Dissolution kinetics of iron from diasporic bauxite in hydrochloric acid solution

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The dissolution of iron in the bauxite ore including diasporite mineral from Kayaderesi region in Muğla-Milas city, Turkey was investigated in hydrochloric acid solution. The bauxite was calcined at different temperatures and periods, and then dissolved in hydrochloric acid solution. After determining the optimum calcination conditions as 1-hour period at 1173 K temperature and the optimum acid concentration as 8 M HCl, dissolution temperature and period for removal of iron from the bauxite were examined experimentally. In calculations of dissolution kinetics of iron, the experimental data showed that the dissolution process was controlled by interfacial chemical reaction with the apparent activation energy of 41.38 kJ/mol. First order reaction kinetics in shrinking core model was found to fit the experimental results. The dissolution of iron from the bauxite was achieved as 96.46% together with 23.40% aluminium.

Keywords: Bauxite, Iron, Acid leaching, Dissolution kinetics, Activation energy

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Bauxite, an important aluminium reserve, include aluminium minerals such as gibbsite (\(\gamma\)-Al\(_2\)O\(_3\).3H\(_2\)O), boehmite (\(\gamma\)-Al\(_2\)O\(_3\).H\(_2\)O), diasporite (\(\alpha\)-Al\(_2\)O\(_3\).H\(_2\)O) and alumina (Al\(_2\)O\(_3\)), and higher concentrations of impurities as iron oxides and silica\textsuperscript{1,2}. Bauxite ore having high iron content is also used as starting material for aluminium production once the removal of iron is achieved. Favourable bauxite ore used in aluminium production must not have high contents of impurities such as iron oxides and silica\textsuperscript{3,5}. Removal of iron from bauxite has recently become the objective of many researchers for two reasons: low-iron bauxite having less than about 2% Fe\(_2\)O\(_3\) finds application in the production of refractory and removal of iron from bauxite prior to the Bayer process reduces the disposal amount of red mud and provides high alumina content\textsuperscript{4}.

For the removal of iron from bauxite ore, different methods are used such as hydraulic classification, magnetic separation, reduction roasting with hydrogen at high temperatures, bioprocessing and leaching with acid solutions\textsuperscript{2,7-10}. Some investigators have reported the removal of iron from bauxite using hydrochloric acid leaching. They found that iron could be removed by hydrochloric acid leaching almost completely. They examined the dissolution kinetics for iron removal and found that the apparent activation energy varied from 48 to 81 kJ/mol\textsuperscript{11,15}. Mergen \textit{et al}.\textsuperscript{13} studied the kinetics of leaching of boehmitic bauxite in hydrochloric acid solution and obtained the results which the dissolution was to fit Jander’s equation in unreacted shrinking core model and the apparent activation energy was 48-51 kJ/mol. Reddy \textit{et al}.\textsuperscript{6} also studied the leaching kinetics of a gibbsitic bauxite with hydrochloric acid. They found that the mechanism for the dissolution of iron followed first order interface chemical reaction and the apparent activation energy was 81 kJ/mol. The removal of more than 98% iron was achieved from hematite together with about 10% aluminium from gibbsitic phases of the ore. Zivkovic and Strbac\textsuperscript{12} studied leaching of low-quality boehmitic bauxite with hydrochloric acid and they obtained dissolution of 95% Fe\(_2\)O\(_3\) and 5% Al\(_2\)O\(_3\). Petermarakis and Paspaliaris\textsuperscript{11} also studied the leaching iron oxides in boehmitic bauxite by hydrochloric acid and suggested that the shrinking core model had an activation energy of 19.6 kJ/mol. Paspaliaris and Tsokalis\textsuperscript{14} investigated the reaction kinetics for the leaching of iron oxides in diasporic bauxite by hydrochloric acid. Their results indicated that the activation energy to dissolve iron oxides was between 62 and 79 kJ/mol in shrinking core model.

The removal of iron oxides from bauxite ores such as boehmitic, diasporic and gibbsitic in hydrochloric acid has high activation energies. On the other hand,
less aluminium dissolution (5-35%) leads to high content of alumina in residues. The obtained residues can be used in the Bayer process for pure alumina or raw material for refractory 5.

In the present work, the dissolution kinetics of iron in the bauxite ore from Kayaderesi region in Muğla-Milas city, Turkey was investigated by hydrochloric acid solution and the apparent activation energy for the dissolution of iron in the bauxite ore was calculated.

**Experimental Procedure**

The powdered bauxite ore from Kayaderesi region in Muğla-Milas city, Turkey was analyzed chemically. Also thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out by a Mettler Thermobalance, under a nitrogen atmosphere, at heating rate of 10 K.min⁻¹ and with 15 mg sample weight.

Bauxite samples were calcined for 1, 2, 3 and 4 h periods at 473, 573, 673, 1273 K temperatures. Then these calcined samples were dissolved in hydrochloric acid solution to determine the optimum calcination temperature and period and hydrochloric acid concentration. Dissolution temperature and period were examined using the optimum calcined sample and acid concentration.

Dissolution experiments were carried out in reflux system on a magnetic stirrer. In the leached solution, iron and aluminium were analyzed by complexometric titration using etylenediaminetetraaceticacid disodium salt as titrant. The used chemicals were reagent grade.

Considering the results obtained from dissolution temperature and period, the apparent activation energy was calculated for iron dissolution.

**Results and Discussion**

**Chemical analysis**

The chemical analysis of the bauxite ore from Kayaderesi region, Turkey gave the following values: SiO₂, 5.64; Fe₂O₃, 21.20; Al₂O₃, 51.36; TiO₂, 5.84; CaO, 1.35 and LOI, 13.00 (%).

