Digestion of Alumina from Non-Magnetic Material Obtained from Magnetic Separation of Reduced Iron-Rich Diasporic Bauxite with Sodium Salts

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Abstract: Recovery of iron from iron-rich diasporic bauxite ore via reductive roasting followed by magnetic separation has been explored recently. However, the efficiency of alumina extraction in the non-magnetic materials is absent. In this paper, a further study on the digestion of alumina by the Bayer process from non-magnetic material obtained after magnetic separation of reduced iron-rich diasporic bauxite with sodium salts was investigated. The results indicate that the addition of sodium salts can destroy the original occurrences of iron-, aluminum- and silicon-containing minerals of bauxite ore during reductive roasting. Meanwhile, the reactions of sodium salts with complex aluminum- and silicon-bearing phases generate diaoyudaoite and sodium aluminosilicate. The separation of iron via reductive roasting of bauxite ore with sodium salts followed by magnetic separation improves alumina digestion in the Bayer process. When the alumina-bearing material in bauxite ore is converted into non-magnetic material, the digestion temperature decreases significantly from 280 °C to 240 °C with a nearly 99% relative digestion ratio of alumina.

Keywords: diasporic bauxite; alumina; digestion; sodium salts; Bayer process

1. Introduction

Bauxite ore is the main raw material used in alumina production. Almost 90% of world’s alumina production is from bauxite using the Bayer process [1,2]. The bauxite ore with high alumina content and a high mass ratio of alumina to silica (A/S ratio) is preferred in the alumina industry. Iron-rich diasporic bauxite ore, usually containing over 15 wt. % iron oxide [3–5], has huge reserves in Australia, Guinea, Brazil, Vietnam, Laos and China [6], but has not yet been exploited to its full potential.

The diasporic bauxite ore requires a high digestion temperature and strong caustic soda solutions during the Bayer process. The digestion temperature of diaspor is about 260–280 °C, much higher than those of boehmite (about 230 °C) and gibbsite (about 140 °C). These features lead to inefficient and costly alumina production from diasporic bauxite using this process. Furthermore, the high iron content in bauxite ore is unfavorable for alumina digestion. The large amount of iron oxide in the red mud also poses a potential environmental risk [7–10]. It is thus more appropriate to separate iron first from the iron-rich diasporic bauxite for the Bayer process.

Many studies have been conducted to separate iron constituents from the iron-rich bauxite by using physical methods [3,11], pyro- and hydro-metallurgical processes [5,12–14], and bio-leaching methods [4,15]. Generally, it is difficult to achieve the sufficient separation of iron due to the complex occurrences and associations of disseminated iron-, aluminum-, and silicon-bearing minerals. The physical methods depend on the specific chemical composition of minerals and are merely
suitable for processing the bauxite ores with simple mineral occurrences. Conversely, pyro- and hydro-metallurgical processes appear to be useful for the treatment of complex bauxite ores. Pickles et al. separated the magnetite from reduced bauxite by magnetic separation after carbothermal reduction which transformed hematite to magnetite. Fifty-eight percent of iron was removed in the non-magnetic material with an alumina recovery of 85% [5].

