

Reaction Kinetic Model for Dissolution of Low Grade Bauxite Rock in Sulfuric Acid

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(Received 31st May 2007, revised 27th October 2007)

Summary: Dissolution kinetics of low-grade bauxite rock in sulfuric acid solution is studied. Using a known acid concentration and particle size of the sample, the influence of various reaction temperatures has been found in order to expound the dissolution kinetics of low-grade bauxite rock. The results show that the dissolution rate increases with increasing concentration of the acid and temperature. A kinetic model is suggested to illustrate the dissolution process of bauxite rock analyzing the kinetic data. The dissolution curves are evaluated in order to test the validity of reaction kinetic models for liquid-solid systems. The experimental data have been analyzed by graphical and statistical methods and it is found that the dissolution of bauxite in the acid is controlled by chemical reaction, i.e., $1 - (1 - \alpha)^{1/3} = 4.2354 \times 10^{-6} e^{-79.3297/RT}$. The apparent activation energy of the dissolution process has been found to be 79.3297 KJmol⁻¹ over the reaction temperature range from 348 to 378 K.

Introduction

Bauxite is a naturally occurring ore, which generally contains aluminium hydroxide minerals along with presence of relatively small amount of silica, iron oxide, titania, aluminosilicate and other impurities depending on the sources. The composition of these ores varies from one deposit to another; therefore, the bauxite ores from different sources may be expected to behave differently in dissolution processes. For the production of aluminium metal, most of the bauxite ore is consumed in the metallurgical industrial areas in the world [1]. However, it may also be mined for direct use in high alumina refractories as well as for the production of aluminum sulfate in different commercial forms and various technical grades depending on the type and nature of bauxite ores. To remove the impurities from the ores, some physicochemical methods such as magnetic separation and reduction roasting are available for up-gradation and beneficiation of bauxite ores, but these techniques and processes could meet with only marginal fruitful results [2]. A number of investigators have reported separation of iron from low-grade bauxite by hydrochloric acid leaching [3-5]. The dissolution of iron and calcium from bauxite ores by hydrochloric acid solution is appreciable as it has the advantage of selectively dissolving bauxite ore contaminating minerals at suitable rates [5]. Magnetic or other physical separation methods may be used to remove iron

from the bauxite ores. However, when the iron materials present in the bauxite ore are too weakly magnetic and/ or too finely divided, they may not be removed significantly by magnetic separation used either alone or in concert with other physical upgradation techniques [5].

After calcination of low-grade bauxite ores at higher temperatures, a number of processes have been carried out using sulfuric acid for the dissolution of the ores to produce alumina [6-8]. A number of low grade bauxite deposits are available in Pakistan. These deposits also contain high aluminous clays in salt range and Kalachatta range of Khushab and Attock areas of the country, which are spread over an area of about 150 sq. miles of these places [9-12]. However, Pakistan has to import a considerable amount of Al(OH)₃ and Al₂O₃ to produce aluminium sulfate (commercially known as Filter Alum) to meet its requirements for sizing paper in paper and pulp industries, for water and sewage treatments as well as for pharmaceutical and various other allied chemical industries. Alum can be produced by reaction of bauxite or clays with sulfuric acid depending on the impurities present in the bauxite ores. However, the role of type and nature of impurities can't 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.

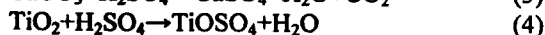
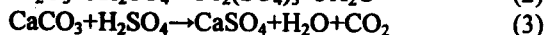
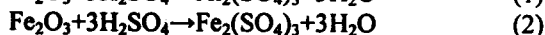
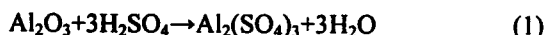
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Without prior calcinations of bauxite ore, aluminium sulfate can be produced from bauxite ore [13]. Fluid solid heterogeneous reactions are of great industrial significance regarding a number of chemical and hydrometallurgical processes. A commercial chemical process can't be developed efficiently and economically unless the reaction kinetic data are established in accordance with the experimental observations. Regarding the leaching of low grade phosphate ores, a number of dissolution processes and kinetic models are available in literature [14-17]. However, no guidelines are available about the dissolution kinetics of low grade indigenous bauxite ores. Therefore, in the present work, the low grade indigenous bauxite ore is treated with sulfuric acid to study the kinetics of the dissolution process.

