Valorisation of Mining and Metallurgical Wastes
the Example of Bauxite Residues

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The Bayer Process for Alumina Production

Bauxite → Digestion → Thickening

Lime + Caustic Soda → Precipitation → Filtration

Seeding

Alumina

Calcination

Milling

Bauxite Residue (Red Mud)
The Bayer Process for Alumina Production

<table>
<thead>
<tr>
<th>Bauxite (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>TiO₂</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>Na₂O</td>
</tr>
<tr>
<td>LOI</td>
</tr>
</tbody>
</table>

| Al₂O₃        | 56 |
| Fe₂O₃        | 25 |
| SiO₂         |  2 |
| TiO₂         |  3 |
| CaO          |  1 |
| Na₂O         |   |
| LOI          | 12 |

<table>
<thead>
<tr>
<th>Al₂O₃</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>48</td>
</tr>
<tr>
<td>SiO₂</td>
<td>6</td>
</tr>
<tr>
<td>TiO₂</td>
<td>6</td>
</tr>
<tr>
<td>CaO</td>
<td>11</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2</td>
</tr>
<tr>
<td>LOI</td>
<td>11</td>
</tr>
</tbody>
</table>
Global Bauxite Residues Production

- Produced as a slurry
- 100 - 120 Mt / year
- Usual handling practice: Disposed in sealed or unsealed artificial impoundments
Bauxite Residues Dam Failure

Hungary 2010
Aluminum and Alumina Production in Greece

– Aluminium of Greece (ALSA), alumina refinery and aluminium production plant

✓ Producing 800,000 tons of alumina and 165,000 tons of aluminium annually
✓ The only vertically integrated bauxite, alumina and aluminium production plant in Europe.

ALSA: 650,000 tons of bauxite residues (red mud)
Bauxite Residues: The case of Aluminium of Greece

- **Dewatering BR in Filter Presses**

- The filter cake has a moisture content to 25%, which makes it easier to handle

- AoG was one of the first Western European plants to apply this technology

- AoG Produces 650,000 t BR per year

Can this BR cake be a potential resource?
Brief History in BR Exploitation

Since 1999 AoG, NTUA are actively participating in RTD projects for BR treatment

AoG BR used in

- Cement Industry (iron source in clinker)
- Brick/Tile Industry (substitution of clay)
- Geopolymer bricks
- Soil Remediation/ Vegetation cover
- Road Base Construction
- Landfill barrier / cover
- Backfilling of Abandoned Mines
New Approaches in Bauxite Residue Valorisation

<table>
<thead>
<tr>
<th></th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>Na$_2$O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bauxite (wt%)</td>
<td>56</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>25</td>
<td>-</td>
<td>12</td>
</tr>
<tr>
<td>Red Mud (wt%)</td>
<td>16</td>
<td>11</td>
<td>6</td>
<td>6</td>
<td>48</td>
<td>2</td>
<td>11</td>
</tr>
</tbody>
</table>

Red Mud contains about 48% iron oxide.

- Iron is a potential element that could be recovered from Red Mud.
- Is it feasible??
Innovative Electric Arc Furnace with a novel feeding system, capable to directly treat finely sized material, without significant material loss in the off-gases. The material is directly fed to the EAF and prior agglomeration is not necessary.
Reductive Smelting of Bauxite Residue

- Pig Iron
- Iron
- Red Mud
- Reductive Smelting of Bauxite Residue
- Bag Filters
  - Dust
  - Coke Fines
  - Fluxes
- Material Feed Mixing
- DUST TREATING EAF
  - Viscous Slag
  - Off-gases
- Exhausted gases
- Red Mud drying
Two test campaigns have been carried out

The first one with NTUA a 750 kVA pilot Electric Arc Furnace of a 600 kg batch capacity

The second at Aluminium of Greece with 1 MVA Electric Arc Furnace of a 1000 kg batch capacity
Case Study with Bauxite Residues

Total charge: 550 kg
Fluxes: 351 kg/tn RM

Molar ratio C:Fe = 2.43
(\%wt \text{CaO+} \%wt \text{MgO}) / (\%wt \text{SiO2}) = 0.94

Experimental conditions

Pre heat slag: 200kg
Feeding Rate: 3 kg/ min
Smelting time: 3.5 h

Optical Pyrometry
Around Electrodes 1700 -2400 C
Melt surface $T = 1400 -1600$ C
“Crust surface” $T = 900-1100$ C
## Case Study with Bauxite Residues

### Pig Iron

<table>
<thead>
<tr>
<th>%Element</th>
<th>Exp %wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Fe</td>
<td>87.09%</td>
</tr>
<tr>
<td>%C</td>
<td>4.05%</td>
</tr>
<tr>
<td>%S</td>
<td>0.05%</td>
</tr>
<tr>
<td>%P</td>
<td>0.20%</td>
</tr>
<tr>
<td>%Si</td>
<td>1.70%</td>
</tr>
<tr>
<td>%Ti</td>
<td>0.45%</td>
</tr>
<tr>
<td>%V</td>
<td>0.28%</td>
</tr>
<tr>
<td>%Cr</td>
<td>4.43%</td>
</tr>
<tr>
<td>TOTAL</td>
<td>99.83%</td>
</tr>
</tbody>
</table>

