Progress in Research and Development of Alumina Production Technology for Low Grade Bauxite in China

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Abstract

Although China has become the largest alumina producer in the world in recent years, it has a shortage of bauxite reserves, and most of what is available is low grade. As a result, it is very important for China to produce alumina economically from its low grade bauxite. Existing alumina production processes for low grade bauxite, such as Bauxite Flotation followed by the Bayer process and the Bayer-Sinter Series process, as well as the progress of research work into other alternative processes are reviewed in this paper. The development directions for alumina production processes from different kinds of low grade bauxite are also proposed.

Keywords: Low grade bauxite, alumina production, desilication, research and development.

1. Definitions of terms

"A/S": mass ratio of Al₂O₃ to SiO₂ in the solid
"N/S": mass ratio of Na₂O to SiO₂ in the solid
"C/S": mass ratio of CaO to SiO₂ in the solid
"αk": molar ratio of caustic Na₂O to Al₂O₃ in liquor
"NK": caustic concentration of the liquor (as Na₂O)
"NT": total Na₂O concentration of the liquor

2. Introduction

Alumina production capacity and output in China has grown to be the largest in the world, even though good quality bauxite reserves are insufficient to maintain this high production level. There is an estimated 55 - 75 billion tones bauxite resources and 28 billion tons of bauxite reserves in the world, but only 0.83 billion tons of the reserves are in China, according to USGS statistics. The grade of bauxite used in refineries in China has been declining for about 10 years with the rapid development and expansion of the alumina industry. The average A/S (alumina to silica ratio) of bauxite has fallen to below 5 in some Chinese refineries.

The alumina production capacity has increased to more than 70 million tonnes in China, and it has become necessary for the Chinese alumina industry to produce alumina from low and medium grade bauxite in China. It is therefore the most important technical objective for alumina production, to be able to economically segregate silica (the most economically significant impurity), from alumina in Chinese bauxites.

The Bayer and Sinter processes are the basis of alumina production processes utilised in China. The alumina production process and desilication product are quite different between these processes. Desilication products most commonly found in Bayer and Sinter processes are shown in Table 1.
Table 1. Desilication products commonly found in Bayer and Sinter processes.

<table>
<thead>
<tr>
<th>Desilication Product</th>
<th>A/S</th>
<th>N/S</th>
<th>C/S</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O·Al₂O₃·1.7SiO₂·H₂O</td>
<td>1</td>
<td>0.608</td>
<td>0</td>
<td>Bayer</td>
</tr>
<tr>
<td>3CaO·Al₂O₃·xSiO₂·(6-2x)H₂O</td>
<td>1.7</td>
<td>0</td>
<td>2.8</td>
<td>Bayer</td>
</tr>
<tr>
<td>2CaO·SiO₂</td>
<td>0</td>
<td>0</td>
<td>1.87</td>
<td>Sinter</td>
</tr>
</tbody>
</table>

Fundamental characteristics of the Bayer process are low energy consumption, low resource utilization efficiency and high alkali consumption. For the Sinter process it is high energy consumption, high resource utilization efficiency and low alkali consumption. Since the size and cost of the energy consumption difference is generally the dominant economic factor, alumina output is produced mainly by the Bayer process globally, including in China, where 95% of alumina produced is by this process.

The basis of research and development on new technology and processes for low grade diasporic bauxite in China is still the Bayer process. One way of classifying existing and new technologies and processes for low grade bauxite based alumina production is to divide them into the categories; Pre-process, Mid-process and Post-process. Pre-process is where bauxite is treated before the Bayer cycle, and the technical and total economic metrics of the subsequent Bayer process are improved in line with the better quality raw material fed to it. Mid-process is where the Bayer cycle is optimized and post-process is where the red mud is reprocessed. A simple diagrammatic sketch of the Bayer process is shown, and the classification of new and existing processes for low grade diasporic bauxite shown in Figure 1.

![Diagram of Bayer process](image)

**Figure 1. Types of new processes for low grade diasporic bauxite.**

Many research and development projects on alumina production from low grade diasporic bauxite have been carried out over many decades, and there has been good progress. Some new processes have been used in refineries. The new technologies for the use of low grade diasporic bauxite are reviewed and some suggestions for the research and development directions for different kinds of low grade diasporic bauxite are presented in this paper.

