An environmentally friendly design for low-grade diasporic-bauxite processing

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\textbf{A R T I C L E   I N F O}

Article history:
Received 30 July 2008
Accepted 7 February 2009
Available online 13 March 2009

Keywords:
Non-ferrous metallic ores
Digestion
Environmental
Mineral economics

\textbf{A B S T R A C T}

A new environmentally friendly design for low-grade diasporic-bauxite processing which is different from the Bayer and sintering processes was proposed in this paper. In the redesign of alumina production technology, a mixture of bauxite ore and sodium hydroxide solution was heated at a higher temperature for the purpose of complete decomposition of bauxite. The products were then extracted by water; the resulting sodium aluminate solution was further purified and used for the gibbsite precipitation, the residue being reacted with a caustic liquor to recover sodium oxide and alumina. The experimental results show that during the new process bauxite decomposition rates approach 100% and the residues can be easily recovered. When diasporic ores with mass ratio of alumina to silica of approximately 5:1 are treated, total alumina recovery efficiency of 86% and a sodium oxide presence below 1.5% in the final red mud will be achieved. This new design surpasses previous approaches in terms of high resource efficiency and low environmental impact.

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1. Introduction

Aluminum is one of most commonly used metallic elements in civilization. Due to its high corrosion resistance and mechanical strength to mass ratio, aluminum alloys are used as a major structural material in aircrafts, buildings, machinery parts, beverage cans and food wraps (Wang et al., 2008; Xu et al., 2004). Bauxite is currently the main resource of alumina/aluminum production. Unlike bauxite ores found in other countries, more than 99% of the bauxite ores in China are diasporic-characterized by tough processing demands, high alumina and silica content, and low alumina to silica mass ratios (hereafter referred to as A/S). In 2003 China's bauxite mineral reserves stood at 2.545 Gt (Luo, 2006). Among these ores, greater than 80% of them have A/S of less than 10 and thus cannot be processed economically through the Bayer process due to their low-grade. An alternative sintering process or a combination of sintering and Bayer processes must be employed (Liu et al., 2007) for these low-grade ores. However, the sintering process is complicated and extremely energy-intensive due to its high reaction temperature of 1200 °C.

In order to bridge the gap between the natural shortage of and the high industrial demand for high quality bauxite, a new technology named ore-dressing Bayer process was developed (Huang and Wang, 2008; Ou et al., 2007; Wang et al., 2004). This process can upgrade the diasporic-bauxite but it creates tailings totaling some 25% of the initial bauxite ores quality that cannot be easily reused due to their complex composition and structure. Furthermore, the tailings produced contain 40% alumina, reducing the total utilization efficiency of bauxite (Li and Pan, 2007). Another alternative solution to solve the shortage of high-grade bauxite is to simply import it from Indonesia, Brazil, etc. to meet the increasing demands of bauxite in China's developing alumina industry. To that end, 880,000 tons of bauxite was imported in 2004. By 2007, high quality bauxite imports had grown to 23.3 million tons – a 25-fold increase in only 3 years. Moreover, the average import price of bauxite has risen from $20/ton in 2004 to $50/ton in 2007. Predictably, this has had a negative effect on alumina production costs and the domestic alumina industry's competitiveness in general. A new process must be developed to utilize China's vast domestic low-grade aluminum resource.

Over the past several decades environmentally friendly design has been applied to an increasingly diverse range of technologies and innovative solutions for the management of resources (Todd et al., 2003; Graedel et al., 2004; Kharel and Charmoudsatis, 2008). Green process design has been recognized as a new significant orientation in the evolution of technology (Lennart and Ljungberg, 2007; Lowenthal and Kastenberg, 1998; Marukawa and Edwards, 2001). This approach not only focuses on raising resource efficiency, but also pays more attention to reducing pollutants and further protecting our plant (Berkel van, 2007; Kobayashi, 2006). Therefore, primary green design can be characterized by high resource efficiency and minimum environmental impacts (Michelini and Razzoli, 2004; Zuidwijk and Krikke, 2008).

At present, China's alumina industry has a very limited supply of high-grade bauxite resources to draw upon and suffers from...
high energy consumption and serious environmental impacts. The processes currently available for low-grade bauxite processing, such as sintering process and flotation-Bayer process, cannot adequately address the related problems of resource efficiency, environmental impacts and energy consumption. However, there is room within China's alumina industry for positive application of green design principles. This paper endeavors to make just such an application by describing a novel method for low-grade diasporic-bauxite treatment.

