Efficient and Sustainable Production of Alumina by Electrolysis of Sodium Carbonate**

Zhanglong Yu, Yongmei Chen, Yinjian Niu, Yang Tang, Pingyu Wan,* Zijian Lv, and X. Jin Yang*

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Supporting Information

Experimental Section

Membrane electrolytic cell

The schematic of the membrane electrolytic cell is illustrated in Fig. S1. The effective area of the cation ion exchange membrane used in the laboratory-scale cell was 120 cm$^2$. The tests for selecting anode materials and the effect of the electrolytic solution temperature were carried out in the laboratory-scale cell using 1.5 mol/L Na$_2$CO$_3$ solution.

In the pilot test the effective area of the membrane was 0.44 m$^2$. The total volume of anode and cathode chambers was 8.8 L. Before the electrolysis was started, 4.4 L Na$_2$CO$_3$ (1.5 mol/L) and 4.4 L NaOH (5.5 mol/L) solutions were filled into the anode and cathode chamber, respectively. After about 1 h electrolysis, the cathode and anode chambers were fed with water and Na$_2$CO$_3$ solution generated from the aluminum hydroxide precipitation. The concentrations of the products from both chambers were controlled by the flow rates. The electrolysis parameters were: IrO$_2$-Co$_3$O$_4$/Ti anode, RuO$_2$/Ni cathode, the electrolysis temperature 75 °C and the current density 1000 A/m$^2$.

Alkali digestion of bauxite

The digestion efficiency by different NaOH concentrations was investigated using a laboratory digestion autoclave of 0.2 L at a pressure of 3.6 MPa, a stirring speed of 90 rpm and 260 °C for 2 h. The amount of diaspore was 40.9 g and caustic soda solution (6.5 M NaOH) was 0.1 L. The digestion efficiency was defined as the amount of Al in the caustic soda solution divided by total amount of Al in the ore digested.

The volume of autoclave employed in the pilot test was 40 L volume. NaOH solution of 20 L produced by the electrolysis and 8.18 kg Diaspore were added to the autoclave, and then were heating to 260 °C for 2 h. Four autoclave digestions were carried out at a time.

Al(OH)$_3$-precipitation

In laboratory studies for Al(OH)$_3$-precipitation using NaHCO$_3$ carbonation, the experiment was carried out in a 2 L container with a mechanical agitation. A solution of 1.2 mol/L NaHCO$_3$ was pumped at a flow rate of 2.0 mL/min to the 200 mL synthetic caustic sodium aluminate solution (1.6 mol/L NaOH and 4.85 mol/L NaAl(OH)$_4$). The solution was stirred by an overhead agitator at 90 rpm. The pH value of the solution was monitored using a pH meter.

In the pilot test, the precipitation was carried out in a 200 L tank. The digestion solution (20 L) from ore digestion was added to the tank and then was neutralized with the NaHCO$_3$ solution from anode chamber of the electrolysis cell. The temperature of the precipitation was controlled at 60 °C.

Analysis and characterization

Samples of aluminum hydroxide were examined by a Hitachi S4700 SEM instrument with an applied voltage of 20 kV. A thin film of gold was coated on the samples prior to examination. The particle size distribution of the precipitates was measured by a Malvern Mastersizer-Laser particle size analyzer. The Al$_2$O$_3$ concentration in the leachate and spent green liquor was determined by EDTA-Zn titration and inductively coupled plasma atomic emission spectrometer (ICP-AES) (Shimadzu ICP S7500), respectively.

Chemicals and Apparatus

The chemicals and reagents employed in laboratory studies were analytical grades and purchased from Beijing Chemicals Company, China. The pH meter was Mettler-Toledo FE20K (Switzerland). The membrane (F6801 perfluoro sulfonated-carboxylate ion exchange membrane) was obtained from Asahi Kasei Corporation, Japan.
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**Figure S1** Schematic illustration of the electrolytic cell.

**Figure S2** The effects of (A) anode materials and (B) temperature on cell voltage.

**Figure S3** (A) Influence of inlet water flow rate on the outlet concentration of NaOH. (B) Influence of the inlet flow rate of Na$_2$CO$_3$ on the outlet concentration of Na$_2$CO$_3$ and NaHCO$_3$.

**Figure S4** The stability of electrolysis of Na$_2$CO$_3$ solution (A) The concentration of NaOH and NaHCO$_3$ and (B) the cell voltage as a function of electrolysis time.

**Figure S5** Effect of initial NaOH concentration on the leaching efficiency of Diaspore ores with different A/S ratios.

**Figure S6** (A) The decomposition efficiency of NaAl(OH)$_4$ in sodium aluminate solution as a function of NaHCO$_3$ dose. (B) The pH value and concentration of dissolved Al in the solution as a function of NaHCO$_3$ dose.