3. **The Progress of Research on Alumina Production from Low Grade Bauxite**

3.1 **Pre-Process**

3.1.1 **Bauxite Washing - Bayer Process**

Washing to improve its grade is not useful for most Chinese diasporic bauxites, but it is useful
for some Chinese diasporic bauxites. For example, the grade can be improved significantly by washing for the diasporic bauxite in Guangxi and Yunnan [1-4].

3.1.2 Bauxite Flotation - Bayer Process

China began to do research work on the bauxite flotation process from the 1970s. A Bauxite Flotation - Bayer process line with a capacity of 300kt/a alumina was constructed and put into operation in Chalco’s Zhongzhou operations in 2004. It was the world’s first industrialization of bauxite flotation followed by the Bayer process, and was a significant landmark.

The bauxite flotation process has been improved continuously in China, and as a result, it has recently been used for low grade bauxite of A/S < 3 [5, 6]. But it is difficult to raise the grade of some low grade bauxites because the silica minerals are too fine and too closely associated with other minerals to be easily separated. For this reason, the bauxite flotation process is not technically or economically feasible for some low-grade bauxites.

3.1.3 Possible Biological Process

Silicates or aluminosilicates can interact with microorganisms to be converted to alumina and silica. Silica is made soluble and separated in this process [7]. The microorganisms, mostly bacteria or fungi, can react with silicate or aluminosilicate selectively at ambient temperatures. This biological process has the potential to relatively simply remove silica from some kinds of bauxite, and if some challenges can be overcome, it may be a useful desilication process.

This process is still in the laboratory, and is far from being used for commercial production, although some related research works are being carried out in some universities or research institutes. The main challenges to this method are: 1) The productivity is less than other methods because of the lower leaching efficiency; 2) the long time periods involved and the rigorous reaction conditions required; 3) Organic material is needed as a nutrient source because the microorganisms are heterotrophic, but a cost effective nutrient medium has not yet been identified; 3) The technical difficulties of purification and regeneration of the required micro-organisms has yet to be mastered.

3.1.4 Chemical Dressing - Bayer Process

3.1.4.1 Calcination, Alkaline Leaching and Desilication

Research on low grade bauxite processing by calcination, alkaline leaching and desilication has been done since the 1950s in China. Marked progress was made in the 1980s [8].

The aluminosilicate in bauxite can react at high temperature to essentially split the silica and alumina by forming separate silica and alumina minerals. The silica minerals so formed are easily dissolved in an NaOH leaching solution owing to their high activity, producing sodium silicate (Na$_2$SiO$_3$). Diaspore in bauxite is converted into α-Al$_2$O$_3$ with an altered corundum structure, which can only be dissolved in an NaOH liquor under high temperature conditions. This allows silica to be partially removed in a leach step at atmospheric temperatures after bauxite calcination, and the A/S of bauxite to be improved [9-11]. Chemical reactions taking place in the calcining process are as follows:

$$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \xrightarrow{450-600\text{°C}} \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O} \quad (1)$$
\[
\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \xrightarrow{900-1150^\circ \text{C}} \alpha \cdot \text{Al}_2\text{O}_3 + 2\text{SiO}_2
\]  

(2)

The key chemical reaction taking place in the leaching step is as follows:

\[
\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}
\]

(3)

Research on the optimization of the bauxite calcination and desilication process by alkaline leaching has been carried out continuously [12 - 15].

### 3.1.4.2 High Concentration Alkali Leaching and Desilication Process

The High Concentration Alkali Leaching and Desilication process was reported in the former Soviet Union [16]. A caustic soda solution of \( N_k = 450 – 500 \text{ g/L} \) is used to treat low grade diasporic bauxite at a liquid - solid ratio of 15 – 20, and a temperature of about 95 °C. As a result, the A/S is increased to about 12, alumina recovery efficiency is 80 – 82 % and desilication efficiency is 75 – 77 %. Some research has been done on the high concentration alkali leaching and desilication of low grade bauxite in China [9]. The bauxite A/S is improved from 7.6 up to over 12 under the conditions of 50% NaOH, bauxite to soda ratio of 2.5, a leaching temperature of 135 °C, and a reaction time of 5 – 20 minutes.

