BAUXITE RESIDUE VALORISATION AND BEST PRACTICES CONFERENCE

Leuven 5-7 October 2015
OPPORTUNITIES FOR HIGH VOLUME COMMERCIAL PRODUCTS CONVERSION FROM BAXITE RESIDUE

Brajendra Mishra

Center for Resource Recovery & Recycling

Bauxite Residue Valorisation and Best Practices

Leuven, Belgium

October 5-7, 2015
Generation of red mud

Bayer-process

- Bauxite
  - crushing
  - milling

- Pressure vessel
  - NaOH

- Na[Al(OH)₄]
  - filtering
  - cooling

- Crystallization
  - Al(OH)₃ as crystallization seed
  - water

- Aluminium oxide
  - rotary kiln

T = 170...180 °C
Red Mud

Industry Processes
(Construction Aggregate, etc.)

Recovery of Value Added Products

Soil Products
REFINERY FACILITY AERIAL

Courtesy: ALCOA – Charles Dobbs

RED MUD
REDMUD

• Production of primary aluminum: 55 mT/yr
• Bauxite mining: 300 mT/yr
• 50% of bauxite is red-mud: a waste-product from the Bayer’s Process

  Fe₂O₃: 70 wt. pct. (35-38% metal value)
  Al₂O₃: 10 wt. pct.
  TiO₂:  7.0 wt. pct.
  CaO:   7.5 wt. pct.

(Sodium-, silicon-, manganese-, chromium-, zinc-oxides)
The legacy......

Global residue production and inventory

residue production rate (Mtpa)

cumulative residue (Mt)

year

0 1900 1920 1940 1960 1980 2000

0 500 1000 1500 2000 2500 3000
## Red mud around the world

<table>
<thead>
<tr>
<th>Country</th>
<th>Main constituents (%)</th>
<th>(ppm) Sc$_2$O$_3$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe$_2$O$_3$</td>
<td>Al$_2$O$_3$</td>
<td>CaO</td>
</tr>
<tr>
<td>Australia</td>
<td>28.5–56.9</td>
<td>15.6–24.0</td>
<td>2.3–5.3</td>
</tr>
<tr>
<td>Brazil</td>
<td>45.6</td>
<td>15.1</td>
<td>1.2</td>
</tr>
<tr>
<td>China</td>
<td>3.0–6.2</td>
<td>5.0–8.6</td>
<td>34.0–39.5</td>
</tr>
<tr>
<td>Germany</td>
<td>44.8</td>
<td>16.2</td>
<td>5.2</td>
</tr>
<tr>
<td>Greece</td>
<td>42.5</td>
<td>15.6</td>
<td>19.7</td>
</tr>
<tr>
<td>Italy</td>
<td>15.2</td>
<td>24.7</td>
<td>4.2</td>
</tr>
<tr>
<td>Jamaica</td>
<td>42.3</td>
<td>16.4</td>
<td>9.1</td>
</tr>
<tr>
<td>Russian</td>
<td>19.7–46.0</td>
<td>11.8–15.4</td>
<td>10.6–30.2</td>
</tr>
<tr>
<td>Spain</td>
<td>37.5</td>
<td>21.2</td>
<td>5.5</td>
</tr>
<tr>
<td>USA</td>
<td>35.5</td>
<td>18.4</td>
<td>7.73</td>
</tr>
</tbody>
</table>
## Mineralogy