Results and Discussion

Leaching of Bauxite Ore

Depending on the type and nature of the solid material as well as the reaction conditions during the leaching process of bauxite ore with sulfuric acid the following reactions may occur:



The kinetics of reaction (1) is the main object of the present work. The reaction (2) may proceed during the course of dissolution 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 bauxite are not discussed. Here it is worth mentioning that any strong acid may not react with calcareous material [15,17] 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. The leaching of hematite during the course of dissolution is also observed depending on the concentration of the acid. At higher concentration of the acid the dissolution of iron is found to be relatively low than the aluminum. Ata et al. [18] investigated the dissolution of malachite ore with sulfuric acid and the results indicated that the dissolution of Cu was about 99.9 %, while the

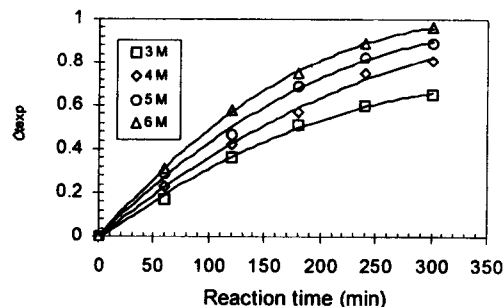


Fig. 1: Effect of acid concentration on dissolution of bauxite ore with 200 rpm at 105°C.

dissolution of Fe in the acid was only up to 40%. However, in the present case the overall share of iron sulfate is not significant due to the lower content of iron in the bauxite ore. The results indicate that the iron containing alum may not be recommended for producing alumina by the Bayer process or for the production of anhydrous aluminum chloride. However, the aluminoferric type of filter alum may be used for water and sewage purification purposes. It may also be used in paper industry depending on the quality of the paper and paper products.

Effect of Reaction Parameters

A number of experiments were carried out to see the effect of leaching reaction time on the dissolution of bauxite ore at varying acid concentration using known particle size and reaction temperature as shown in Fig. 1. Depending on the dissolution conditions, the results show that the dissolution rate of bauxite ore increases with increasing the acid concentration. However, at higher concentration of the acid the rate of dissolution is relatively slow, a situation which may be attributed to the increase in the polarity of the acid O-H bond decreasing the number of hydrogen ions due to the decrease in water amount more and more in the medium [17]. At various reaction temperatures, a number of experiments were carried out to see the effect of reaction time on the leaching of bauxite ore at known reaction conditions as shown in Fig. 2. The bauxite leaching rate curves show that the rate of dissolution of the ore increases by increasing the temperature of the process. The efficiency of the dissolution process may increase with a decrease in particle size of the bauxite ore. The liquid solid ratio as well as stirring speed may

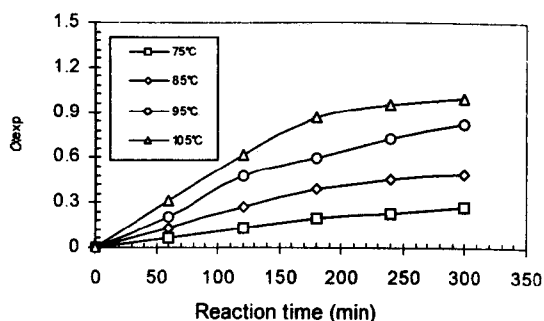


Fig. 2: Effect of temperature on dissolution of bauxite ore with 5M acid at 200 rpm.

influence the dissolution process. Therefore, these parameters also need to be studied so that the optimum process conditions may be determined.

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 shrinking core of the solid particles [19]. 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:



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,

$$t = t^* [1 - (1 - \alpha)] \quad (6)$$

for chemical reaction control,

$$t = t^* [1 - (1 - \alpha)^{1/3}] \quad (7)$$

and for ash layer diffusion control,

$$t = t^* [1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)] \quad (8)$$

The value of t^* depends on the reaction parameters in accordance with the kinetic models.

For example, for a chemical reaction controlled model, eq. (7) t^* is:

$$t^* = \rho_B R_o / bk_s C_A \quad (9)$$

Where t^* is the time for complete dissolution (sec), ρ_B is the molar density of the solid reactant (mol m^{-3}), R_o is the radius of the solid particle (cm), b is the stoichiometric coefficient of the solid, k_s is the surface reaction rate constant (cm sec^{-1}) and C_A is the acid concentration (mol m^{-3}). In the analysis, the dissolution fraction of bauxite ore was calculated by Eq. (10):

$$\alpha_{\text{exp}} = \frac{\text{Amount of } Al^{3+} \text{ in the solution}}{\text{Total amount of } Al^{3+} \text{ in original sample}} \quad (10)$$