### 3.1.5 Predesilication-classification Process

The Predesilication-Classification process was proposed by the Zhengzhou Light Metal Research Institute at the end of last century [17, 18]. Bauxite is ground and treated with spent liquor of \( N_k = 140 – 300 \text{ g/L} \), at a temperature of 80 – 120 °C. Kaolinite in bauxite is changed into sodium aluminosilicate hydrate in the process. The beneficiated bauxite is obtained by classification according to the difference in particle size and density in the slurry. The tailings are treated by the addition of lime, and more than 75% of soda can be recovered.

### 3.2 Mid-Process

#### 3.2.1 Iron Hydrogarnets

The reaction mechanism of adding hydrated calcium ferrite \((\text{CaO})_3 \cdot \text{Fe}_2\text{O}_3 \cdot (\text{H}_2\text{O})_6\), hereafter called \( \text{C}_3\text{FH}_6 \)), and the preparation principles and methods of \( \text{C}_3\text{FH}_6 \) have been studied systematically in the Zhengzhou Light Metal Research Institute in China [19 - 21]. When \( \text{C}_3\text{FH}_6 \) is dosed at a C/S of 1.5, after digestion of Henan bauxite \((\text{A/S} = 6.0)\) at 260 °C for 60 minutes, the A/S and N/S in the resulting red mud are 0.7 and 0.17 respectively. The red mud also settles well. Because the process of \( \text{C}_3\text{FH}_6 \) preparation is complicated, the Zhengzhou Light Metal Research Institute demonstrated that \( \text{C}_3\text{FH}_6 \) could be successfully replaced by \((\text{CaO})_3 \cdot \text{Fe}_2\text{O}_3\) [22].

### 3.3 Post-Process

#### 3.3.1 Series Process

Initially, the Bayer process is used to treat bauxite and the majority of \( \text{Al}_2\text{O}_3 \) is extracted. The Sinter process is then used to treat the red mud. Alumina and soda is recovered from the mud, and the sodium aluminate solution produced is recycled into the Bayer process. When using the Series method to treat low grade bauxite, the recovery of alumina is high, alkali consumption is low, and energy consumption is obviously lower than the Sinter method [23 - 26].
There are two refineries using the Series process in China now [27].

3.3.2 The New Wet Series Process

A double stage wet digestion, called the “New Series” process was proposed by the Zhengzhou Research Institute of Chalco [28]. The flow sheet is shown in Figure 2. The bauxite is digested under the current Bayer conditions with the molar ratio of caustic soda to alumina in leaching liquor ($a_k$) of 1.35 - 1.60, the alumina to silica mass ratio (A/S) of 1.00 - 1.60 in the red mud after digestion. In the second stage, the red mud from the first stage was leached at 200 – 300 °C with an optimised liquor caustic concentration and caustic soda to alumina molar ratio. The lime added was controlled to a CaO to SiO$_2$ mass ratio of 1.5 - 2.5, resulting in a mass ratio of alumina to silica (A/S) of 0.2 - 0.8, and soda to silica (N/S) of 0.01 - 0.20 in the red mud for disposal.

![Figure 2. Flow sheet of the New Wet Series process.](image)

3.3.3 Coal-based Reduction Sinter Process

A coal-based Reduction Sinter process was studied to treat high ferric Bayer red muds [29]. An amount of coal is added as a reducing agent to the traditional batch formula in the Sinter process. As a result, Fe-containing minerals in Bayer red mud are transformed into elementary Fe by controlling the temperature and the reducing conditions in the Sinter process. The laboratory test results show that the recovery efficiency of Fe, Al$_2$O$_3$ and Na$_2$O is 94.4%, 75% and 80% respectively. The purity of iron recovered is 93.7%.