<table>
<thead>
<tr>
<th>MINERAL</th>
<th>Bauxite</th>
<th>Redmud</th>
</tr>
</thead>
<tbody>
<tr>
<td>GIBBSITE, Al(OH)$_3$</td>
<td>65-70</td>
<td>5-8</td>
</tr>
<tr>
<td>BOEHMITE, AlOOH</td>
<td>3-5</td>
<td>5-8</td>
</tr>
<tr>
<td>GOETHITE, FeOOH</td>
<td>8-10</td>
<td>3-5</td>
</tr>
<tr>
<td>HEMATITE, Fe$_2$O$_3$</td>
<td>5-8</td>
<td>45-50</td>
</tr>
<tr>
<td>ANATASE, TiO$_2$</td>
<td>2-3</td>
<td>1-2</td>
</tr>
<tr>
<td>APATITE, Ca$_5$(PO$_4$)$_3$ (OH,Cl,CO$_3$)</td>
<td>1-2</td>
<td>4-5</td>
</tr>
<tr>
<td>CALCITE, CaCO$_3$</td>
<td>1-2</td>
<td>1-2</td>
</tr>
<tr>
<td>QUARTZ, SiO$_2$</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>Also iron and calcium titanate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Recovery Processes of Red mud

<table>
<thead>
<tr>
<th>Process</th>
<th>Products</th>
<th>Note</th>
</tr>
</thead>
</table>
| 1) Pyro only     | Pig iron, Ti-rich slag (REE)/Metallic iron | ✓ Pyro method  
① smelting: Iron oxide Reduction in blast furnace or similar reactor  
② solid state reduction  
✓ Disadvantage  
• High Na contents in Red Mud: sodium oxide deposition -.  
• High drying cost of red mud |
| 2) Pyro + Hydro  | Pig iron, REE (from REE slag)               | ✓ Pig iron by reductant, Concentration of REE in slag  
✓ Recovery of Concentrated REE by hydro method  
✓ High sodium contents and Waste water problem |
| 3) Hydro only    | REE                                         | ✓ Selective leaching of REE (Fe$_2$O$_3$ is not leached, Using HNO$_3$, Y 96%, Sc 80%, light lanthanides 30-50%)  
✓ Selective precipitation and Solvent Extraction |

**Main targets:** Scandium(Sc), Gallium(Ga), Titanium(Ti)  
**By-products:** Iron(Fe), Aluminum(Al)
A fundamental choice

Options:

- Capacity, demand & supply,
- economics, environmental impacts, transport

BR → construction aggregate
BR → metal(s) + building material
BR → metal(s) + oxides + building material
What are the suggested paths forward?

**Use BR as an admixture in standard OPC**

Done, also industrially, max 3wt% because of OPC chemistry (low iron!)

**High-Fe hydraulic cement**

Two groups foreseen, i.e. ferrite-rich cements and sulfo-ferroaluminate-rich.

Comparable mechanical properties to OPC but also unique characteristics (niche market)

**Fe-rich inorganic polymers**

See work already taking place in CR³.

Inorganic polymers are more and more industrially acceptable...
Real life applications of inorganic polymers

A fundamental choice: is BR core business or not?

25 tons of Red Mud Treated

16 tons of Slag Produced

5 tons of Pig Iron Produced

Walker & NTUA Development
Pig iron & other products

- Blast Furnace route
- Other smelting options
- Applications for slag
Potential applications

Value-added Products: Alternatives

- Alumina and an iron-rich BF feed material (100 pct.)
- Alumina, pig-iron and titanium oxide (75 pct.)
- Alumina and ferro-titanium (70 pct.)

KEY FACTORS: Cost, material and energy balance for the number of processes required.
Process Flow

Dry

Simultaneous Sinter and Reduction

Magnetic Separation

Magnetic Fraction

Compare with DRI

Acceptable

Iron Recovery

Not Acceptable

Smelting

Non-Magnetic Fraction

Leaching and Drying

Alumina Recovery

Residue

Slag Analysis for further Recovery
**Process Material Flow (without magnetic separation):**

- **Red Mud Analysis:** 70% Fe$_2$O$_3$, 10% Al$_2$O$_3$, 7% CaO, 7% TiO$_2$, 2% SiO$_2$ and 4% other constituents

- 1 kg dried redmud after sintering, leaching, drying and reduction yields **725 g of product**.

