From Red to Grey: Revisiting the Pedersen Process to Achieve Holistic Bauxite Ore Utilisation

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In the broad sense an **alkaline process** for extraction of alumina from low grade aluminous materials.

- Divergence from other alkaline (sintering) processes:
  1. Pig Iron by-product
  2. Solidification of aluminous phase from slag

- Raw materials with **low Al$_2$O$_3$:Fe$_2$O$_3$** ratio preferred.
- Flexibility in TiO$_2$ and SiO$_2$ concentrations of raw materials.
- One known industrial application of the process (1928 – 1969).
Pedersen Process Timeline

- **1915**
  - Harald Pedersen experiments: smelting of iron ore with low quality aluminous materials, lime and coke.
  - **Main Products:** Pig Iron low in sulfur and a calcium aluminate slag to be treated for Al extraction.

- **1920**
  - Harald Pedersen experiments: smelting of iron ore with low quality aluminous materials, lime and coke.
  - **Main Products:** Pig Iron low in sulfur and a calcium aluminate slag to be treated for Al extraction.

- **1924**
  - Patents of the Pedersen Process

- **1925**
  - Plant built at Høyanger (Norway) to recover alumina from anorthosite consisting predominantly of labradorite.

- **1928**
  - Alumina production of 17,000 mtpy continued until the stop of operations at Høyanger due to economic reasons.

- **1940**
  - Alumina production 12,000 mtpy was based on Greek bauxite.

- **1969**
  - Alumina production of 17,000 mtpy continued until the stop of operations at Høyanger due to economic reasons.

- **2017**
  - ENSUREAL will study the possibility of revisiting and updating the Pedersen Process to address the 21st century needs.
Grey Mud – Definition & Known facts

Grey Mud is the solid slag residue from the leaching stage of the Pedersen Process, consisting predominantly of CaCO₃ and all the unreactive elements present in the slag.

Issues to be considered:

1. In the plant at Høyanger the quantity of Grey Mud produced was 2 times the quantity of Al₂O₃ produced.
2. Originally the mud was disposed off since it was considered a harmless residue.
3. Settling and Cleaning operations of the residue are major contributors to the operating costs of the Pedersen Process.

*Actual percentages may vary depending on the composition of the raw materials.
Factors influencing quality and properties of Grey Mud:

1. Modelling of Leaching Process
2. Modelling of solidified slag properties (chemical and mineralogical composition, particle size)
Slag Modelling

Goal 1: Formation of leachable calcium aluminates to ensure calcium carbonate formation.

- The binary system CaO – Al$_2$O$_3$ presents numerous crystalline compounds: C$_3$A, C$_{12}$A$_7$, CA, CA$_2$ and CA$_6$. Important in cement production.

- Issues to be considered:
  1. A solidification from the melt may not follow exactly the thermodynamic binary phase diagram.
  2. Possibility of glass formation near the eutectic (critical cooling rate $\approx$ 5°C / s)
  3. Effect of the atmosphere during cooling and impurities
Slag Modelling

Goal 1: Formation of leachable calcium aluminates to ensure calcium carbonate formation.

- As an example of the effect of the cooling atmosphere to the distribution of phases in the CaO – Al₂O₃ we present the binary phase diagram of the system as has been assessed in vacuum (absence of humidity). The $C_{12}A_7$ phase is not forming under these conditions.
Slag Modelling

Goal 2: Formation of target calcium silicate phases to ensure no unreacted lime and Al losses.

Issues to be considered:
1. Silica is the main contaminant in aluminate solutions for the production of metallurgical alumina.
2. Keeping $\text{SiO}_2$ content below $\approx 10\%$ ensures no loss due to the formation of gehlenite.
3. Dicalcium silicate is the desired phase due to its “dusting” effect on the slag.
It is desirable for the silica content of the slag to be obtained in the form of the dicalcium silicate phase, \(2\text{CaO} \cdot \text{SiO}_2\), for two reasons:

1. It undergoes several phase transformations from one polymorph to another when the slag is cooled. As the athermal, martensitic-like transformation of the monoclinic \(\beta\)-polymorph to the orthorhombic \(\gamma\)-polymorph is accompanied by a volume expansion of about 12%, high internal stresses are built up in the slag during this transformation, finally causing the disintegration of the slag. This phenomenon is called “dusting” it is desirable for economic reasons related to the subsequent size reduction processes.

2. To avoid the formation of gehlenite \((2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2)\), which leads to alumina losses.
# Slag phases in Grey Mud

<table>
<thead>
<tr>
<th>Bauxite Compound</th>
<th>Desired Compound after Smelting</th>
<th>Furnace Phase</th>
<th>Found in Grey Mud as is</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>Metallic Fe</td>
<td>Pig Iron</td>
<td>No</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>CaO·Al$_2$O$_3$, 3CaO·Al$_2$O$_3$, 12CaO·7Al$_2$O$_3$</td>
<td>Slag</td>
<td>No</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2CaO·SiO$_2$</td>
<td>Slag</td>
<td>Yes</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>CaO·TiO$_2$</td>
<td>Slag</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Minor Components</strong></td>
<td>Insoluble compounds</td>
<td>Slag</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Leaching Stage Modelling