3.3.4 Calcification-Carbonation Process

The Calcification-Carbonation process for alumina production from Bayer red mud or low grade bauxite was presented by the Northeast University in China. The flowsheet is shown in Figure 3.
There are three main steps in the process; 1) In the Calcification step, the calcification and alkaline-recovery of soda and alumina from Bayer red mud mixed with lime or calcium aluminate take place in a high Na solution (100 - 300g/L) at a temperature of 80 -180°C and with a reaction time of 10 – 60 min. As a result, all the silica-containing minerals in the mud are transformed into hydrogarnet, and a high Na concentration solution is produced. 2) The Carbonation step in which water and CO₂ are added, with the CO₂ partial pressure controlled at 0.8 - 1.8 MPa, a reaction temperature of 80 - 160°C, and reaction time of 10 – 240 minutes. The main minerals in the solid phase after the Carbonation reaction are calcium silicate, CaCO₃ and Al(OH)₃. 3) Digestion of Al(OH)₃ at low temperature. The solid phase from the Carbonation step is digested in sodium aluminate solution with the Na concentration 50-150g/L and then the Al₂O₃ in the solution is precipitated as calcium aluminate which is returned to calcification reaction section and cycled [30, 31].

**Figure 3. Experimental procedure for Calcification-Carbonation processing of red mud.**

### 3.4 Other Technologies

#### 3.4.1 Sinter Process

The Sinter process, including the soda-lime and limestone processes, can in theory be used to treat any Al₂O₃-containing resources for alumina production. It has a high coefficient of resource utilization and low soda consumption when low grade bauxite is treated by this process. But it requires a huge investment, is a complicated production process and has a high specific energy consumption.
3.4.2 Two Stage Sinter Process

A two-stage sinter process suitable for Chinese low grade bauxite was put forward in the 1970s in China [32]. In the first stage only Na$_2$CO$_3$ is added and sintered with bauxite, SiO$_2$ is converted to sodium aluminosilicate, and Al$_2$O$_3$ converted to Na$_2$O·Al$_2$O$_3$. Limestone is added and sintered with the first red mud in the second stage, SiO$_2$ is converted to 2CaO·SiO$_2$, and Al$_2$O$_3$ is converted to Na$_2$O·Al$_2$O$_3$.

The major advantage of the two-stage sinter process is that the batch formula of Al$_2$O$_3$, Na$_2$O and SiO$_2$ in first stage and that of CaO and SiO$_2$ in the second need not be very strict. The use of the two stage sinter process has become less and less feasible, following the continued drop in Chinese bauxite grades.

3.4.3 Technologies Based on Hydrochemical or Hydrothermal Processes

Researchers in the former USSR, Hungary and Czech Republic have been studying the extraction of alumina from high silica materials containing aluminium using wet-processes since the 1950s. The theory of high pressure hydrochemical processes is that the silica in ore is transformed into minerals without, or with low alumina and soda content at high temperatures (260-350°C), such as sodium-calcium silicate hydrate, calcium silicate hydrate, Fe-containing hydrogarnets, etc. Alumina is extracted into liquor in the form of sodium aluminate. The main feature of the high pressure hydrochemical process is that the liquor caustic soda concentration is high (300 - 500g/L Na$_2$O), and the caustic ratio is also high ($\alpha_K$ 30-35). The reactions of the hydrothermal process take place at high temperatures (over 240 °C) with a lower caustic soda in liquor, and with a lower caustic ratio compared to the High Pressure Hydrochemical Process.

Researchers in China have studied technologies based on hydrothermal or hydrochemical processes systematically since the 1980s and proposed a series of new processes, such as Low temperature digestion-High pressure hydrochemical process, and new “Wet Series” process and so on, according to characteristics of Chinese bauxite resources.

The researchers from the Institute of Process Engineering at the Chinese Academy of Science proposed the process of digesting diasporic bauxite at low temperature [33]. The flowsheet is shown in Figure 4. A higher alumina extraction rate of over 90% could be reached while digestion was carried out at 150-200°C for 0.5 - 3 hours with an NaOH concentration of 40 – 70 %. The main forms of silica in the red mud were sodium aluminosilicates such as Na$_8$Al$_6$Si$_6$O$_{24}$(OH)$_2$(H$_2$O)$_2$ and Na$_9$Al$_9$Si$_{15}$O$_{48}$(H$_2$O)$_{27}$ [34]. A new process for producing alumina with low grade bauxite, called the low temperature digestion-high pressure hydrochemical process, had been proposed in which the process above was combined with High Pressure Hydrochemical Process [35]. A higher alumina extraction rate of over 95 % and N/S ratio of lower than 0.20 in the red mud could be reached when low grade bauxite with an A/S ratio of 3 to 7 was treated with the low temperature digestion-high pressure hydrochemical process.
New Sinter Process