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. The validity of the experimental data into the integral rate has been tested by statistical and graphical methods. The kinetic analysis results for the dissolution process is found to be consistent with a chemically controlled reaction and the integral rate expression has been determined to obey the following rate equation:

$$1 - (1 - \alpha)^{1/3} = kt \quad (11)$$

Where k is the overall reaction rate constant (sec^{-1}). Using the conversion values the apparent rate constant, k , has been evaluated at different reaction temperatures by plotting $1 - (1 - \alpha)^{1/3}$ vs. t as shown in Fig. 3. To evaluate the activation energy and pre-exponential factor, the Arrhenius equation (12) can be used:

$$k = A_o e^{-E_a/RT} \quad (12)$$

A plot between $\ln k$ and $1/T$ should be a straight line with a slope of $-E_a/RT$ and an intercept of $\ln A_o$ if the experimental data are fitted well by the Arrhenius equation. The values of pre-exponential factor and activation energy have been estimated from the plot of $\ln k$ vs. $1/T$ as shown in Fig. 4. The values are:

$$E_a = 793297 \text{ J mol}^{-1}; \quad A_0 = 4.2354 \times 10^6 \text{ s}^{-1}$$

Such a value of activation energy indicates that the dissolution of bauxite ore with sulfuric acid is a chemically controlled reaction, which agrees with the reported findings in the similar research of liquid-solid reaction systems [15,17,20-23]. Putting the values of the pre-exponential factor and activation energy in the Arrhenius Eq. (12), it follows that:

$$k = 4.2354 \times 10^6 e^{-79.3297/RT} \quad (13)$$

Comparing Eq. (11) and (13), the semi empirical kinetic model for the dissolution of bauxite ore can be given:

$$1 - (1 - \alpha)^{1/3} = 4.2354 \times 10^6 e^{-79.3297/RT} t \quad (14)$$

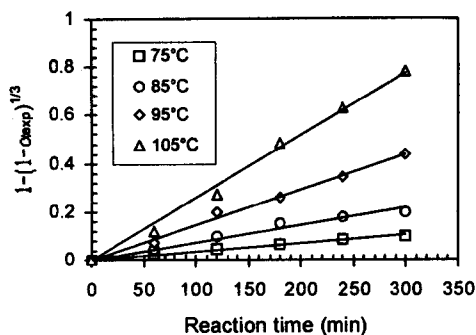


Fig. 3: $1 - (1 - \alpha)^{1/3}$ vs. t at different reaction temperatures.

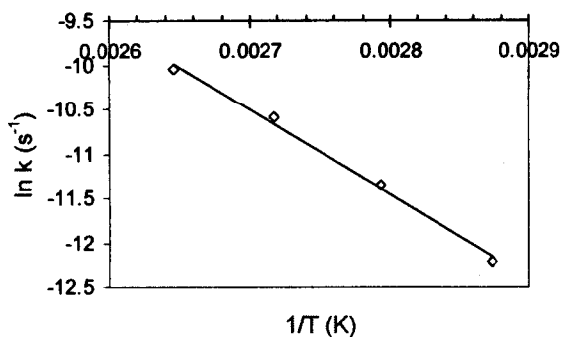


Fig. 4: Arrhenius plot for the dissolution of bauxite ore.

The applicability of the suggested semi empirical kinetic model can be checked by the agreement between the experimental and calculated conversion values. To test the agreement between the experimental conversion and the values calculated from the semi empirical kinetic model, the graph of α_{exp} versus α_{cal} is plotted as shown in Fig. 5. It is observed that the agreement between the experimental and calculated values is good with a correlation coefficient of 0.9879 and standard deviation of ± 0.03187 . The value of the standard deviation of regression or standard error of estimate of α_{cal} on α_{exp} indicates that the degree of scatter of the observed values about the regression line is small. Using the statistical analysis for the experimental data, a relative mean square of errors of 0.0804 was calculated by Eq. (15):

$$ER = \left[\frac{1}{N} \sum_{i=1}^N \frac{(\alpha_{cal} - \alpha_{exp})^2}{(\alpha_{cal})^2} \right]^{1/2} \quad (15)$$

The value of relative mean square of errors shows that, in probabilistic models, such a value of the random errors is not significant.

Experimental

Sample Preparation and Analysis

The present work aimed to study the leaching kinetics of low-grade bauxite ore from Khushab (Pakistan). The low grade bauxite sample was crushed and sieved using U. S. Tyler standard sieves to collect -32+42# (-0.495+0.351 mm) size fraction for analysis. The +32# (+0.495 mm)

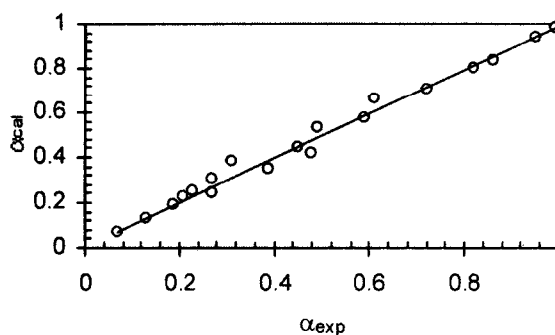


Fig. 5: Agreement between the experimental and calculated conversion values.