Calcium Aluminates Leaching Reactions

\[(CaO \cdot Al_2O_3)_s + (Na_2CO_3)_{aq} \rightarrow (NaAl(OH)_4)_{aq} + (CaCO_3)_s\]
\[(3CaO \cdot Al_2O_3)_s + 3(Na_2CO_3)_{aq} + 2H_2O \rightarrow (NaAl(OH)_4)_{aq} + 3(CaCO_3)_s + 4NaOH\]
\[(12CaO \cdot 7Al_2O_3)_s + 12(Na_2CO_3)_{aq} + 5H_2O \rightarrow 7(NaAl(OH)_4)_{aq} + 12(CaCO_3)_s + 10NaOH\]
\[Al(OH)_3 + OH^- \rightleftharpoons Al(OH)_4^-\]

- CaCO₃ precipitation the driving force
- Al present in the form of Al(OH)₄⁻ due to alkaline pH during leaching
- NaOH addition to sustain alkalinity avoid precipitation of Al(OH)₃
- In the original Pedersen Process leaching takes place in atmospheric pressure and mild temperatures (40°C – 60°C)
Leaching Stage Modelling

Calcium Silicates Side Reactions

\[(2CaO \cdot SiO_2)_s + 2(Na_2CO_3)_{aq} + H_2O \rightarrow (Na_2SiO_3)_{aq} + 2(CaCO_3)_s + 2NaOH\]

\[(2CaO \cdot SiO_2)_s + 2(NaOH)_{aq} + H_2O \rightarrow (Na_2SiO_3)_{aq} + 2\text{Ca(OH)}_2_s\]

• Ideally all silica is fixed as insoluble residues in this process. However, dissolution of small amounts of silicon during leaching is unavoidable.

• In the Lime Sinter Process the silica content of PLS is reported in 2% - 3% (Alumina basis) necessitating a desilication/purification step prior to precipitation.

• In the original Pedersen Process a two stage leaching process was applied, with excess of slag in the second stage acting as a desilication step.
# Red Mud – Grey Mud: Differences & Potentials

<table>
<thead>
<tr>
<th>Residue</th>
<th>Grey Mud</th>
<th>Red Mud</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Main Components</strong></td>
<td>CaCO$_3$, CaO, SiO$_2$</td>
<td>Fe-Oxides, Al$_2$O$_3$, SiO$_2$</td>
</tr>
<tr>
<td><strong>Al$_2$O$_3$ Losses</strong></td>
<td>$\approx 2%$</td>
<td>$\approx 15%$</td>
</tr>
<tr>
<td><strong>Na$_2$O Losses</strong></td>
<td>$\approx 1%$</td>
<td>$\approx 5%$</td>
</tr>
<tr>
<td><strong>Mud : Alumina</strong></td>
<td>2:1</td>
<td>1:1</td>
</tr>
<tr>
<td><strong>Alkalinity</strong></td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>

Grey Mud has the potential to overcome difficult implementation barriers in which Red Mud struggles, i.e. the risks associated with 2 main techno-environmental components: **soda** and **alkalinity**.
Grey Mud Valorisation Prospects

Agricultural Sector
Lime Fertiliser / Soil Additive

Construction Sector
Cement and other construction materials

Reuse in the Process
Lime and CO$_2$ Source
Greek Bauxite Case: Grey Mud as REEs Source

- BR from Greek Bauxites (700,000 tons/year) is considered a possible REEs resource.
- Scandium represents 95% of the REE economic value and is found at exploitable levels.
- Greek BR processing could meet 10% of the annual EU demand in REE mainly as Ce, La, Nd and Y.
- Processing Greek Bauxites in will produce a Grey Mud enriched in REEs.
- Research will be undertaken in to assess the possibility of REEs extraction.
Greek Bauxite Case: Grey Mud as REEs Source

BR Combined Process Routes for REEs recovery

- REE’s extraction from BR by combined pyro- and hydrometallurgical treatment has been extensively studied in NTUA.
- Mineral acid leaching provides high recovery yields but large concentration of co-dissolved metals interfere with the downstream REE’s purification process, essentially Al and Fe.
- Grey Mud is depleted of Al and Fe. Its high CaCO₃ content is a challenging aspect.
Conclusions

- The Pedersen Process is a combined pyro- and hydrometallurgical process, originally designed to treat various alternative aluminous raw materials with low Al₂O₃:Fe₂O₃ ratio.
- Industrially the process used Greek bauxite high in Fe-content until 1969.
- Grey Mud is called the solid slag residue from the leaching stage of the Pedersen Process, consisting predominantly of CaCO₃ and all the unreactive elements present in the slag.
- Grey Mud composition is affected by the modelling of both the solidification of the slag and the leaching operations.
- Grey Mud as a product overcomes certain implementation barriers in which Red Mud struggles, i.e. the risks associated with soda content and alkalinity.
- Grey Mud, due to its high calcium content could be potentially marketed in the agricultural and construction sectors, or could be recycled in the process to lower costs.
- Grey Mud from Greek bauxites could prove to be a REEs resource.
Thank you for your attention