the temperature influence, it may be better to use temperatures up to about 60–70 °C for avoiding the solvent loss due to evaporation. Generally, temperature is the most effective parameter regarding reaction kinetics of chemical processes. Most of industrial reactions are carried out relatively at higher temperatures to increase the overall efficiency of a process as well as to avoid the side reactions. In the present case, the reaction conditions have been used in accordance with industrial operations. At higher temperature the rate of dissolution is relatively low, a situation that may be attributed to the decrease in solubility of the product at higher temperatures causing the formation of solid product and/or of saturated solid/liquid interface on the surface of the particle.

4.2. Kinetic analysis

For a liquid/solid reaction system, the reaction rate is generally controlled by one of the following steps: diffusion through the liquid film, diffusion through the ash/product layer or the chemical reaction at the surface of the solid particles [26]. The rate of the process would be controlled by the slowest of these sequential steps. The reaction model between a liquid and a solid may be given as:

$$A_{(\text{liquid})} + \text{bB}_{(\text{solid})} \rightarrow \text{Products} \tag{6}$$

Let the time of completion of the leaching process be t^*, the fractional conversion of bauxite be α and at any time t the integrated equations for liquid/solid heterogeneous reactions are:

for film diffusion control,

$$t = t^*[1 - (1 - \alpha)] \tag{7}$$

for chemical reaction control,

$$t = t^*[1 - (1 - \alpha)^{1/3}] \tag{8}$$

and for ash diffusion control,

$$t = t^*[1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)] \tag{9}$$

The value of t^* depends on the reaction parameters in accordance with the kinetic models. For example, for a chemical reaction controlled model, Eq. (8) t^* is:

$$t^* = \frac{\rho_B R_o}{b k_s C_A} \tag{10}$$

where t^* is the time for complete dissolution (min), ρ_B is the molar density of the solid reactant (mol m^{-3}), R_o is the radius of the solid particle (m), b is the stoichiometric coefficient of the solid, k_s is the surface reaction rate constant (m min^{-1}) and C_A is the acid concentration (mol m^{-3}). To determine the kinetic parameters and rate-controlling step for the dissolution of bauxite ore, the experimental data have been analyzed on the basis of liquid/solid heterogeneous reaction models, Eqs. (7)–(9). The data did not fit these models. However, for a diffusion-controlled reaction through a non-porous product layer to a shrinking core of unreacted spherical particle, with the assumption that the product layer has the same volume as the reactant, the data may be analyzed by Jander's equation [27].

The validity of the experimental data into the integral rate was tested by statistical and graphical methods. The kinetic analysis results for the dissolution process were found to be consistent with the Jander's model and the integral rate expression was determined to follow the following rate equation:

$$[1 - (1 - \alpha)^{1/3}]^2 = kt \tag{11}$$

where k is the overall reaction rate constant (min^{-1}). Using the conversion of Al^{+3} the values for rate constant, k, can be determined at different reaction temperatures by plotting $[1-(1-\alpha)^{1/3}]^2$ versus t as shown in Fig. 8. After the estimation of activation energy and pre-exponential factor, the kinetic model for the dissolution of bauxite ore may be expressed as:

$$[1 - (1 - \alpha)^{1/3}]^2 = A_o \, e^{-E_a/RT} t \tag{12}$$

The Arrhenius plot can be used to evaluate the activation energy if the reaction mechanism is assumed to remain unchanged over the temperature range of the experiments. To explain the dissolution of bauxite ore, the above kinetic model, Eq. (12) is not expected to hold good for different parameter conditions as its applicability is limited by the specific values used

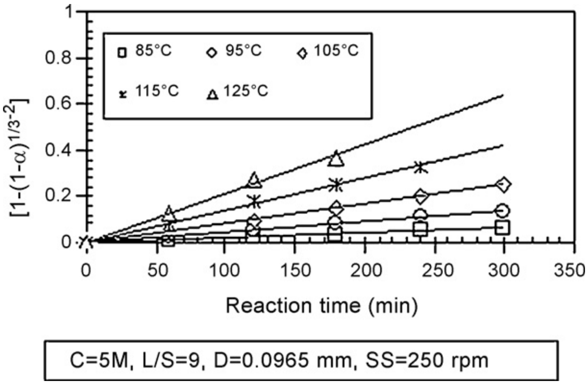

Fig. 8. Plot between $[1-(1-\alpha_{\mathrm{exp}})^{1/3}]^2$ and reaction time.

in the dissolution process. The results show that, along with temperature, the other parameters also affect the rate of dissolution and they may be included in the model, Eq. (12). Therefore, to study the parametric cumulative effect on the Arrhenius parameters all the reaction parameters have been included in the model, Eq. (12).

