Dissolution kinetics of iron and aluminium from red mud in sulphuric acid solution

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Dissolution kinetics for the removals of iron and aluminium from red mud, a by-product or waste of the Bayer Process, with sulphuric acid were studied. The process parameters studied include calcination temperature, sulphuric acid concentration, particle size, agitation rate, dissolution temperature and time. Temperature and acid concentration had strong influence on the dissolution of iron and aluminium. The mechanism for the dissolution of both iron and aluminium followed first order kinetic model equation (F1), \(-\ln(1-\alpha) = kt\), controlled by interfacial chemical reaction, with the apparent activation energies of 61.42 and 7.39 kJ/mol, respectively. Using 6 M acid, the removals of 97.46% iron and 64.40% aluminium were achieved from red mud calcined at 873 K.

Keywords: Dissolution kinetics, Red mud, Iron, Aluminium, Sulphuric acid

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Red mud is an unwanted by-product or waste of the Bayer Process and causes serious disposal problems for the environment due to the high alkalinity and the large amount of the waste. Depending on the quality of bauxite used in the Bayer Process, the quantity of red mud generated varies between 55-65% of the bauxite. A lot of research and developmental activities are going on throughout the world to find effective utilization of red mud, which involves various product developments1. Its usage can be broadly classified into three categories: (i) bulk utilization in terms of landfill, land reclamation, etc., (ii) specific use as building materials, inorganic chemicals, adsorbents, pH modifier etc. and (iii) recovery of major metallic constituents1-3.

Since, bulk and specific uses can consume only a small part of the red mud generated, total utilization would need the recovery of major metallic constituents1-3. Residues from different bauxites have a wide range of composition: Fe₂O₃, 20-60%; Al₂O₃, 10-30%; SiO₂, 2-20%; Na₂O, 2-15%; CaO, traces-8%; TiO₂, traces 28% (ref.1,4).

Red mud includes valuable metallic contents and alkalinity. After Bayer Process, a basic process, acid leaching can lead to the recovery of iron, more aluminium, titanium and others. At the end of acid leaching, silica will be a second by-product and it will have bigger surface area and less impurities. So acid leaching of red mud will decrease the waste of basic process.

Intensive research has been conducted on the recovery of metallic constituents from red mud and other uses. Ercag & Apak3 studied the total evaluation of red mud to obtain pig iron and a slag useful for the recovery of TiO₂, Al₂O₃ etc. by carbon-lime-soda sintering and electric furnace smelting. Sulphuric acid5,6 and ultrasound-assisted sulphuric acid7 leaching of Ti content in red mud were modeled statistically by Sayan & Bayramoglu. Other examples of Ti recovery were studied by some researchers8-11. In addition, the recoveries of Al(III), Fe (III), Na(I) and Ti(IV) from red mud by the Donnan dialysis system12,13, of aluminium4 and of scandium14 etc. were examined.

However, dissolution kinetics of metallic values from red mud has not been studied enough. The present work deals with the dissolution kinetics of iron and aluminium from red mud. Red mud was calcined at different temperatures and dissolved in sulphuric acid solution. The apparent activation energies \((E_a)\) for iron and aluminium dissolutions from red mud were calculated.

Experimental Procedure

Red mud was supplied by the Etibank Seydisehir Aluminum Plants in Turkey and includes sodium aluminosilicate (sodalite), kaolinite, chamosite, haematite, goethite, amorphous metal oxides and hydroxides, mineralogically3. It was calcined at different temperatures in muffle furnace and then
dissolved in sulphuric acid solution. In the dissolution experiments, a 250-mL glass balloon on a magnetic stirrer was equilibrated to a temperature of 298 to 378 K in an oil bath thermostatically controlled. Also, the reactor was fitted with a condenser to prevent losses by evaporation. After each leaching test, an amount of a sample taken from the leach slurry was filtered immediately, iron and aluminium contents in the leach solutions were determined complexometrically by EDTA titration. Distilled water and reagent grade chemicals were used to make up all required solutions.

Results and Discussion

Chemical analysis

The chemical analysis of red mud and theoretically calculated chemical composition of calcined red mud for 1 h at 873 K are given in Table 1. The calcined sample at 873 K was used in the leaching experiments after effect of calcination.