**Product analysis:**

- Fe: 60%, FeO: 8%, SiO$_2$ and Al$_2$O$_3$: 4.5%, CaO: 11.5%, TiO$_2$: 9%, Na$_2$O: 1% and others: 6%.

- LOI of as-received redmud is approx. 27 wt. pct. at 400°C
Blast Furnace Addition

- **BASIS:** 100 Kg redmud added through tuyeres per tonne of hot metal.

- Coke required: 338 kg (357 kg): *Saving 5 %*
- Slag produced: 252 kg (245 kg)
- Lime required: 82 kg (93 kg): *Saving 12 %*
- Iron Ore required: 1317 kg (1429 kg): *Saving 8 %*
- Higher productivity due to less ore, coke and lime charged from the top.
- Hearth protection from titanium oxide in the slag
Recovery of Iron oxides

• Iron is major constituent of red mud. Iron oxide varies between 10-75% in red mud.
• Hematite conversion to magnetite and later magnetic separation was tried. It was observed that the fine particle size of red mud particles required high magnetic field intensity.
• Smelting/roasting could be performed in Fluidized beds, rotary kiln etc. To recover pig iron/iron from the red mud.
• The slag generated has applications to recover Titania, rare earths.
Recovery of Metals - Iron

Soda ash + Red mud + Coke Breeze

- Pugmilling
- Roasting, 750 °C
- Leaching
- Filtration

Leach residue

- Magnetic separation
  - Magnetic fraction
  - Non magnetic fraction
    - Smelting
    - Pig iron
    - Ti Recovery

Precipitation by CO₂

- Calcination
  - Al₂O₃
Iron Removal - Reduction

\[ Fe_2O_3 + 2C = 2Fe + CO(g) + CO_2(g) \]

• Carbon in the form of Petcoke is added varied from 100% to 300% excess. CaO powder layer is placed on top of the mixture in the furnace in N₂ atmosphere. The temperature of reduction ranges from 900°C to 1100°C. The iron thus reduced is separated by magnetic separation.

<table>
<thead>
<tr>
<th>Reduction Conditions</th>
<th>Weight Loss</th>
<th>Mossbauer Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp #</td>
<td>Time</td>
<td>Temp</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>900</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>1050</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1050</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>1050</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>1050</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>1050</td>
</tr>
</tbody>
</table>

• As temperature increases, reduction increases. At 1050 °C complete reduction occurs.
• Minimum time for complete reduction was achieved at 2 hours.
• As Carbon content increases from 100 % to 200 % excess complete reduction occurs.
Iron Removal – Magnetic Separation

Results from a Typical Wet or Dry Magnetic Separation Performed on Reduced Red Mud

- It is observed that Iron, calcium, titanium and aluminum segregate to the magnetic product while sulfur, manganese and sodium segregate to the non-magnetic product. Iron also distributes to the non-magnetic portion of the red mud.
- CaO is supplemented to the Bayer process and can react with titanium oxide to form perovskite. The pervoskite attaches with Iron and is separated into the magnetic portion.
- The presence of iron in the non-magnetic product could be due to residual FeO remaining from reduction.
- Smeltig operation can be applied to the non magnetic portion containing reduces iron oxides and Ca, Al, Na, Ti, Mn, Si, P, S, Zn.
**TITANIA RECOVERY**: *Perovskite to rutile*

The concentration of antas or rutile titania in red mud varies between 2.5 wt% and 22.6 wt%. 