**Pig Iron Phase:** 120 kg  
**Fe % Recovery:** 97%

### Slag

<table>
<thead>
<tr>
<th>%Element</th>
<th>Exp %wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Na₂O</td>
<td>1.89%</td>
</tr>
<tr>
<td>%MgO</td>
<td>4.65%</td>
</tr>
<tr>
<td>%Al₂O₃</td>
<td>24.23%</td>
</tr>
<tr>
<td>%SiO₂</td>
<td>32.62%</td>
</tr>
<tr>
<td>%SO₃</td>
<td>1.09%</td>
</tr>
<tr>
<td>%CaO</td>
<td>29.65%</td>
</tr>
<tr>
<td>%TiO₂</td>
<td>6.79%</td>
</tr>
<tr>
<td>%Cr₂O₃</td>
<td>0.41%</td>
</tr>
<tr>
<td>%Fe₂O₃</td>
<td>1.11%</td>
</tr>
<tr>
<td>%C</td>
<td>0.49%</td>
</tr>
<tr>
<td>TOTAL</td>
<td>102.43%</td>
</tr>
</tbody>
</table>

**Slag Phase:** 280 kg  
**Basicity:** 1.05

*High Cr presence due to initial refractory dissolution*
Results from 750 kVA experiments

- Proved the feasibility of producing Pig Iron from Bauxite Residues
- High Cr presence due to initial refractory dissolution need to change refractory type
- Determination of appropriate operation conditions to be used in the second experimental campaign at the 1 MVA EAF of Aluminium of Greece

Questions raised
What can we do with the produced slag from the smelting process?
New Approaches in Bauxite Residue Valorisation
Case Study with Bauxite Residues

Slag fiberization

✓ Preliminary slag blowing tests has shown that the slag produced can be fiberized.
✓ The chemical composition of the slag is within mineral wool industry’s specs.
Pilot Tests in Aluminium of Greece

AoG Pilot Plant

- 1 MVA AMRT-EAF (AC, 3-electrode, dust treating, batch capacity 1t)
- Melt Fiberizing Line
- Static Bed Electric Dryer

- During a two year long experimental campaigns treated more than 25 t of BR
- More than 5 t of Pig Iron produced and tested in secondary steel production
- High Quality mineral wool product produced from the slag
The ENEXAL Bauxite Residue Treatment Process – AoG’s 1st Pilot Plant

Red Mud EAF Carbothermic Smelting

- Open bath operation
- Continuous feeding 6.65 kg/min
- Melt Temperature app 1600°C
- Energy Consumption: 1508 kWh/t of BR
- Dust in filters 4% wt of feed

Feed Batch

<table>
<thead>
<tr>
<th>Feed</th>
<th>Batch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry BR (kg)</td>
<td>700</td>
</tr>
<tr>
<td>Silica (kg)</td>
<td>126</td>
</tr>
<tr>
<td>Lime (kg)</td>
<td>105</td>
</tr>
<tr>
<td>Coke (kg)</td>
<td>140</td>
</tr>
<tr>
<td>Total Feed (kg)</td>
<td>1071</td>
</tr>
</tbody>
</table>
ENEXAL BR Treatment

Pig Iron Production
- Produced metal within specification for use in secondary steel industry, as an up to 20% steel scrap substitute
- More than 5t pig iron produced in total

<table>
<thead>
<tr>
<th>Pig Iron</th>
<th>Refr1</th>
<th>Refr2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (%wt)</td>
<td>95.47</td>
<td>93.44</td>
</tr>
<tr>
<td>C (%wt)</td>
<td>3.36</td>
<td>4.59</td>
</tr>
<tr>
<td>S (%wt)</td>
<td>0.26</td>
<td>0.07</td>
</tr>
<tr>
<td>P (%wt)</td>
<td>0.08</td>
<td>0.22</td>
</tr>
<tr>
<td>Si (%wt)</td>
<td>0.01</td>
<td>1.12</td>
</tr>
<tr>
<td>Cr (%wt)</td>
<td>0.82</td>
<td>0.50</td>
</tr>
<tr>
<td>Total</td>
<td>99.99</td>
<td>99.94</td>
</tr>
</tbody>
</table>

White Iron grinding balls produced from BR iron (21%wt subs)
**ENEXAL BR Treatment**

**Mineral Wool Production**

- Slag melt within empirical indexes
- Fibre with good quality:
  - $\lambda = 0.034 \text{ W/(mk)}$ [UNI EN 12667]
  - Average fiber diameter 7 micron
  - Bright color (low Mn content)
  - High Mechanical resistance due to high TiO$_2$