4.3. Parametric cumulative effect on the Arrhenius parameters

Based on the rate constant determined by the temperature along, the designing of industrial equipments may not be fruitful if the reaction parameter conditions affect the kinetic rate constant in the liquid/solid dissolution systems. The distribution of active reaction sites may cause the variation in the apparent value of activation energy depending on the type and nature of materials. In a number of heterogeneous reactions, the experimentally determined activation energy has been found to vary with various factors such as particle size, heating rate, presence of impurities, acid concentrations and pretreatment of the samples. Such factors may generally be categorized as those concerned with the experimental procedure and those connected with the type and nature of materials to be treated in the process. The literature survey reveals that a number of semi empirical models have been suggested for liquid/solid heterogeneous systems [17,18,28–31]. However, no guidelines are available to highlight the interesting aspect of parametric cumulative effect (PCE) on the Arrhenius parameters. Therefore, to see the parametric cumulative effect on the Arrhenius parameters the following semi empirical models may be considered including the Arrhenius law:

$$k = A_{\mathrm{o}}\mathrm{e}^{-E_{\mathrm{a}}/\mathrm{RT}} \quad (13)$$

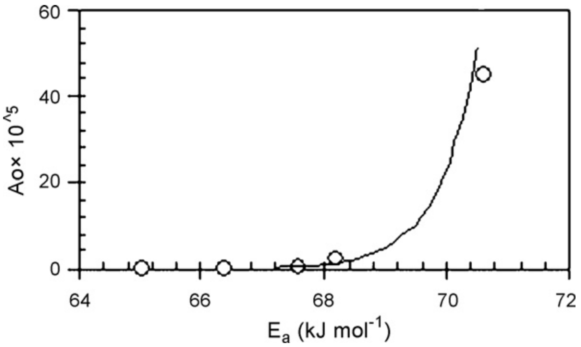

Fig. 9. Plot between A_{o} and E_{a}.

$$k = A_{\mathrm{o}}\mathrm{SS}^{\mathrm{d}}\mathrm{e}^{-E_{\mathrm{a}}/\mathrm{RT}} \quad (14)$$

$$k = A_{\mathrm{o}}(L/S)^{\mathrm{c}}\mathrm{SS}^{\mathrm{d}}\mathrm{e}^{-E_{\mathrm{a}}/\mathrm{RT}} \quad (15)$$

$$k = A_{\mathrm{o}}C^{\mathrm{b}}(L/S)^{\mathrm{c}}\mathrm{SS}^{\mathrm{d}}\mathrm{e}^{-E_{\mathrm{a}}/\mathrm{RT}} \quad (16)$$

$$k = A_{\mathrm{o}}D^{\mathrm{a}}C^{\mathrm{b}}(L/S)^{\mathrm{c}}\mathrm{SS}^{\mathrm{d}}\mathrm{e}^{-E_{\mathrm{a}}/\mathrm{RT}} \quad (17)$$

To evaluate the regression coefficients and constants, these equations may be analyzed by simultaneous multiple regression. For simultaneous multiple regressions a computer program was used to evaluate the regression coefficients in the above mentioned kinetic models. After simultaneous multiple regression, the values of the constants and the Arrhenius parameters have been calculated as shown in Table 2. The results show that the amount of estimated activation energy decreases along with the decrease in the Arrhenius pre exponential factor due to the cumulative effect of parameters on the reaction kinetics of the dissolution process. The results of Table 2 show that the parametric cumulative effect also affects the values of the multiple regression constants along with the change in the Arrhenius parameters.