2. Brief description of Bayer process

In order to compare and contrast with the new process, the traditional Bayer process is first briefly described (Fig. 1). The Bayer process is widely used for producing of alumina from bauxite. In most diasporic-bauxite refineries, the ground bauxite and a small amount of lime are initially mixed with caustic liquor and held at approximately 100 °C for a few hours to achieve pre-desilication. Formulas (1)–(4) represent the main chemical reaction of Bayer process. At temperature, usually between 240 and 280 °C, the soluble diasporic-bauxite treatment.

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\[
\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 + 2(\text{Na}_2\text{O} \cdot \text{SiO}_2) + (n + 2)\text{H}_2\text{O} = \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O} + 4\text{NaOH}
\]

(4)

\[
\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O} = 2\text{Al(OH)}_3 + 2\text{NaOH}
\]

(5)

\[
\begin{align*}
\text{2AlOOH} + 2\text{NaOH} + 2\text{H}_2\text{O} &= \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O} \\
\text{SiO}_2 + 2\text{NaOH} &= \text{Na}_2\text{O} \cdot \text{SiO}_2 + \text{H}_2\text{O} \\
\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + 6\text{NaOH} &= \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 + 2(\text{Na}_2\text{O} \cdot \text{SiO}_2) + 5\text{H}_2\text{O}
\end{align*}
\]

(1)–(3)

Fig. 1. Illustrative flowsheet of the traditional Bayer process.

3. New environmentally friendly design for low-grade diasporic processing

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(2), (3), (6), (7), and (8) represent the main chemical reactions during digestion.

The resulting sodium aluminate is extracted by water and separated from the residues. The residues may contain varying amounts of sodium aluminosilicate, hydrated ferric oxide produced during dissolution, sodium titanate and other impurities in the bauxite resources, as shown in Reactions (4) and (9). The solid impurities are treated to recover sodium oxide and alumina. And the sodium aluminate solution is further purified and then used for the gibbsite precipitation after cooling and adding of seed materials, which can be seen in Reaction (5).

The spent liquor from gibbsite precipitation is condensed in order to crystallize sodium aluminate. The produced sodium aluminate crystal is dissolved in water and incorporated into the former green sodium aluminate liquor before seed precipitation. The second spent liquor is sent to recover soda and alumina in the solid impurities, as illustrated by Reactions (10) and (11). Finally, the liquor from recovery unit is recycled to digest bauxite after filtration. The solid waste which is also named final red mud, is removed from the system after washing and can be used without further modification as a raw material in cement production because of its low alkaline content.

4. Material and reagents

The bauxite ores in this study supplied by Zhejiang Jinjiang Group in China were firstly ground to 74 \( \mu m \) and then the minerals was sampled for composition analysis by a Perlin–Elmer Optima 5300 DV ICP-OES and for phase identification by X-ray diffraction with a Rigaku D/max-2400 X-ray diffractometer using Cu K\( \alpha \) radiation. It was scanned over a (5–90\(^\circ\)) 2\( \theta \) scan range. The solid impurities separated from the sodium aluminate solution after digestion were washed, dried and analyzed by X-ray diffraction and ICP-OES in the same fashion. Their chemical compositions are given in Table 1 and their structures illustrated in Fig. 3.

Table 1

<table>
<thead>
<tr>
<th>Material source</th>
<th>Composition (wt.%)</th>
<th>A/S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Al_2O_3 )</td>
<td>SiO(_2)</td>
</tr>
<tr>
<td>Jinjiang Group</td>
<td>58.91</td>
<td>12.07</td>
</tr>
<tr>
<td>Residue</td>
<td>25.61</td>
<td>23.24</td>
</tr>
</tbody>
</table>

Note: LOI means loss of ignition; A/S means alumina to silica mass ratio.
Above analysis showed that about 70% of the bauxite ore is dias- 
spore. Other phases include ~12% silicon dioxide in the form of 
kaolinite and less than 10% quartz, titanium and iron impurities.
At 4.88, A/S is relatively low clearly identifying it as low-grade 
diasporic-bauxite. It also indicated that the ores can almost com-
pletely react with alkaline during the digestion, as can be con-
cluded by almost amorphous structure of the solid residues. As a 
result of it, A/S of the residues drops to 1.10, which is close to 
the theory proportion of 1.