The recent studies indicated that metallization reductive roasting followed by magnetic separation is efficient for separating and recovering iron from refractory iron-containing ores, and sodium salts (e.g., sodium carbonate and sodium sulfate) are the appropriate additives for improving the iron separation in the process [16–21]. A recent study by the authors [22] has confirmed that 92.51% of iron was separated and a powdered direct reduction iron (DRI) with 88.17% total iron content (TFe) was obtained under the optimal conditions. Meanwhile, the alumina, silica, and other valuable components such as titanium and rare earth in non-magnetic material could be selectively recycled. As the major component, the extraction of alumina is important and it is also conducive to further enriching and recovering titanium and rare earth. Several authors proposed that the alumina in the Bayer red mud can be recovered via alkali roasting followed by water leaching. During the alkali roasting, the reaction of sodium aluminosilicate hydrate in red mud with Na$_2$CO$_3$ forms NaAlO$_2$, due to the conversion of SiO$_2$ into CaSiO$_3$ via the addition of CaO-bearing substances [23–25]. However, during the reductive roasting of high aluminum and silicon ores with sodium salts, but without CaO, the Al$_2$O$_3$ and SiO$_2$ react with Na$_2$CO$_3$ and form other sodium aluminosilicates such as Na$_3$O-Al$_2$O$_3$·6SiO$_2$, Na$_2$O·Al$_2$O$_3$·4SiO$_2$ and Na$_{1.55}$Al$_{1.55}$Si$_{0.45}$O$_4$, which are not dissolved in water [9,18]. Moreover, there is lack of research on the alumina extraction from these materials with various sodium aluminates and aluminosilicates, and the effectiveness of alumina extraction has been unclear heretofore.

In the present study, the digestion of alumina from non-magnetic material via the Bayer process was investigated. For comparison, the direct digestion of alumina from iron-rich diasporic bauxite ore was also considered by using the Bayer process. The superiority of alumina digestion from non-magnetic material was discussed intensively.

2. Materials and Methods

2.1. Materials

Non-magnetic material used in this study was prepared via reductive roasting of iron-rich diasporic bauxite with sodium salts followed by magnetic separation. Iron-rich diasporic bauxite was taken from the southwest Yunnan, China. Its chemical composition is shown in Table 1. The total iron content was 17.43% and much higher than that of the conventional bauxite ore. The contents of alumina and silica were 41.83% and 15.10%, respectively.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fe$_{\text{total}}$</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Na$_2$O</th>
<th>CaO</th>
<th>MgO</th>
<th>LOI 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bauxite ore</td>
<td>17.43</td>
<td>41.83</td>
<td>15.10</td>
<td>3.81</td>
<td>0.05</td>
<td>0.09</td>
<td>0.08</td>
<td>13.10</td>
</tr>
<tr>
<td>Non-magnetic material</td>
<td>4.55</td>
<td>43.20</td>
<td>18.11</td>
<td>4.25</td>
<td>17.58</td>
<td>0.11</td>
<td>0.09</td>
<td>10.03</td>
</tr>
</tbody>
</table>

1 LOI: Loss on ignition.

The chemical composition of non-magnetic material was also determined. The result in Table 1 demonstrates that the contents of Al$_2$O$_3$, SiO$_2$ and TiO$_2$ in non-magnetic material are higher than those of bauxite ore after separating of iron. The addition of sodium salts caused increase of the Na$_2$O content from 0.05% to 17.58% and decrease of the total iron content to 4.55%.

2.2. Methods

The ground bauxite ore mixed with sodium salts including 35 wt. % sodium carbonate, 10 wt. % sodium sulfate and 2 wt. % borax was briquetted into cylinders. The stainless tube (dimensions
of Φ50 mm × 200 mm) loaded the dried briquettes with size of Φ10 mm × 10 mm was filled with lignite as reductant and placed in the vertical resistance furnace to perform the reductive roasting at 1050 °C for 60 min. Then the cooled briquettes were crushed and ground in a ball mill to preparation of pulp with 98 wt. % particles passing −0.074 mm. The non-magnetic material was obtained after magnetic separation of pulp in a XCGS-73 Davis magnetic tube (Changsha, China) with magnetic field intensity of 1000 Gs. The procedure for reduction and magnetic separation of bauxite ore was detailed described in the literature [22]. Under the optimized conditions, 83.6 wt. % non-magnetic fraction with 86.3 wt. % alumina occupation was obtained for the followed alumina digestion.