The resultant data given in Table 2 were analyzed by graphical and statistical methods in order to see the parametric cumulative effect on the Arrhenius parameters as shown in Fig. 9. The results show that the parametric cumulative effect on the Arrhenius parameters follows an exponential relation, i.e.

$$A_{\mathrm{o}} = f(E_{\mathrm{a}}) = A\mathrm{e}^{Z_{\mathrm{iz}}\mathrm{E}_{\mathrm{o}}} \quad (18)$$

where A is pre-exponential factor and Z_{iz} is energy sensitivity coefficient of the reaction parameters involved the dissolution process:

$$Z_{\mathrm{iz}} = 1.5582\,\mathrm{mol\,kJ^{-1}\,min^{-1}}$$
$$A = 9.65595 \times 10^{-42}\,\mathrm{min^{-1}}$$

Table 2
The regression results for the parametric cumulative effect on the Arrhenius parameters

Model	$\ln A_{\mathrm{o}}$	E_{a}/R	*a*	*b*	*c*	*d*	SE	R^2
Eq. (13)	15.31124	8493.652568	–	–	–	–	0.0883	0.9892
Eq. (14)	12.33345	8200.522849	–	–	–	0.39237	0.1066	0.9732
Eq. (15)	10.78339	8129.48158	–	–	0.65816	0.37558	0.0911	0.9734
Eq. (16)	9.107586	7983.42054	–	0.9483	0.62896	0.34106	0.0959	0.9648
Eq. (17)	6.639807	7823.38389	−1.01137	0.9105	0.59698	0.30324	0.0987	0.9549

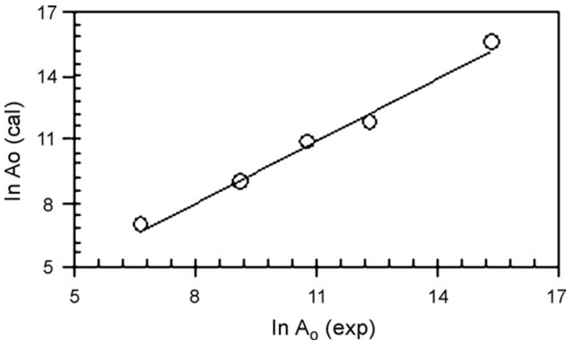

Fig. 10. Agreement between the values of pre-exponential factor.

The agreement between the experimental values and the calculated ones from the suggested exponential model, Eq. (18) has been tested by plotting $\ln A_{o(\exp)}$ versus $\ln A_{o(\mathrm{cal})}$ as shown in Fig. 10. The scatter diagram shows that the agreement between the experimental and calculated values is fairly good with a correlation coefficient of 0.9946 and standard error of the estimate of 0.0598. It is worth mentioning that the applicability of the suggested model Eq. (18) can also be tested in terms of the activation energy as shown in Fig. 11. Again, the results show a good relationship between the variables with a correlation coefficient of 0.9946 and standard error of the estimate of 0.0605. The coefficient of determination has been found to be 0.9891 for both of the relations tested. The value of the energy sensitivity coefficient shows the parametric contribution effect on the Arrhenius parameters, affecting the overall reaction kinetics of the dissolution process. It might be expected that the liquid/solid dissolution systems may show a specific energy sensitivity coefficient, depending on the parameter conditions as well as the type and nature of materials.

To illustrate the dissolution process of bauxite ore, the semi empirical models can be suggested using the regression analysis results. Putting the values of parameters, after the comparison of Eq. (11) with Eqs. (13–17), it follows that:

$$[1-(1-\alpha)^{1/3}]^2 = 4.4626 \times 10^6 \mathrm{e}^{-70.6162/\mathrm{RT}} t \tag{19}$$

$$[1-(1-\alpha)^{1/3}]^2 = 2.2998 \times 10^5 \mathrm{SS}^{0.3924} \mathrm{e}^{-66.2803/\mathrm{RT}} t \tag{20}$$

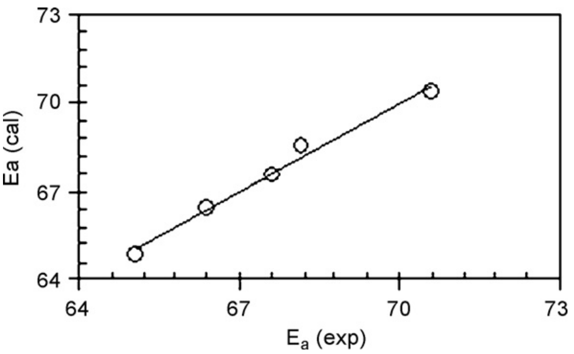

Fig. 11. Agreement between the values of activation energy.