The reagent sodium hydroxide and calcium oxide employed in 
this work were of analytical grade and made by Beijing Chemical 
Plant. Distilled water was used throughout the experiments when-
ever needed.

5. Evaluation of the new process

5.1. Environmental impact

5.1.1. Choice of resources

This new reaction path was designed for low-grade diasporic-
bauxite. It differs from the Bayer process in two key aspects. Firstly, 
no solid additives are needed during the digestion of ores. The ores 
can almost completely react with alkaline under proper conditions 
despite the absence of additives, remarkably reducing the amount 
of waste residue left after leaching. Alumina losses caused by syn-
thesis of calcium aluminate, which often occurs during Bayer 
leaching, can be avoided. Secondly, the spent liquor produced by 
sodium aluminate crystallization can be reused to recover sodium 
oxide in the new process almost exclusively lie in two kinds of andradites – 3CaO·Al2O3·0.5Fe2O3·0.5SiO2·SiO2·4H2O and 3CaO·0.13Al2O3· 
0.87Fe2O3·1.65SiO2·2.7H2O. According to the composition of the 
two andradites, it can further be seen that A/S is lower than that 
of the Bayer process. Furthermore, A/S in the final red mud can 
be reduced to 0.2 if pure sodium hydroxide is applied to recover 
valuable elements in the recovery unit. Doing so would elevate 
the final low-grade bauxite recovery rate to 95%.

Moreover, it is well-documented that 6–10% sodium oxide re-
 mains in the red mud in the Bayer process, whereas the presence 
of sodium oxide drops to 1.5% in the new process for the same rea-
son as above. The reduction of sodium oxide content in the red 
mud greatly alleviates the environmental problems caused by its 
caustic nature (Liu et al., 2007). In the meantime, the lower content 
of sodium oxide in the red mud also leads to a lower consumption of 
sodium hydroxide. Plant operations would now require 0.021 t 
per ton alumina product, approximately 84% less than the 0.13t re-
quired by Bayer process excluding normal mechanical losses.

Next, sodium aluminate crystal produced by the process of 
evaporation and crystallization, after dissolving with water, is 
recycled and mixed with the pregnant liquor for gibbsite precipita-
 tion. Thereby a big loop of remaining alumina in the spent liquor is 
avoided, which occurs in the Bayer process.

5.1.3. Waste

Although other components in the bauxite, such as silicon oxide 
(SiO2), ferric oxide (Fe2O3) and titanic oxide (TiO2) can also react 
with sodium hydroxide or one another, they hardly have any im-
 pact on the separation of sodium aluminate with the exception of 
silicon oxide. To explain, the solubility of synthesized ferric 
oxide and titanic oxide becomes very low within certain ranges of 
sodium hydroxide concentration and temperature and almost 
all of them can be precipitated as main solid residues. Conversely, 
a fraction of silicon oxide can be dissolved into the aqueous solu-
tion, which damages the sodium aluminate liquor and has to be re-
moved from the solution by adding calcium oxide or other addi-
tives. Sophisticated technologies can easily help to finish the 
desilication process.
Table 2
Difference between Bayer process and the new design.

<table>
<thead>
<tr>
<th>Process</th>
<th>New design</th>
<th>Bayer process</th>
<th>Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Difference</td>
</tr>
<tr>
<td>Digesting temperature (°C)</td>
<td>375</td>
<td>260</td>
<td>115</td>
</tr>
<tr>
<td>Process pressure (MPa)</td>
<td>0</td>
<td>5</td>
<td>–5</td>
</tr>
<tr>
<td>Leaching time (min)</td>
<td>30</td>
<td>60</td>
<td>–30</td>
</tr>
<tr>
<td>Recovery of Al₂O₃ (%)</td>
<td>86</td>
<td>70</td>
<td>16</td>
</tr>
<tr>
<td>Reaction medium</td>
<td>NaOH</td>
<td>NaOH</td>
<td>Same</td>
</tr>
<tr>
<td>Amount of red mud (t/t Al₂O₃)</td>
<td>1.09</td>
<td>1.58</td>
<td>–0.49</td>
</tr>
<tr>
<td>Na₂O in red mud (%)</td>
<td>8</td>
<td>8</td>
<td>–6.5</td>
</tr>
<tr>
<td>Water consumption (t/t Al₂O₃)</td>
<td>7.39</td>
<td>10.24</td>
<td>–2.85</td>
</tr>
<tr>
<td>Soda consumption (t/t Al₂O₃)</td>
<td>0.021</td>
<td>0.13</td>
<td>–0.109</td>
</tr>
<tr>
<td>Bauxite consumption (t/t Al₂O₃)</td>
<td>1.98</td>
<td>2.45</td>
<td>–0.47</td>
</tr>
<tr>
<td>Energy consumption (GJ/t Al₂O₃)</td>
<td>20</td>
<td>17</td>
<td>3</td>
</tr>
</tbody>
</table>