**Figure S7** The percentage concentration of impurities (Na$_2$O, SiO$_2$ and Fe$_2$O$_3$) and loss on ignition (LOI) and the fraction of <45 μm particles in the Al(OH)$_3$ product at different total precipitation time.

**Figure S8** Standard material flow diagram and energy intensity of the Bayer, sinter and the proposed process based on production of 1 ton alumina.

**Table S1** The basic chemistries of the Bayer, sinter and proposed processes.

**Table S2** Energy consumption for the major steps of the Bayer and proposed process for processing diaspore ores (unit in GJ, based on 1 ton alumina production)
Figure S1 Schematic illustration of the electrolytic cell. The effective surface area of the membrane in the cell used in laboratory studies and pilot test is 120 cm$^2$ and 4400 cm$^2$. The membrane is F6801 perfluorosulfonated-carboxylate ion exchange membrane (Asahi Kasei Corporation), and the anode and cathode are IrO$_2$-Co$_2$O$_3$/Ti and RuO$_2$/Ni, respectively.

Figure S2 The effects of anode materials (A) and temperature (B) on cell voltage. RuO$_2$/Ni was used as cathode in both (A) and (B), and IrO$_2$-Co$_2$O$_3$/Ti was used as anode in (B). Current density, 1000 A/m$^2$. The variation of cell voltage for RuO$_2$-Ni$_2$O$_3$/Ti anode was the largest among the four anode materials.

Figure S3 (A) Influence of inlet water flow rate on the outlet concentration of NaOH. (B) Influence of the inlet flow rate of Na$_2$CO$_3$ on the outlet concentration of Na$_2$CO$_3$ and NaHCO$_3$. The temperature of electrolyte, 75 °C; the current density, 1000 A/m$^2$; anode, IrO$_2$-Co$_2$O$_3$/Ti; cathode, RuO$_2$/Ni.
**Figure S4** The stability of electrolysis of Na$_2$CO$_3$ solution. (A) The concentration of NaOH and NaHCO$_3$ and (B) the cell voltage as a function of electrolysis time. The electrode was IrO$_2$-Co$_3$O$_4$/Ti anode–RuO$_2$/Ni cathode pair; the temperature of the electrolyte: 75 °C; the current density: 1000 A/m$^2$; the flow rates: water 1 L/h, 1.5 M Na$_2$CO$_3$ solution 8.5 L/h.

**Figure S5** Effect of initial NaOH concentration on the leaching efficiency of Diaspore ores with different A/S ratios. Temperature, 260 °C; duration of leaching, 2 h; the (MR)$_a$ was controlled to be 1.35. Initial concentration of NaOH: a - 3.23 mol/L, b - 4.84 mol/L, c - 6.45 mol/L, d - 8.06 mol/L, e - 9.68 mol/L.

**Figure S6** (A) The decomposition efficiency of NaAl(OH)$_4$ in sodium aluminate solution as a function of NaHCO$_3$ dose. (B) The pH value and concentration of dissolved Al in the solution as a function of NaHCO$_3$ dose. Twenty liters of aluminate solution [1.6 M NaOH and 4.85 M NaAl(OH)$_4$] was added to the reactor and NaHCO$_3$ solution (1.3 M) was pumped to aluminate solution at a flow rate of 10 L/h. The reaction temperature was 60-70 °C;
**Figure S7** The percentage concentration of impurities (Na$_2$O, SiO$_2$ and Fe$_2$O$_3$) and loss on ignition (LOI) and the fraction of <45 μm particles in the Al(OH)$_3$ product at different total precipitation time.