$$[1-(1-\alpha)^{1/3}]^2 = 1.2601 \times 10^4 (L/S)^{0.6582} \mathrm{SS}^{0.3756} \mathrm{e}^{-64.0321/\mathrm{RT}} t \tag{21}$$

$$[1-(1-\alpha)^{1/3}]^2 = 3.9024 \times 10^3 C^{0.9483} (L/S)^{0.6289} \mathrm{SS}^{0.3411} \mathrm{e}^{-64.6973/\mathrm{RT}} t \tag{22}$$

$$[1-(1-\alpha)^{1/3}]^2 = 7.6495 \times 10^2 D^{-1.0114} C^{0.9105} (L/S)^{0.5969} \times \mathrm{SS}^{0.3032} \mathrm{e}^{-65.0436/\mathrm{RT}} t \tag{23}$$

In the above equations α is the conversion fraction of Al^{+3}, *D* the particle size, *C* the acid concentration, *L/S* the liquid/solid ratio, SS the stirring speed, *R*, k_o, *a*, *b*, *c*, *d* constants, *T* the reaction temperature, E_a the activation energy, *t* the reaction time for the dissolution process. The above Eq. (23) shows the effect of all the parameters included in the Arrhenius expression. For the semi empirical model, Eq. (23), the simultaneous multiple regressions gave the following values for the constants:

$$E_a = 65043.6137\,\mathrm{Jmol}^{-1},\ k_o = 7.649473 \times 10^2,$$

$$a = -1.01137,\ b = 0.9105,\ c = -0.59698 \text{ and } d = 0.30324.$$

With multiple correlation coefficient of 0.9772 and standard error of estimate of 0.0987, the regression analysis indicates that the deviation between the experimental and the calculated conversion values is not significant. The value of activation energy is found to be $65043.6137\,\mathrm{Jmol}^{-1}$, which is consistent with the values reported for the leaching of bauxite ores [3,6]. For the dissolution of bauxite ore, the literature survey indicates the different reaction mechanisms depending on the reaction conditions as well as the type and nature of the ores. The kinetic analysis for the rate production of Al^{+3} in the leach solution indicates the diffusion-controlled mechanism, which agrees with the reported findings in the similar work of bauxite ore dissolution systems [3,8,32].

The regression results show that the effect of temperature on the dissolution rate is the highest as compared to the other parameters. Higher temperature may be preferred to increase the efficiency of an industrial process by increasing the reaction rate constant. The experimental results indicate that at higher temperature the change in the rate of dissolution is relatively low, which may be attributed to the formation of solid product and/or solid/liquid interface on the surface of the particle. The results show that the effect of particle size on the dissolution kinetics is relatively higher as compared to the other parameters, which indicates the role of size reduction and the increase in surface area of the particles per unit weight of the sample. It may be attributed to the fact that the aluminium material is not freely available and lies in the pockets of the ore matrix.

As described before, the concentration has a significant effect on the rate of dissolution of the bauxite ore. The values of the constants show that the effect of acid concentration is nearly equal and opposite to the effect of particle size on the dissolution process. As compared to the other parameters, the stirring speed shows the lowest effect on the dissolution of the bauxite ore, which indicates that the leaching kinetics of the sample is diffusion-controlled process. In the dissolution of bauxite ore, Mergen et al. [32] concluded that, for diffusion-controlled reactions, the stirring speed does not affect the dissolution amounts. As compared to the stirring speed, the effect of liquid/solid ratio is significant and it is about two times the effect of stirring speed on the dissolution process.

Keeping in view the data fitting, ionization of the leaching agent and the solubility of $Al_2(SO_4)_3$ at the reaction conditions, it is expected that the diffusion of hydronium ions may control the overall kinetics of the leaching process. For the dissolution of calcined bauxite ore with sulfuric acid, Hulbert and Huff [2] investigated that the rate-controlling step could be the diffusion of hydronium ions to the phase boundary at 80 and 95 °C. The rate-determining slowest step needs further studies; however, the results show that the rate-controlling step for the overall dissolution process of the heterogeneous system is a diffusion-controlled reaction.