Dissolution reactions

When red mud is added into sulphuric acid solution, the reactions taking place in the medium can be written as follows:

\[
\begin{align*}
\text{Fe}_2\text{O}_3(s) + 3\text{H}_2\text{SO}_4(aq) & \rightarrow \text{Fe}_2(\text{SO}_4)_3(aq) + 3\text{H}_2\text{O}(l) \quad \ldots(1) \\
\text{Al}_2\text{O}_3(s) + 3\text{H}_2\text{SO}_4(aq) & \rightarrow \text{Al}_2(\text{SO}_4)_3(aq) + 3\text{H}_2\text{O}(l) \quad \ldots(2)
\end{align*}
\]

Calcination of red mud

Thermal characteristics of red mud can vary sample to sample. In general, red mud contains some minerals which cause mass loss at different temperatures, if it is calcined. These minerals are goethite FeO(OH), sodalite Na₆[Al₆Si₆O₂₄(CO₃)₂-2H₂O, boehmite AlO(OH), gibbsite Al(OH)₃ and kaolinite Al₄(Si₄O₁₀)(OH)₈.15,16.

In the experimental studies, the red mud sample was calcined at 473-1273 K temperatures and weight decreases are noted. The obtained results are given in Fig. 1. The maximum total dissolution was obtained at 873 K temperature. The sample calcined at this temperature lost major quantity of releasable constituents and had more surface area. In addition, some phases conversions from gibbsite-boehmite, goethite-hematite completed. The dissolution at high temperatures decreased, since less soluble oxides form above 873 K temperature.

\[
\begin{align*}
\text{Al(OH)}_3(s) & \rightarrow \text{AlO(OH)}(s) + \text{H}_2\text{O}(g) \quad \text{(573 K)} \quad \ldots(3) \\
\text{Al}_2\text{O}_3.3\text{H}_2\text{O}(s) & \rightarrow \text{Al}_2\text{O}_3.\text{H}_2\text{O}(s) + 2\text{H}_2\text{O}(g) \quad \text{(573 K)} \quad \ldots(4) \\
2\text{AlO(OH)}(s) & \rightarrow \text{Al}_2\text{O}_3(s) + \text{H}_2\text{O}(g) \quad \text{(above 573 K)} \quad \ldots(5) \\
2\text{FeO(OH)}(s) & \rightarrow \text{Fe}_2\text{O}_3(s) + \text{H}_2\text{O}(g) \quad \text{(544 K)} \quad \ldots(6)
\end{align*}
\]

Table 1 — Chemical analysis of red mud

<table>
<thead>
<tr>
<th>Component (%)</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>CaO</th>
<th>Na₂O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>14.99</td>
<td>34.02</td>
<td>23.06</td>
<td>4.80</td>
<td>0.06</td>
<td>13.50</td>
<td>8.66</td>
</tr>
<tr>
<td>Calcined at 873K</td>
<td>16.04</td>
<td>36.40</td>
<td>24.67</td>
<td>5.14</td>
<td>0.06</td>
<td>14.44</td>
<td>2.35</td>
</tr>
</tbody>
</table>

Fig. 1 — Weight decreases of red mud at different temperatures (1 g red mud)

Effect of calcination

To examine the effect of calcination on the dissolution, the calcined red mud samples were dissolved in sulphuric acid solution. The obtained results are given in Fig. 2. The maximum total dissolution was obtained at 873 K temperature. The sample calcined at this temperature lost major quantity of releasable constituents and had more surface area. In addition, some phases conversions from gibbsite-boehmite, goethite-hematite completed. The dissolution at high temperatures decreased, since less soluble oxides form above 873 K temperature.
Effect of sulphuric acid concentration

Effect of sulphuric acid concentration on the dissolution was examined using 2, 4, 6, 8 and 10 M sulphuric acid solutions and the red mud sample calcined at 873 K temperature, and the obtained dissolution results for iron and aluminium are given in Fig. 3. It was found that sulphuric acid concentration was more effective at high dissolution temperature than room temperature. According to the results, the optimum sulphuric acid concentration was determined as 6 M. Moreover, iron dissolution increased from 3-5% to above 80%, but aluminium dissolution was from 25-30% to nearly 60% when dissolution temperature increased from 298 to 378 K. It was concluded that sulphuric acid concentration and temperature is an effective factor for the dissolution process.

Effect of agitation rate

The experimental results of agitation rate are given in Table 2. When agitation rate was examined, the total dissolution increased from 5% to 23.18% up to 400 rpm, but the increase was lesser above this agitation. It was found that agitation was not as effective as the temperature.