**Table S1** The basic chemistries of the Bayer, sinter and proposed processes $[^a]$.  

<table>
<thead>
<tr>
<th>Step</th>
<th>Bayer process</th>
<th>Sinter process</th>
<th>Proposed process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Digestion and Leaching</td>
<td>$0.25$Al$_2$O$_3$H$_2$O + $0.5$H$_2$O + NaAl$_2$O$<em>4$OH$</em>{1.5-1.3}$ $[^b]$</td>
<td>$0.5$Al$_2$O$_3$H$_2$O + $0.65$Na$_2$CO$_3$ = $Na_2$Al$_2$O$<em>4$CO$</em>{2.5-0.65}$ + $2.15$H$_2$O = $Na_2$Al$<em>2$(OH)$</em>{1.5-1.3}$</td>
<td>$0.5$Al$_2$O$_3$H$_2$O + $1.3$NaOH + H$_2$O = $Na_2$Al$<em>2$(OH)$</em>{1.5-1.3}$</td>
</tr>
<tr>
<td>Al(OH)$_3$ precipitation</td>
<td>$Na_2$Al$<em>2$(OH)$</em>{1.5-1.3}$ + $1.3$NaOH (seed) = ($ß+0.5$)Al(OH)$_3$↓ + $Na_2$Al$<em>2$(OH)$</em>{1.5-1.3}$ $[^c]$</td>
<td>$Na_2$Al$<em>2$(OH)$</em>{1.5-1.3}$ + $0.65$CO$_2$ = Al(OH)$_3$↓ + $0.65$Na$_2$CO$_3$</td>
<td>$Na_2$Al$<em>2$(OH)$</em>{1.5-1.3}$ + $1.3$NaHCO$_3$ = Al(OH)$_3$↓ + $1.3$Na$_2$CO$_3$ + $1.3$H$_2$O</td>
</tr>
<tr>
<td>Spent green liquor treatment</td>
<td>$Na_2$Al$<em>2$(OH)$</em>{1.5-1.3}$ (dilute) $→$ Na$_2$CO$_3$ (dilute) $→$ Na$_2$CO$_3$</td>
<td>Evaporation (No chemical changes) $→$ Evaporation (No chemical changes) $→$ Electrolysis</td>
<td>Na$_2$CO$_3$ + $2$H$_2$O $→$ NaHCO$_3$ + NaOH + H$_2$ + $1$CO$_2$</td>
</tr>
</tbody>
</table>

$[^a]$ Diaspore (Al$_2$O$_3$.H$_2$O) is used as an example to express the chemistries of the processes. The mole ratio (MR) of Na$_2$O to Al$_2$O$_3$ in the caustic liquor ([NaOH+NaAl(OH)$_4$] before the digestion (MR)$_d$, and after digestion (MR)$_i$ in the Bayer process is important and typical values of (MR)$_d$ and (MR)$_i$ are 2.6 and 1.3 respectively in the Bayer process. Thus the formula of sodium aluminate and caustic soda composite is written as Na$_2$Al$_2$(OH)$_{3y-x}$ (x/y=MR) for comparison of the chemistries of the three processes and the comparison clearly demonstrates the differences in digestion capacity and aluminum hydroxide precipitation.  

$[^b]$ The chemistry of digestion is generally expressed by Al$_2$O$_3$.H$_2$O + 2NaOH +aq $→$ NaAl$_2$(OH)$_{1.5-1.3}$ + NaOH where $ß$ is seed ratio.

$[^c]$ The chemistry of seeded precipitation is usually written as NaAl$_2$(OH)$_{1.5-1.3}$ + $ß$NaAl(OH)$_3$ (seed) = ($ß+1$)Al(OH)$_3$ + NaOH $→$ Al(OH)$_3$↓ + Na$_2$O + $ß$H$_2$O.

**Table S2** Energy consumption for the major steps of the Bayer and proposed process for processing diaspore ores (unit in GJ, based on 1 ton alumina production).

<table>
<thead>
<tr>
<th>Step</th>
<th>Bayer process Energy</th>
<th>Literature data</th>
<th>The proposed process Energy</th>
<th>Note</th>
</tr>
</thead>
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<tr>
<td>Digestion</td>
<td>3.99 $[^a]$</td>
<td>2.7-5 $[^1]$</td>
<td>2.74</td>
<td>Measured $[^b]$</td>
</tr>
<tr>
<td>Precipitation</td>
<td>0.23</td>
<td>3.2-5.0 $[^2]$</td>
<td>0.18</td>
<td>Estimated</td>
</tr>
<tr>
<td>Evaporation</td>
<td>4.45</td>
<td></td>
<td>0.00</td>
<td>NA</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>-</td>
<td></td>
<td>6.66</td>
<td>Measured, 1850 kWh</td>
</tr>
<tr>
<td>Calcination</td>
<td>3.38</td>
<td>3-5 $[^3]$</td>
<td>0.23</td>
<td>$[^c]$</td>
</tr>
<tr>
<td>Total</td>
<td>12.05</td>
<td>9.3-14.7 $[^4]$</td>
<td>9.81</td>
<td></td>
</tr>
</tbody>
</table>

$[^a]$ The energy for digesting diaspore is generally higher than that for gibbsite ores.  

$[^b]$ The electrolysis of carbonate produces pure and concentrated NaOH of caustic digestion liquor (6.5 mol/L NaOH). The volume of this digestion liquor required for digesting and leaching out the same amount of Al$_2$O$_3$ from the ores is reduced by 40-50% in comparison with the volume of spent green liquor (mixtures of 4.0 mol/L NaOH and 2.5 mol/L aluminate) in the Bayer process. Accordingly, the energy for digestion is significantly reduced.  

$[^c]$ Refer to footnote $[^c]$ of Table 2.  

$[^d]$ This is for all-inclusive energy consumption for all the steps of the Bayer process, including bauxite ore grinding, mixing, digestion, red-mud separation, desilication, precipitation, evaporation and calcination.

**References**