The digestion process was performed in a self-designed reactor equipped with four 150 mL stainless steel pots that rotate in a molten salt bath (Figure 1). The molten salts included sodium nitrate, potassium nitrate and sodium nitrite. Synthetic pregnant liquor was prepared by dissolving sodium hydroxide and aluminum hydroxide in deionized water. The pregnant liquor and the non-magnetic material were transferred into the pots before digestion in which the sealed pots were immersed in the bath with the specified temperature. The reactor was rotated at 30 rpm. After digestion, the sealed pots were taken out and cooled to 80–90 °C with the cooling rate of 20 °C/min, then the suspension in pots was immediately separated and the residue cake was washed using hot water (about 80–90 °C). The dried residue was collected for determination of chemical composition.

The actual and relative digestion ratios of alumina, and the yield of residue are used as the evaluation indexes. Their calculations are given as follows:

\[
\eta_1 = \frac{A_1 - S_1}{A_1} \times 100\% = [1 - \left(\frac{1}{A_1/S_1}\right)] \times 100\% \quad (1)
\]

\[
\eta_2 = \frac{A_1 - A_2 \times Y}{A_1} \times 100\% \quad (2)
\]

\[
\eta_3 = \frac{\eta_2}{\eta_1} \times 100\% \quad (3)
\]

where \(\eta_1\) is the theoretical digestion ratio of alumina, its value is the constant for a specific feed as A/S ratio is fixed; \(\eta_2\) is the actual digestion ratio of alumina; \(\eta_3\) is the relative digestion ratio of alumina. \(A_1\) and \(A_2\) represent the alumina contents in the feed and red mud, respectively, wt. %; \(S_1\) and \(S_2\) represent the SiO\(_2\) contents in the feed and red mud, respectively, wt. %, and \(Y\) is the yield of red mud, %.
3. Results and Discussion

3.1. Digestion Alumina from Non-Magnetic Material

3.1.1. Effects of Caustic Soda Concentration and Caustic Ratio

The caustic soda concentration and caustic ratio in pregnant liquor strongly influence the digestion of alumina in the Bayer process. Generally, a high caustic ratio and caustic soda concentration are beneficial to the alumina digestion, because of the unsaturation of Al₂O₃ in the pregnant liquor. The effect of the caustic soda concentration on the alumina digestion in the non-magnetic material was verified, and the results are shown in Figure 2. The other conditions were kept at the digestion temperature of 240 °C, the digestion time of 60 min, the caustic ratio of 3.0 in the pregnant liquor, and the liquid-to-solid ratio of 4.0 mL/g. The results indicate that the alumina digestion from the non-magnetic material increases first and then decreases with the increasing caustic soda concentration. The digestion of alumina reaches a maximum at the caustic soda concentration of 260 g/L. Note that there is a small difference in alumina digestion when the caustic soda concentration varies between 240 g/L and 260 g/L.

![Figure 2. Effect of caustic soda concentration on the alumina digestion.](image)

The effect of the caustic ratio on the alumina digestion was also examined. The conditions were a caustic soda concentration of 240 g/L in the pregnant liquor, a digestion temperature of 240 °C, a digestion time of 60 min, and a liquid-to-solid ratio of 4.0 mL/g. As shown in Figure 3, increasing the caustic ratio has a favorable impact on the alumina digestion. The relative digestion ratio of alumina improves from 58.08% to 71.43% when the caustic ratio increases from 3.0 to 4.5. Meanwhile, the yield of red mud decreases from 92.30% to 83.56%.
3.1.2. Effect of Digestion Temperature

The above results suggest that the alumina digestion is satisfactory at a low digestion temperature in spite of the high caustic soda concentration or caustic ratio. Hence the effect of the digestion temperature was further explored. The conditions were a digestion time of 60 min, a caustic soda concentration of 240 g/L with a caustic ratio of 4.0 in the pregnant liquor, and a liquid-to-solid ratio of 4.0 mL/g.

As seen from Figure 4, the alumina digestion increases significantly when the temperature increases. Only 30.93% of alumina is digested from the non-magnetic material at 220 °C, with the yield of red mud exceeding 92.6%, indicating the precipitation of sodium aluminosilicates instead of the digestion of alumina during the digestion process. However, the relative digestion ratio of alumina increases from 53.35% to 94.72% when the temperature varies from 220 °C to 280 °C. With the increasing digestion temperature, more alumina is dissolved in the pregnant liquor, and the yield of red mud reduces significantly. However, generally, it is impractical to use a too-high digestion temperature in the view of energy consumption and preparation.