Effect of particle size

The red mud samples having different particle size were dissolved in sulphuric acid solution. It was found that the dissolution rate increases with decreasing particle size and consequently it was seen that it wasn’t effective in the dissolution as temperature as.

Effect of dissolution temperature

The temperature dependence of the dissolution of iron and aluminium were determined by the experiments in 6 M sulphuric acid solution for different periods. The obtained results are given in Figs. 2 and 4. The results presented in Fig. 4 show that the dissolution rates for iron and aluminium are extremely increased by temperature and the best results were recorded at 378 K temperature for the calcined red mud.

Dissolution kinetics

In order to establish the kinetic parameters and rate-controlling step about the dissolutions of iron and aluminium in sulphuric acid solution, the experimental data were analyzed on basis of the unreacted shrinking core model. According to this model, reaction rate may be controlled by one of the following steps: diffusion through a fluid film, diffusion through ash or interfacial chemical reaction.

Since, temperature is very effective in the dissolutions of iron and aluminium according to the experimental results, it was concluded that the dissolutions of iron and aluminium from the red mud were controlled by interfacial chemical reactions. For the iron and aluminium dissolution kinetics, two equations (Eq. 7 and 8) were used, which are interfacial chemical reaction controlled.

\[
y = [1-(1-\alpha)^{1/3}] = kt \quad \text{(Spherical particle, R3 model)} \quad \ldots (7)
\]
\[
y = [-\ln(1-\alpha)] = kt \quad \text{(First-order kinetics, F1 model)} \quad \ldots (8)
\]
Fig. 4 — Effect of dissolution temperature and time (1 g calcined red mud for 1 h at 873 K in 100 mL 6 M H$_2$SO$_4$; agitation rate, 400 rpm)

Fig. 5 — $[1 - (1 - \alpha)^{1/3}] - t$ plots (R3) for Fe$_2$O$_3$

where $\alpha$ is the fraction of iron or aluminium dissolved at time, $t$ and $k$ is the overall rate constant$^{18,20,21,23,24}$.

Using the experimental data, the kinetic plots were drawn as shown in Fig. 5 (R3 model for Fe$_2$O$_3$), Fig. 6 (F1 model for Fe$_2$O$_3$), Fig. 8 (R3 model for Al$_2$O$_3$) and Fig. 9 (F1 model for Al$_2$O$_3$). The rate constants ($k$) were calculated from these plots.

The relationship between the rate constant, $k$ and temperature, $T$ is given by the Arrhenius equation;

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad \ldots(9)$$

where $A$ is the frequency factor and $E_a$ is the apparent activation energy. The apparent activation energies were calculated as 54.76 and 61.42 kJ/mol using R3.
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Fig. 9 — \[-\ln(1-\alpha)\]– t plots (F1) for Al₂O₃

Fig. 10 — Arrhenius plots for Al₂O₃

Table 3 — Kinetics values for Fe₂O₃ versus Al₂O₃

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k</td>
<td>R²</td>
</tr>
<tr>
<td>298</td>
<td>0.000080</td>
<td>0.5329</td>
</tr>
<tr>
<td>313</td>
<td>0.000300</td>
<td>0.9112</td>
</tr>
<tr>
<td>333</td>
<td>0.000700</td>
<td>0.8797</td>
</tr>
<tr>
<td>353</td>
<td>0.006800</td>
<td>0.8840</td>
</tr>
<tr>
<td>378</td>
<td>0.006100</td>
<td>0.5448</td>
</tr>
</tbody>
</table>

R²(Average) 0.7505 0.7837 0.6503 0.6698

F₁ = First-order kinetics model equation

\[y = [-\ln(1-\alpha)] = kt\]
\[\alpha = \text{The fraction of iron or aluminium dissolved}\]
\[A = \text{The frequency factor}\]
\[E_a = \text{Activation energy, kJ mol}^{-1}\]
\[F_1 = \text{First-order kinetics model equation}\]
\[g = \text{Gram}\]
\[h = \text{Hour}\]
\[J = \text{Joule}\]

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$k =$ Reaction rate constant, min$^{-1}$

$kJ =$ Kilojoule

$K =$ Kelvin temperature

$M =$ Molarity, mole/L

$\text{mL} =$ Milliliter

$R^2 =$ Regression coefficient

$R^3 =$ Spherical particle model equation

$R =$ Gas constant

$t =$ Time, min.

$T =$ Temperature, K

References