Some patents from the Chang’an University in China propose that sodium carbonate or sodium hydroxide can react with the silica or alumina in low-grade bauxite with high selectivity by controlling the roasting temperature and residence time. On the basis of these findings, a series of Chinese patents for the production of alumina with low-grade bauxite have been lodged. One such patent (CN201010231520.5) involves increasing the A/S ratio of bauxite by roasting a mixture of low-grade bauxite and sodium carbonate at 120 – 500 °C for 20 - 40 minutes so as to make the sodium carbonate react with the silica in the bauxite with high selectivity. Another patent (CN201110002674.1) is for producing sodium aluminate by roasting a mixture of low-grade bauxite and sodium carbonate at 620 – 990 °C for 10 - 60 minutes so as to make the sodium carbonate react with the alumina. The patent CN201110002305.2) is for producing sodium aluminate by roasting the mixture of low grade bauxite and sodium hydroxide at 520 – 1000 °C for 10 - 60 minutes so as to make the sodium hydroxide react with the alumina in the bauxite at a high selectivity.

The Technology Development Direction for Alumina Production using Low Grade Bauxite in China

Only the Bayer-Sinter Series process and the Flotation-Bayer process have been used in some refineries in China, even though many efforts had been made to develop alumina production processes using low grade bauxite.

Chinese bauxite resources are mainly distributed in Henan, Shanxi, Shandong, Guangxi, Guizhou, Yunnan and Chongqing. The characteristics of each region’s bauxite resources vary between the mining areas, such as that the silica containing minerals in the bauxite in Henan are...
mainly non-kaolinite silica, while those in Shanxi are mainly kaolinite. The bauxite in some Guizhou mining areas and most of the mining areas under the coal contains high sulfur minerals, and these sulfur minerals which have detrimental effect on the production process which need to be eliminated or mitigated. The content of Fe$_2$O$_3$ in the bauxite in Guangxi and Yunnan is higher, so the comprehensive recovery and utilization of Fe$_2$O$_3$ simultaneously in the process of extraction of alumina should be considered.

For the bauxite where the silica containing minerals are non-kaolinite minerals, such as the low grade bauxite in Henan, the further systematic optimization of flotation desilication technology should be the development direction to maximize economic benefit. Both the A/S and N/S ratio in red mud could be reduced when Flotation is followed by the Bayer process.

For the bauxite in which the main silica containing mineral is kaolinite, such as the low grade bauxite in Shanxi, it is difficult to control both the A/S and N/S ratio in red mud at lower levels when using the Bayer process to produce alumina, so the further systematic optimization of flotation desilication technology, new technology of wet series process, chemical desilication technology and series process should be regarded as the development direction of alumina production technology. For the bauxite resources in some mining area, the comparison of different technologies should be carried out to determine the optimal process. In the process of optimization of series process, it is necessary to focus on the dry-feeding technology in order to reduce the energy consumption of the production system greatly.

The accumulation of sulfur in the production system will not only affect product quality but also cause the corrosion of equipment for preheating and digestion when fed to the Bayer process directly. Consequently, for the low-grade bauxite with high sulphur, such as some mining areas in Chongqing and Guizhou, new or improved desulphurization and desilication processes using ore beneficiation or desulphurization by calcination followed by chemical desilication prior to the Bayer process is recommended to use the high sulfur bauxite efficiently and economically.

For the low grade bauxite with high iron, such as some mining areas in Guangxi and Yunnan, the extraction and recovery of iron should be integrated with the alumina production process, to use the high iron bauxite comprehensively and to realize the maximum economic benefits.

5 References

20. Xin-hua Li, et al, The mechanism, research progress and application prospect of the new process that calcium hydrate was added in the Bayer process, Proceedings of the 6th annual academic conference of the Nonferrous Metals Society of China (C), Beijing, 2005, 373-375.
21. Xin-hua Li, et al, Dissolution tests of the new process that calcium hydrate was added in the Bayer process, Journal of Chinese Rare Earths, 2006, 24 (Special Issue), 553-555.