Table-1. Analysis of the ore sample.

Composition	wt (%)
Al ₂ O ₃	63.5
SiO ₂	13.7
Fe ₂ O ₃	3.9
TiO ₂	1.7
CaO	3.5
LOI	13.5

fraction was further crushed using Mortar Grinder to obtain the desired size fraction. 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, Al₂O₃, SiO₂, Fe₂O₃, TiO₂, CaO and loss on ignition (LOI) contents as shown in Table-1. Atomic Absorption Spectrophotometer (AAS) and conventional methods [24, 25] were used for analysis. Fig. 6 shows a SEM photograph of the raw bauxite particles. At the first glance, it can be observed that the material under study is granular. In addition, the material seems to be impure due to dark and bright reflectance. The particles are not of definite size but mostly of mixed nature morphology. The results indicate the homogeneity of the original bauxite,

which basically consists of boehmite, hematite, kaolinite and anatase. The white areas show a relatively high concentration of the light element (Al) as boehmite and diaspore on the surface. The bright black ground shows the presence of siliceous and calcareous grains present in the ore matrix.

Experimental Procedure

In the present study, -32+42# (-0.495+0.351 mm) fraction was used in a well-mixed spherical batch reactor (500 mL) heated by a constant temperature bath and equipped with a mechanical stirrer. A known amount of sulfuric acid was slowly added into the reactor vessel containing 5.0 g of the sample for each run at the stirring speed of 200 rpm. 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 Al³⁺ content in the leach solution was determined by using Atomic Absorption Spectrophotometer. The dissolution fraction of bauxite ore in the leach slurry was calculated by Eq. (10). The experimental data were analyzed by graphical and statistical methods to determine the kinetic parameters for the dissolution of bauxite ore.

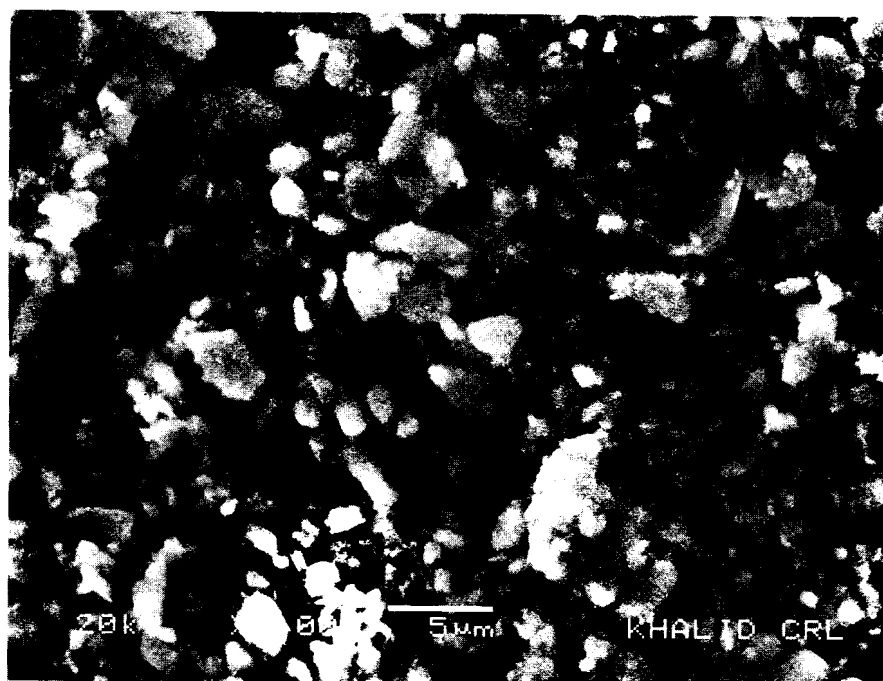


Fig. 6. Scanning electron microphotograph of raw bauxite particles.

Conclusions

The low grade bauxite ore can be treated with sulfuric acid to produce alumino ferric type of filter alum for water and sewage purification purposes. It may also be used in paper industry depending on the quality of the paper and paper products. Analysis of the kinetic data by different kinetic models indicates a chemically controlled process. The activation energy of the dissolution process is found to be 79.33 KJ mol⁻¹, which is consistent with a chemically controlled reaction. A semi empirical kinetic model is developed, and this model can estimate the bauxite material reacted with a relative mean square of error of 0.0804.

Acknowledgment

The authors would like to thank the Department of Chemistry, B. Z. University, Multan for providing the facilities to complete the work.

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