As mentioned above, almost all components in the bauxite can react with alkaline during digestion, making it possible for sodium oxide and alumina in red mud to be recovered effectively. Because ferric oxide transforms from hematite or magnetite to ferrite in the digestion process, and further to hydrated ferric oxide in the subsequent leaching, it becomes active enough to react with sodium aluminosilicate and calcium oxide to form andradites with low sodium and alumina.

In addition, complete reaction of alumina in bauxite with recycled alkaline also results in an obvious decrease of the residue amount. According to test results, the solid waste output is only 1.09 t per ton alumina product for the bauxite with A/S of 4.88, 45% less than that of the Bayer process.

The other advantage of this new design is that the final-stage residues can be used as feedstock in the cement industry due to its low sodium content (Shi and Zhao, 2005) or for iron extraction by reduction and magnetic separation since ferric oxide has been enriched (Liu et al., in press).

5.1.4. Water consumption
In an alumina plant, fresh water is often employed to wash alumina hydroxide and the final red mud. Reductions in red mud output are naturally followed by reductions in the amount of washing water. Total water consumption is about 7.39 t per ton alumina product, significantly lower than that of the Bayer process.

5.2. Energy efficiency
Energy conservation plays an important role in the new process design. In this new one for low-grade bauxite processing energy consumption analysis cannot quantified properly as necessary thermodynamic data are not available till now. But a rough estimation on energy consumption of this process has been made. Firstly, the whole process is operated at atmospheric (units of digestion, evaporation and crystallization, precipitation) or near atmospheric pressure (recovery of sodium oxide and alumina unit), instead of a leaching operation at high pressure ranging from 4 to 6 MPa as used by the Bayer process. Resultantly, energy consumption can be sharply lowered. Secondly, energy consumption reduction is also possible as a result of high utilization efficiency of bauxite and the alumina's nearest recycling route (from spent liquor after seed precipitation through crystallization to pregnant liquor, not to digestion unit). On the other hand, condensation of caustic solution till almost desiccation in the process and the first step-digestion are undoubtedly energy-intensive which will compromise the energy efficiency. By comparing to the energy consumption in Bayer process, it is estimated that the energy consumption is ~20 GJ per ton alumina product for the bauxite with A/S of 5, ~18% higher than that of Bayer process – 17 GJ. Energy saving is an urgent mission for this new process.

5.3. Final products
One challenge of green design is the creation of new living products capable of supporting the demands of human society. This new process generates gibbsite and sodium aluminate. Gibbsite is the ideal raw material for producing sandy alumina, and sodium aluminate is often utilized as an adjunct in treatment of potable and industrial water and also an additive in paper processing.

5.4. Summary
A summary of the differences between the Bayer process and the introduced greener design for low-grade diasporic-bauxite is shown in Table 2.

6. Conclusions
A novel and environmentally friendly design for low-grade diasporic-bauxite processing has been developed. It applies the theory of green design to a fundamental redesign of alumina industry technology, rather than a simple revision of the traditional method. The new design focuses not only on higher resource efficiency and more efficient products, but also on maximum reduction of environmental impacts. The detailed characteristics analysis shows that, when compared with the traditional Bayer process, this new project remarkably increases the efficiency of resources and decreases water consumption. Moreover, it creates fewer environmental impacts because of the lower sodium content of red mud and minimal solid waste produced. At the same time, this process can provide us with a desirable product – sandy alumina.

At present, this bauxite digestion process is in the early stages of development. Energy consumption is till higher than that of Bayer process. So the process’ optimization on this new process is needed. Moreover, deeper exploration of recovery of sodium and alumina from the red mud is necessary, since it may be of help to address the Bayer process pollution.

Acknowledgement
The authors gratefully acknowledge the financial supports from the Key Project Program of the National Natural Science Foundation of China (Grant No. 50234040).
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