<table>
<thead>
<tr>
<th>Slag</th>
<th>Refr1</th>
<th>Refr2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>5.0</td>
<td>1.1</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>27.6</td>
<td>26.5</td>
</tr>
<tr>
<td>CaO</td>
<td>25.3</td>
<td>23.4</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>20.9</td>
<td>31.1</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>3.0</td>
<td>0.1</td>
</tr>
<tr>
<td>MgO</td>
<td>8.89</td>
<td>8.3</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>5.6</td>
<td>6.1</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>2.4</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Mineral wool used inside the plant
ENEXAL BR Treatment

BR Mineral Wool

Commercial Mineral Wool
The ENEXAL Bauxite Residue Treatment Process – AoG’s 2nd Pilot Plant

- Smelting energy 14.5% in excess of thermodynamic requirement
- Overall plant consumption 2 MWh/t BR
BR Treatment results

- Up-scaling will bring higher energy efficiency, especially in BR drying
- Initial studies show the process to be profitable
- Break-even point is achieved with a fairly low mineral wool price

**but**
- Pig iron revenues accounts only for 25% of the operating costs
- Treating the AoG annual BR production can produce 0.5 Mt of Mineral Wool products
On Going Research

• The AoG BR also contains approximately 0.1% wt REE (mainly as Sc, Ce and Nd)

• What could be a possible technology for their recovery?
Selective leaching of REE from Red Mud

On-going RTD effort for the selective leaching of REE from red mud using Ionic Liquids

REE in Red Mud ~1200 ppm

Direct leaching of red mud with HbetTf2N in water at 60°C with 10% pulp density
In the framework of EURARE a IL pilot plant is being set up in NTUA.

The pilot will demonstrate the full processing chain from concentrate to REE metal using IL.

- **REE concentrate / Red Mud**
- **IL Leaching stage**
  - 2 X 1.0 lt reactors
  - 0.1 kg batch
  - 220 C
- **S/L separation**
  - 1-2 lt/hour
  - 95 C
- **Precipitation Unit**
  - 2 X 1.0 lt reactors
  - 95 C
- **IL Separation Mixer-Settlers Units**
  - 20 stages
  - Up to 100 C
  - Flow rate 1 lt/h
  - 100 ml volume
- **IL electro-winning**
  - REE Metal
Holistic Approach

Al-Sc Alloy

REE industry

Safe disposal

REE and Th Removal and Separation

Holistic Approach

Red Mud

Steel Industry

Pig Iron Production

REE industry

Slag Valorization

Cement

Mineral Wool

Geopolymers
Other Potential Applications

• The case of Laterites and the Ferro-Nickel Industry
Case Study with Fe-Ni slag

Fe-Ni Slags in LARCO:

- Annual production is approximately 2 million tons of Fe-Ni slag
- There are no special processing issues
- Treating the slag in-situ, before cooling would mark significant energy savings.
Proposed Solution

Both by-products are chemically similar

– Originating from lateritic weathering deposits in Greece
– Containing high amount of iron oxides (40-50%wt)
– Containing at least 30% wt alumino-silicates

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<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>V₂O₅</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Mud</td>
<td>16.22</td>
<td>10.73</td>
<td>6.08</td>
<td>5.93</td>
<td>47.74</td>
<td>2.51</td>
<td>0.21</td>
<td>10.42</td>
</tr>
<tr>
<td>Fe-Ni slag</td>
<td>9.69</td>
<td>3.47</td>
<td>38.27</td>
<td>5.13</td>
<td>39.78</td>
<td>2.47</td>
<td>0.10</td>
<td>0.95</td>
</tr>
</tbody>
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EAF Carbothermic Smelting

Produce Mineral Wool
Produce Pig-Iron = Zero Waste Process
Bauxite Residue Geopolymeric Tiles/Bricks

Bauxite Residues 85% - Metakaolin 15%

- Compression Strength: 20.5 MPa - MW (Moderate Weathering Conditions)
- Bending strength: 600 N (good for tiles)
- Water Absorption 1.28%
- Negligible water permeability
- \textit{Low resistance to Freezing-Thawing Cycles}

Suitable building material for moderate climates (e.g. Mediterranean)
Combined Geopolymers for Bricks and Tiles

Bauxite Residues 50% - FeNi Slag 50%

- Excellent Mechanical properties
  - Comp. Strength: > 40MPa
  - Bending Strength: 4MPa
- Density: 2350 kg/m³
- Water absorption: 0.57%
- Water permeability: Negligible
- High resistance to Freezing-Thawing Cycles

Suitable building material for almost any climate
Research Projects

2010 - 2014 AoG / NTUA Coordinated the FP7 ENEXAL Project, demonstrating the complete conversion of Bauxite Residues to pig-iron and mineral wool products.

2013 - 2017 NTUA Coordinates the FP7 EURARE Project, researching technologies for REE extraction from BR.

From 2015 AoG and NTUA will undertake 4 PhD studies under the recently approved Marie Currie project on “European Training Network for Zero-Waste Valorisation of Bauxite Residue (Red Mud)”
The ENEXAL Bauxite Residue Treatment

Preliminary Economic Evaluation

- Pig Iron revenues (fixed market price 400 EUR/t) amount to 38% of operational costs
- Mineral wool revenues depend on market price (depends on product quality and market demand)