- **Sulfation**
- **Leaching**
- **Precipitation** $\text{TiOSO}_4\cdot\text{H}_2\text{O}$
- **Dissolution & Iron Reduction**
- **Hydrolysis**
- **Pigment Washing and Bleaching**
Recovery of Titanium Oxide
Recovery of Alumina

- Red mud contains 2.2-33% alumina.
- Alumina is recovered by converting to sodium aluminate.
- Hydrometallurgically Alumina can be recovered by forming a hydro-garnet.
- Li Zhong et al have conducted a multiple stage caustic leaching process to recover Al$_2$O$_3$ and Na$_2$O.
- Simultaneous roasting employing Sodium Carbonate/ Soda ash to form Sodium Aluminate and reduce Hematite to magnetite was performed.
Recovery of Alumina

\[ \text{Na}_2\text{O}.m\text{Al}_2\text{O}_3.n\text{SiO}_2.x\text{H}_2\text{O}+2n\text{CaO}+(m-1)\text{Na}_2\text{CO}_3 = m\text{Na}_2\text{O}.\text{Al}_2\text{O}_3+n2\text{CaO}.\text{SiO}_2+x\text{H}_2\text{O}+(m-1)\text{CO}_2 \]
Sintering and Leaching of Alumina

**Sintering**
\[ \text{Al}_2\text{O}_3 + \text{Na}_2\text{CO}_3 = 2\text{NaAlO}_2 + \text{CO}_2(g) \]
*Temperature of operation: 850-1100°C*
*Time: 2 hours*

**Leaching**
\[ \text{NaAlO}_2(s) = \text{NaAlO}_2(aq) \]
*Temperature of operation: 25-100°C*
*Time: 5-30 minutes, Red Mud to water: 2-50 gpl*
## Sintering and Leaching of Alumina

<table>
<thead>
<tr>
<th>Run #</th>
<th>Temperature</th>
<th>Excess Soda</th>
<th>A/C Ratio</th>
<th>Excess Caustic</th>
<th>Recovery</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>850</td>
<td>50</td>
<td>0.6</td>
<td>100</td>
<td>66.7</td>
<td>76.8</td>
</tr>
<tr>
<td>2</td>
<td>950</td>
<td>50</td>
<td>0.6</td>
<td>100</td>
<td>67.4</td>
<td>81.4</td>
</tr>
<tr>
<td>3</td>
<td>1050</td>
<td>50</td>
<td>0.6</td>
<td>100</td>
<td>69.6</td>
<td>83.1</td>
</tr>
<tr>
<td>4</td>
<td>950</td>
<td>0</td>
<td>0.6</td>
<td>100</td>
<td>62.7</td>
<td>66.2</td>
</tr>
<tr>
<td>5</td>
<td>950</td>
<td>50</td>
<td>0.6</td>
<td>100</td>
<td>66.9</td>
<td>75.3</td>
</tr>
<tr>
<td>6</td>
<td>1050</td>
<td>50</td>
<td>0.6</td>
<td>0</td>
<td>59.9</td>
<td>76</td>
</tr>
<tr>
<td>7</td>
<td>1050</td>
<td>50</td>
<td>0.6</td>
<td>150</td>
<td>39.9</td>
<td>54.3</td>
</tr>
</tbody>
</table>

- Concentration of sodium hydroxide solution, time, temperature of leaching and A/C ratio are kept constant.
- The washing conditions are kept constant at 100°C for 15 minutes using a ratio of 10g/l of red mud to distilled water.
- As temperature increases, extraction efficiency increases
- Excess sodium carbonate and caustic added increases the formation of sodium aluminate and extraction of alumina respectively.
Caustic leaching of Red Mud

- Experiments conducted at Temp: 60 °C, 80 °C; Leaching time: 3h, 6h; NaOH Concentration: 10%, 50% and 100% excess, pH 9~10
- Only could get 1% of Aluminum of red mud out.
Iron Removal-Concentrating Magnetite (Proposed)
Conclusions

♦ Redmud generated from Jamaican bauxite has approx. 60 % iron oxide in hematite form
♦ Alumina can be recovered with over 90 % efficiency by soda-ash sintering and caustic leaching
♦ Iron oxide can be reduced by carbothermic reduction with over 92 % metallization
♦ The product after leaching can possibly be used as a feed to the blast furnace