The agreement between the observed values of conversion and the calculated ones from the suggested model has been tested by plotting α_{exp} versus α_{cal} as shown in Fig. 12. The scatter diagram shows that the agreement between the experimental and calculated values is good with a correlation coefficient of 0.9917 and standard error of estimate of 0.0189. The value of standard error of estimate indicates that the deviation between the experimental and the calculated conversion values is small. The data in Fig. 12 shows a positive tendency to cluster around the regression line indicating the presence of a good relationship between the variables. The standard deviation of regression or standard error of estimate of α_{cal} on α_{exp} reflects that the degree of scatter of the observed values about the regression line is not significant. The relative mean square of errors of 0.02884 has been calculated by using Eq. (24):

$$\text{ER} = \left[\frac{1}{N}\sum_{i=1}^{N}\frac{(\alpha_{\text{cal}} - \alpha_{\text{exp}})^2}{(\alpha_{\text{cal}})^2}\right]^{1/2} \tag{24}$$

The calculated value of relative mean square of errors shows that, in the suggested model, such a value of the random errors is not significant.

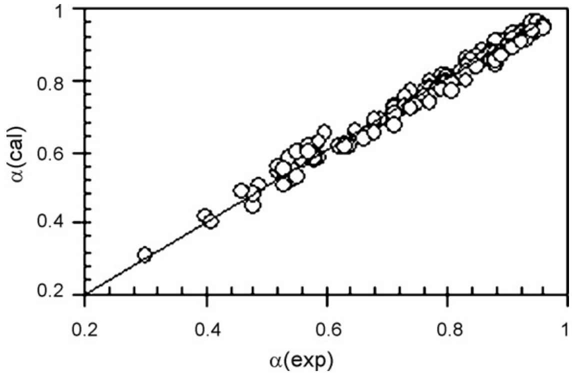

Fig. 12. Agreement between experimental and calculated conversion values.

5. Conclusions

Sulfuric acid can be used to dissolve the bauxite ore depending on the type and nature of impurities present in the ore matrix. The results show that the alumino ferric type of filter alum can be produced for water and sewage treatment purposes as well as for paper industry depending on the quality of the paper and paper products. It is found that the dissolution rate of bauxite material increases with increasing the acid concentration, liquid/solid ratio, stirring speed and temperature and decreasing particle size.

In order to see the parametric cumulative effect (PCE) on the Arrhenius parameters, the data given in Table 2 have been analyzed by graphical and statistical methods and the results show that the parametric cumulative effect on the Arrhenius parameters follows an exponential relation. The validity of the exponential model has been tested and the results show a good relationship between the variables. The energy sensitivity coefficient can be used to highlight the interesting aspect of the overall parametric contribution effect on the Arrhenius parameters. The results show that the reaction parameters may affect the reaction kinetics of liquid/solid dissolution processes. It might be expected that the energy sensitivity coefficient may depend on the parameter conditions as well as the type and nature of liquid/solid dissolution systems.

Analysis of the kinetic data by different kinetic models indicates that the dissolution of bauxite ore with sulfuric acid follows the shrinking core model with diffusion-controlled process. The value of activation energy is found to be 65043.61367 J mol^{-1}, which agrees with the values reported in literature for the dissolution of bauxite ores. A semi-empirical kinetic model, including the parameters in the dissolution process, is developed, and the model can estimate the aluminium fraction reacted with a relative mean square of errors of 0.02884. According to the analyzed results it can be recommended that the parameter values for the optimum dissolution rate are $C = 5$ M, $L/S = 9\ \text{cm}^3\,\text{g}^{-1}$, $T = 388$ K, $\text{SS} = 250\ \text{min}^{-1}$ and $D = 0.0965$ mm.

Acknowledgements

The author thanks the unknown referee for the constructive comments and improvements to the manuscript. The author would like to thank Prof. Dr. M. Shakirullah, Institute of Chemical Sciences, University of Peshawar for the analysis of samples. The author is thankful to B. Z. University, Multan for financial support and M. Ashraf for helping in the experimental work. At last but not least, he would like to appreciate the patience of his wife for the time that he spent in the department regarding the present work.