**Thermal analysis**

Thermogravimetric (TG) and differential thermal (DTA) analyses were done for the bauxite ore and the results are given in Fig. 1. It was noted that weight losses were 8.55% between 780-814 K, 3.14% between 814-965 K and 1.01% between 965-1063 K temperatures. The biggest weight loss was between 780-814 K. This is due to the fact that Al₂O₃.H₂O mineral in the bauxite decomposes to Al₂O₃ and H₂O. In other words, it can be explained as dewatering of the bauxite ore. Release of crystalline water doesn’t finish up to 814 K. The process continues above 814 K at low rate 1, 2.

**Effect of calcination on dissolution**

The calcined samples were dissolved in hydrochloric acid solution to examine effect of calcination on the dissolution. The possible chemical reactions that occur during the dissolution of the bauxite with hydrochloric acid are as follows 6:

\[ \text{Fe}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O} \]  \hspace{1cm} (1)

\[ \text{CaO} + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (2)

\[ \text{Al}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O} \]  \hspace{1cm} (3)

\[ \text{TiO}_2 + 2\text{HCl} \rightarrow \text{TiCl}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (4)

Reaction indicated as Eq. (1) is of special interest for the dissolution process. The obtained experimental results for examining the effect of calcination conditions on the dissolution of the bauxite are given in Fig. 2. It was found that the dissolution slowly increased up to 1073 K but faster above this temperature. The dissolution increased with time. The calcined samples have bigger surface area because of dewatering. This situation results in the fact that hydrochloric acid solution reacts rapidly with iron minerals or other minerals. The optimum calcination temperature and period were determined as an hour at 1173 K temperature. The bauxite sample calcined at 1173 K was used in the subsequent dissolution experiments.
Effect of acid concentration on dissolution

The experimental results examining the effect of hydrochloric acid concentration to the dissolution are given in Fig. 3. It seems that 8 M HCl solution is the optimum acid concentration. It is important that the optimum concentration is close to azeotropic HCl concentration, 6.93 M or 20.2%. The acid can be regenerated after it is used in the dissolution.

Effect of temperature and time of dissolution

The effects of dissolution temperature and period on iron and aluminium dissolutions were studied and the results are given in Table 1 and Fig. 4. The maximum dissolutions found were 96.46% Fe2O3 and 23.40% Al2O3. In these conditions, leaching residue includes 0.86% Fe2O3 and more than 72% Al2O3. This means that high aluminium and less iron content in the bauxite can be obtained by hydrochloric acid leaching.

Temperature has a significant effect on the dissolution of iron from the bauxite. On the other hand, dissolution period is not so effective as temperature. The fact that temperature is effective in dissolution kinetics shows that the dissolution rate is controlled by interface chemical reaction16-23. Therefore the dissolution was considered to follow first order kinetics, F1 \{-ln(1-\alpha)=kt\} or contracting volume model, R3 \{1-(1-\alpha)^{1/3}=kt\}. F1 plots are given in Fig. 5a and R3 plots are in Fig. 5b as a function of time at different temperatures.

When the regression analyses of both the kinetics models (F1 and R3) were examined, \( r^2 \) squares showed that first order kinetic model controlled the dissolution of iron in the bauxite. Hence, the rate constants \( k \) at different temperatures were calculated from Fig. 5a and are given in Table 2.

Equations (5) and (6) give relationship between the rate constant, \( k \) and temperature, \( T \)

\[
k = A \exp(-E/RT) \quad \ldots (5)
\]

\[
\ln k = \ln A - (E/RT) \quad \ldots (6)
\]

where \( A \) is the frequency factor and \( E \) is the apparent
The activation energy for the F1 model was calculated as 41.38 kJ/mol from Fig. 6. The fact that the dissolution process is controlled by interfacial chemical reaction is confirmed with the activation energy above 20 kJ/mol. If the activation energy was under 20 kJ/mol, the dissolution could be controlled by diffusion processes. So the reaction represented by Eq. (1) can be suggested for the kinetic process.

Many investigators found that the apparent activation energies were above 48 kJ/mol for different bauxite types. In this study, the activation energy is lower than 48 kJ/mol. This is due to the calcination of the bauxite. In addition, different mineralogical bauxite samples were used in experimental studies. Not only calcination effects the dissolution but the origin of bauxite was also effective.

Conclusions
The following conclusions can be drawn from the studies:

(i) Temperature has a significant effect on the dissolution of iron in the bauxite.

(ii) Iron in the bauxite can be removed by hydrochloric acid leaching and the residue with high aluminium content can be used for the aluminium processes.

(iii) Under optimum conditions it is possible to achieve 96.46% dissolution of iron with 23.40% aluminium.

(iv) The rate of iron dissolution followed first order reaction mechanism, \( F1 \{-\ln(1-\alpha) = kt\} \) with an apparent activation energy of 41.38 kJ/mol.

Nomenclature
- \( \alpha \) = Fractional conversion of iron dissolution
- \( A \) = Frequency factor
- \( DTA \) = Differential thermal analysis
- \( E \) = Activation energy
- \( F1 \) = Equation of first order kinetics model
- \( g \) = Gram
- \( J \) = Joule
- \( h \) = Hour
- \( K \) = Kelvin temperature
- \( k \) = Rate constant
- \( kJ \) = Kilojoule
- \( M \) = Molarity, mole/liter
- \( mg \) = Milligram
- \( mL \) = Milliliter
- \( R \) = Gas constant
- \( r \) = Regression coefficient
- \( R3 \) = Equation of interfacial chemical reaction model
- \( T \) = Temperature
- \( t \) = Time
- \( TG \) = Thermogravimetric analysis

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References