3.1.3. Effect of Lime Addition

Lime is widely applied in the Bayer process for improving the digestion efficiency. The effect of the addition of lime on the digestion of the non-magnetic material was investigated. The other experimental parameters were a digestion temperature of 240 °C, a digestion time of 60 min, a caustic soda concentration of 240 g/L with a caustic ratio of 3.0 in the pregnant liquor, and a liquid-to-solid ratio of 4.0 mL/g.
The results presented in Figure 5 indicate that the digestion of alumina improves obviously with the increasing addition of lime. The relative digestion ratio of alumina reaches 99.58% with the red mud yield of 56.59% when the lime dosage is 4.0%. Further increasing the lime dosage leads to a slight change in alumina digestion. Obviously, the addition of lime is beneficial to reducing the digestion temperature in the Bayer process. It is found that the digestion temperature is only 240 °C under the lime dosage of 4.0% when the alumina extraction is complete.

![Figure 5. Effect of lime dosage on the alumina digestion.](image)

### 3.2. Mechanisms on Improvement of Alumina Digestion of Non-Magnetic Material

#### 3.2.1. Digestion Characteristics Comparison between Iron-Rich Diasporic Bauxite and Non-Magnetic Material

Table 2 compares alumina digestion from iron-rich diasporic bauxite and non-magnetic material. Obviously, it is feasible to digest the non-magnetic material at a lower temperature than that of iron-rich bauxite ore. Compared with bauxite ore, the digestion temperature of non-magnetic material decreases from 280 °C to 240 °C on the premise of a nearly 99% relative digestion ratio of alumina, with the simultaneous reduction of the caustic ratio from 4.0 to 3.0. Besides, due to the separation of iron, the yield of red mud reduces from 78.19% to 56.59%. The results confirm that the digestion of alumina from the non-magnetic material is superior to that of the iron-rich bauxite ore.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Iron-Rich Bauxite Ore</th>
<th>Non-Magnetic Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Digestion temperature/°C</td>
<td>240</td>
<td>280</td>
</tr>
<tr>
<td>Digestion time/min</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Caustic soda concentration/g/L</td>
<td>240</td>
<td>240</td>
</tr>
<tr>
<td>Caustic ratio</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Lime dosage/wt. %</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>η₂/,%</td>
<td>13.09</td>
<td>63.10</td>
</tr>
<tr>
<td>η₃/,%</td>
<td>20.48</td>
<td>98.75</td>
</tr>
<tr>
<td>Y/,%</td>
<td>104.36</td>
<td>78.19</td>
</tr>
</tbody>
</table>

#### 3.2.2. Improving Mechanisms of Alumina Digestion of Non-Magnetic Material

According to Figure 6, the alumina in iron-rich bauxite ore occurs in the phases of diaspore (α-AlOOH), boehmite (γ-AlOOH) and kaolinite (Al₂O₃·2SiO₂·2H₂O) (Figure 6 A). During the reductive roasting, the hematite is reduced to metallic iron (Equation (4)), and the alumina and silica, produced from the decomposition of diaspore (Equation (5)) [26], boehmite and kaolinite in the iron-rich bauxite...
ore, react with sodium salts and generate sodium aluminates and aluminosilicates [18,27,28]; in the case of sodium carbonate as the primary additive, the reactions are as seen in Equations (6) and (7).

In the present system, the aluminum-bearing phases in the non-magnetic material transform into diaoyudaite (NaAl₁₁O₁₇) and sodium aluminosilicate (Na₁₁₂₅₁₁₅₅Si₁₄₅O₄) (Figure 6B).