References

[1] A. Russel, Ind. Miner. 361 (1997) 39–43.
[2] S.F. Hulbert, D.E. Huff, J. Clay. Miner. 8 (1970) 337–345.
[3] Y. Paspalliaris, Y. Tsolakis, Hydrometallurgy 19 (1987) 259–266.
[4] G. Patermarakis, Y. Paspaliaris, Hydrometallurgy 23 (1989) 70–90.

[5] Z.D. Zivkovic, N.D. Strbac, Hydrometallurgy 36 (1994) 247–258.

[6] B.R. Reddy, S.K. Mishra, G.N. Banerjee, Hydrometallurgy 51 (1999) 131–138.

[7] L.Y. Sadler, C. Venkataraman, Int. J. Miner. Process. 31 (1991) 233–246.

[8] A. Mergen, Br. Ceram. Trans. 103 (2004) 42–46.

[9] Ya.Ya. Dodonov, G.V. Medoks, E.M. Soshestvenskaya, J. App. Chem. (USSR) 20 (1940) 870.

[10] L. Dubnil, Verre Silic. Ind. 12 (1947) 22.

[11] F.H. Aly, I.El. Shawarby, S.H. Eissa, M.F. Chalabi, J. Min. Met. Fuel. 29 (1981) 316.

[12] M.R. Cheema, Geol. Surv. Pak. Inf. Release No. 76, 1973.

[13] T. Hussain, A.A. Naqvi, Geol. Surv. Pak. Inf. Release No. 59, 1973.

[14] S.M.I. Shah, Geol. Surv. Pak. Rec. 52 (1980) 91.

[15] Persons/RUJV, Feasibility Study of Bauxite Preleminary Survey Report under Technical Services Project US Aid Loan No. 391-W-165, PUNJMIN, 1981.

[16] A.K. Shah, H. Mumtaz, J. Chem. Soc. Pak. 17 (1995) 216–231.

[17] M. Ashraf, Z.I. Zafar, T.M. Ansari, Hydrometallurgy 80 (2005) 286–292.

[18] Z.I. Zafar, M. Ashraf, Chem. Eng. J. 131 (2007) 41–48.

[19] B. Liang, Li. Chun, C. Zhang, Y. Zhang, J. Hydrometall. 76 (2005) 173–179.

[20] O.N. Ata, S. Colak, Z. Ekinci, M. Copur, Chem. Eng. Technol. 24 (2001) 409–413.

[21] W.W. Scott, Standard Methods of Chemical Analysis, D. Van Nostrand Company, NY, 1956.

[22] N.H. Furmann, Standard Methods of Chemical Analysis, D. Van Nostrand Company, New Jersey, 1963.

[23] E.D. Economou, T.C. Vaimakis, E.M. Papamichael, J. Colloid Interf. Sci. 245 (1) (1998) 164–171.

[24] E.D. Economou, T.C. Vaimakis, E.M. Papamichael, J. Colloid Interf. Sci. 245 (1) (2002) 133–141.

[25] C.N. Fredd, H.S. Fogler, J. Chem. Eng. Sci. 53 (1998) 3863–3874.

[26] O. Levenspiel, Chemical Reaction Engineering, second ed., Wiley, New York, 1972, pp. 357–377.

[27] W. Jander, Z. Anorg. Allg. Chem. 163 (1927) 1–52.

[28] C. Ozmetin, M.M. Kocakerim, S. Yapici, A. Yartasi, Ind. Eng. Chem. Res. 35 (1996) 2355–2359.

[29] F. Demir, B. Donmez, S. Colak, J. Chem. Eng. Jpn 36 (2003) 683–688.

[30] H. Demir, C. Ozmetin, M.M. Kocakerim, S. Yapici, M. Copur, Chem. Eng. Proc. 43 (2004) 1095–1100.

[31] L. Oral, D. Bunyamin, D. Fatih, Int. J. Miner. Proc. 75 (2005) 91–99.

[32] A. Mergen, M. Bilen, A. Buyukburc, M. Gunduz, Silic. Ind. 67 (2002) 75–80.