Soda Sintering Process for the Mobilization of Aluminum and Gallium in Red Mud

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Motivation

Red Mud from landfill Lünen (ex VAW), Germany contains high amounts of aluminum → Utilization as alumina and gallium source

<table>
<thead>
<tr>
<th>Components in wt.-%</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>TiO₂</th>
<th>Na₂O</th>
<th>Cr₂O₃</th>
<th>Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Mud</td>
<td>27</td>
<td>28.5</td>
<td>13.1</td>
<td>3.8</td>
<td>8</td>
<td>7</td>
<td>0.35</td>
<td>65 ppm</td>
</tr>
</tbody>
</table>

- **Requirements for processing:**
  - High recoveries of gallium and aluminum
  - High selectivity (low effort for purification)
  - Stable and simple process

- **Aim of the treatment:**
  - Aluminum recovery: > 80 %
  - Gallium recovery: > 80 %
Extraction Processes

- **Bayer-Process**
  - simple and economical process
  - High selectivity
  - poor aluminum recoveries at mild digestion conditions

- **Acidic leaching**
  - Simultaneous leaching of minor elements
  - Not selective → Need of leachate purification
  - Losses of acid due to alkaline red mud

- **Na$_2$CO$_3$ Sintering (Dry digestion)**
  - High selectivity and Al-recoveries
  - Cost-intensive: Energy, grinding, Na$_2$CO$_3$ recovery
Thermodynamic basics: Soda fusion

Principle: Soda-potash fusion

→ Silicates and metal oxides are digested in fused salt

For trivalent ions like Al2O3

\[
\text{M}_2\text{O}_3(\text{s}) + \text{Na}_2\text{CO}_3(\text{s}) \rightleftharpoons 2 \text{NaMO}_2(\text{s}) + \text{CO}_2(\text{g})
\]

\[
\text{M}_2\text{SiO}_5(\text{s}) + 3 \text{Na}_2\text{CO}_3(\text{s}) \rightleftharpoons 2 \text{NaMO}_2(\text{s}) + 3 \text{CO}_2(\text{g}) + \text{Na}_4\text{SiO}_4(\text{s})
\]

For tetravalent ions like TiO2, SiO2

\[
\text{MO}_2(\text{s}) + \text{Na}_2\text{CO}_3(\text{s}) \rightleftharpoons \text{Na}_2\text{MO}_3(\text{s}) + \text{CO}_2(\text{g})
\]

→ equilibrium constant can be influenced by the CO2 partial pressure

CO2 partial pressure can be reduced by carbon addition due to

Boudouard reaction: \( \text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2 \text{CO}(\text{g}) \)

→ Carbon addition shifts equilibrium to water soluble compounds
Thermodynamic basics: Lime addition

Principle: Immobilization of reactive silica

- Silica from split (sodium)aluminum silicates (DSP) is bonded by lime to insoluble calcium silicates

\[
2 \text{Ca(OH)}_2(aq) + \text{Si(OH)}_4(aq) \rightleftharpoons \text{Ca}_2\text{SiO}_4(s) + 4 \text{H}_2\text{O}(l)
\]

- Less dissolved silica in solution

Attention: Too much lime leads to formation of hardly soluble calcium aluminates

For comparison molar ratio C/S:

\[
\frac{\text{CaO}}{\text{SiO}_2}
\]
**Process flowchart and Parameter**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$CO$_3$</td>
<td>15 - 80 wt.-% of Red mud input</td>
</tr>
<tr>
<td></td>
<td>Stoichiometric: Al$_2$O$_3$: 16%</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$ + TiO$_2$: 28%</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$ + TiO$_2$ + Fe$_2$O$_3$: 47%</td>
</tr>
<tr>
<td>Lime (C/S)</td>
<td>0.35 – 1.5</td>
</tr>
<tr>
<td>Carbon addition</td>
<td>0, double stoichiometric Fe$_2$O$_3$ $\rightarrow$ Fe</td>
</tr>
<tr>
<td>Temperature</td>
<td>480 – 1070 °C</td>
</tr>
</tbody>
</table>
Sintering

- Resistance heated furnace:
  - 330 ml clay crucible
  - Air atmosphere
  - Continuous temperature control by 3 type K thermocouples
  - Holding time at process temperature to maintain equilibrium
Leaching

- Crushing in disc mill
- Agitated leaching
  - 50 °C (exothermic reaction with water)
  - 100 g red mud with additives in 640 ml water (avoiding solubility limit)
  - Leaching time 30 min
- Instant vacuum filtration after leaching
Results: Recoveries of Al and Ga

- At 1000 °C; C/S = 1.3
- Soda addition < 60 %: Increasing recovery of Al and Ga
- Soda addition > 60 %: Falling recovery of Al & Ga

- 15 % coke (double stoichiometric \( \text{Fe}_2\text{O}_3 \rightarrow \text{Fe} \))
- At 60 % \( \text{Na}_2\text{CO}_3 \); C/S = 1.4
- Increasing recovery of Al and Ga with increasing temperature up to 1070 °C
- Addition of carbon improves Al and Ga recovery by 10 - 15 %
Results: Recoveries of Al and Ga

- With 60% Na₂CO₃ addition
  - C/S < 1.1: Increasing recovery of Al
  - C/S > 1.1 slightly falling Al recovery
  - Ga recovery falling with increasing C/S

- With 60% Na₂CO₃ addition
  - Lower concentration of dissolved silicon with higher C/S
  - Silicon concentration very low → good selectivity
Summary

- Na$_2$CO$_3$ addition sufficient for the total transformation of Fe$_2$O$_3$, TiO$_2$ and Al$_2$O$_3$ into sodium compounds (> 50 %) is necessary for a complete aluminum extraction.
- C/S rations > 0.8 lower the concentration of dissolved silicon in the liquor significantly.
- C/S ratio of 1.2 seems to be the best for aluminum recovery.
- Higher C/S ratios lower the Ga recovery.
- Carbon addition improves Al and Ga recovery by 10-15 %.
- Sinter temperature should be in the range of 1050-1100 °C.
- Best Recoveries

Al: 84 % ; Ga: 85 %
Thank you for your attention!