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + 3\text{CO} & \rightarrow 2\text{Fe} + 3\text{CO}_2 \\
\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} & \rightarrow \text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O} \\
x\text{Na}_2\text{CO}_3 + y\text{Al}_2\text{O}_3 & \rightarrow 2\text{Na}_2\text{Al}_x\text{O}_{(x+3y)} + x\text{CO}_2 \\
x\text{Na}_2\text{CO}_3 + y\text{Al}_2\text{O}_3 + z\text{SiO}_2 & \rightarrow x\text{Na}_2\text{O} \cdot y\text{Al}_2\text{O}_3 \cdot z\text{SiO}_2 + x\text{CO}_2
\end{align*}
\]

Furthermore, it is observed from Figure 7A that the occurrences of hematite, kaolinite and diaspore in iron-rich bauxite ore are more complex. Especially, the main iron-bearing mineral, hematite, is surrounded by the matrix phases of diaspore and kaolinite. It is necessary to destroy the original structure of the minerals for extracting alumina. Figure 7B shows that the aggregation of metallic iron during reductive roasting. Due to the reduction of iron-bearing mineral, the structure of matrix minerals is destroyed, and the aluminum-bearing phases are independent.

The above analysis indicates that it is more difficult to extract alumina using the Bayer process when the bauxite ore is directly digested with the occurrence of closed minerals. Besides, the digestion
of diaspore, as the main aluminum-bearing mineral, is also limited at low temperatures. The strict digestion conditions such as a high temperature and high caustic ratio are required (Table 2).

For the non-magnetic material, the satisfactory separation of iron and aluminum-bearing minerals can be achieved via reduction roasting followed by magnetic separation. The independent phases diaoyudaote and sodium aluminosilicate, obtained via the magnetic separation of reduced bauxite with sodium salts, are original alumina sources when the non-magnetic material is used as the Bayer digestion feed. The separation and transformation of aluminum-bearing minerals is in favor of the alumina digestion at low digestion temperatures (Table 2). On the other hand, the high content of Na$_2$O in the non-magnetic material can be introduced into pregnant liquor during the digestion of diaoyudaote and sodium aluminosilicate, and during the increase of caustic soda concentration and caustic ratio.

It should be pointed out that the actual digestion ratio of alumina is only 60% in spite of the high relative digestion ratio of alumina (up to 99.5%). This is explained by the low A/S ratio of the feeds (only 2.77 and 2.39 for iron-rich bauxite ore and non-magnetic material, respectively). It can be inferred that the actual digestion ratio of alumina is improved significantly when the raw material bauxite ore has a high A/S ratio. In other words, the technology proposed in this study reveals a new direction for exploitation of iron-rich diasporic bauxite ore.

4. Conclusions

The digestion of alumina from non-magnetic material obtained after reductive roasting of an iron-rich diasporic bauxite ore with sodium salts followed by magnetic separation was investigated in the present study. The digestion temperature significantly decreases from 280 °C to 240 °C and the yield of red mud also reduces from 78.19% to 56.59% in the Bayer process using a non-magnetic material as the feed compared with the direct digestion of alumina from the iron-rich bauxite ore. When the optimum conditions are a digestion temperature of 240 °C and a time of 60 min, a caustic soda concentration of 240 g/L, a caustic ratio of 3.0 and a lime dosage of 4.0%, the relative digestion ratio of alumina in the non-magnetic material is 99.58%. It indicates that the alumina in the non-magnetic material can be extracted almost completely. During the reductive roasting, the sodium salts react with aluminum- and silicon-bearing minerals, destroying the original structures of the minerals in the bauxite ore. Meanwhile, the generation of diaoyudaote and sodium aluminosilicate in reductive roasting is further beneficial to alumina extraction at a relatively low digestion temperature, contributing to satisfactory alumina digestion.

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Author Contributions: Guanghui Li and Tao Jiang conceived and designed the experiments; Jun Luo and Zhuoxuan Li performed the experiments, analyzed the data and wrote the paper; Zhiwei Peng and Yuanbo Zhang supervised experimental work and reviewed the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References
