Iron recovery and production of high added value products from the metallurgical by-products of primary aluminum and ferronickel industries

Efthymios Balomenos, Dimitrios Panias
The “Greek” Metallurgical problem

- Two major primary metallurgical plant operate in Greece:
  - Aluminium of Greece (ALSA), alumina refinery and aluminium production plant

- Producing **810,000 tons of alumina** and **165,000 tons of aluminium** annually
- The leading industrial producer of alumina and aluminium in **South East Europe**
- The only vertically integrated bauxite, alumina and aluminium production **plant in Europe.**
The “Greek” Metallurgical problem

- Two major primary metallurgical plant operate in Greece:
  - General Mining and Metallurgical company (LARCO), primary ferro-nickel plant

- Producing 100,000 tons of Fe-21Ni annually
- The largest ferronickel producer (mining and smelting) in Europe and one the 5 largest ferronickel producers in the world.
- The company holds about 6% of the Fe-Ni European market share
Both plants produce significant amount of by-products
- **ALSA:** 650,000 tons of bauxite residues (red mud)
- **LARCO:** 2 million tons of Fe-Ni slag

Since 2012, sea disposal of by-products has been prohibited

Potential for land disposal is limited due to geographical and other constraints

No proper areas (location and size) in short distances from plants
Proposed Solution

Both by-products are chemically similar
- Containing high amount of iron oxides (40-50%wt)
- Containing at least 30% wt alumino-silicates

<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>V$_2$O$_5$</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Mud (wt%)</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 (wt%)</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>
</table>
Mineral Wool production

Mineral wool

Is an excellent inorganic thermo- and sound-insulating material for commercial and industrial use.

Mineral and glass wool currently dominate the thermo-insulation market in Europe.

<table>
<thead>
<tr>
<th>Material</th>
<th>Approx. Max Operating Temperature °C</th>
<th>Range of Bulk Density kg/m³</th>
<th>Range of Thermal Conductivity W/m.K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Mineral Wool</td>
<td>230 to 250</td>
<td>9 to 120</td>
<td>0.032 to 0.040 (At 20°C)</td>
</tr>
<tr>
<td>Stone Mineral Wool</td>
<td>700 to 850</td>
<td>23 to 200</td>
<td>0.033 to 0.035 (At 10°C)</td>
</tr>
</tbody>
</table>

EU THERMO-INSULATION MARKET

Mineral and glass wool currently dominate the thermo-insulation market in Europe.

Loose Fill
Blanket
Carbothermic Reductive Smelting

Process Design Issues:

- Define conditions for optimum iron recovery (temperature, carbon addition)
- Define physico-chemical properties of the slag through appropriate fluxes in order to produce a melt suitable for mineral wool production

Empirical indexes for mineral wool production

<table>
<thead>
<tr>
<th>Index</th>
<th>Formula</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( \frac{(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2)}{\text{(CaO+MgO)}} )</td>
<td>&lt; 1.8</td>
</tr>
<tr>
<td>P</td>
<td>( \frac{4.9}{[(\text{MgO}+\text{CaO}+\text{Fe}_2\text{O}_3 + \text{Na}_2\text{O} + \text{TiO}_2)/(\text{SiO}_2 + \text{Al}_2\text{O}_3)]} -0.45 )</td>
<td>&lt; 15</td>
</tr>
<tr>
<td>k2</td>
<td>( [100 - (\text{SiO}_2 + \text{Al}_2\text{O}_3)]/(\text{SiO}_2 + \text{Al}_2\text{O}_3) )</td>
<td>0.8 - 1</td>
</tr>
<tr>
<td>SHG</td>
<td>( \frac{(\text{SiO}_2 + \text{Al}_2\text{O}_3)}{(1.4 \text{MgO}+ 0.4 \text{Fe}_2\text{O}_3 + \text{CaO} + \text{TiO}_2)} )</td>
<td>1.3 - 1.4</td>
</tr>
<tr>
<td>KNB</td>
<td>( \text{Na}_2\text{O} + \text{MgO} + \text{CaO} )</td>
<td>30 – 40</td>
</tr>
<tr>
<td>N</td>
<td>( \text{Na}_2\text{O} )</td>
<td>&lt; 5%</td>
</tr>
<tr>
<td>F</td>
<td>( \text{Fe}_2\text{O}_3 )</td>
<td>&gt; 5%</td>
</tr>
</tbody>
</table>

Pig iron standards

<table>
<thead>
<tr>
<th>%C</th>
<th>~ 4%</th>
</tr>
</thead>
<tbody>
<tr>
<td>%S</td>
<td>&lt;0.02%</td>
</tr>
<tr>
<td>%P</td>
<td>&lt;0.05%</td>
</tr>
<tr>
<td>%Si</td>
<td>0.4-0.8%</td>
</tr>
</tbody>
</table>
Case Study with Bauxite Residues

### Bauxite residues in ALSA:
- Annual production is approximately 650,000 tons
- Over the last years four (4) filter Presses are used for drying residues to moisture content close to optimum value (28% w/w dry basis) (considered as BAT)

### Processing issues:
- Red mud is an extremely fine material ($d_{50} \approx 5\mu m$)
- It still necessitates drying prior to be fed in an EAF
- It contains almost 0.5% Na$_2$O which can cause damages to the refractories
  - Dust treating EAF
  - Double skin dryer
  - EAF with high area to height ratio in relation to a blast furnace
Case Study with Bauxite Residues

- 100% Utilization of Red Mud - no solid wastes
- Production of two marketable products

Diagram:
- Bag Filters
  - Dust
  - Coke Fines
  - Fluxes
- Red Mud drying
- Material Feed Mixing
- DUST TREATING EAF
- Off-gases
- Viscous Slag
- Fiberization
- Pig Iron
- Mineral Wool Fibers
II. Innovative feeding system allows direct processing of dusty material (<10 mm) by regulating the rate of feeding in relation to power supply.

operation under totally open bath mode

Continuous feeding directly in the hot zone in-between the three electrodes.

The furnace is tilted for melt pouring.
Batch mode operation.

Grid Power
AC Transformer
Prebaked Graphite Electrodes
Suction on the top Feeder of fines under the suction level.
Case Study with Bauxite Residues

Experiments in the 400 kVA AMRT EAF

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

Molar ratio C:Fe = 2.43  [Stoichiometric reduction ratio C:Fe = 1.5]

(\%wt CaO + \%wt MgO) / (\%wt SiO2) = 0.94  [Neutral Slag = 1.0]

Experimental conditions

Pre heat slag: 200 kg
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 Properties

<table>
<thead>
<tr>
<th>Component</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 Properties

<table>
<thead>
<tr>
<th>Component</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>% O</td>
<td>0.49%</td>
</tr>
<tr>
<td>TOTAL</td>
<td>102.43%</td>
</tr>
</tbody>
</table>

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

Contains **31%wt** of the initial Red Mud

Contains **43% wt** of the initial Red Mud
Case Study with Bauxite Residues

Elemental Mass Balance (kg)

Feed

Products

Sodium evaporation: 41% wt

Dissolved Cr/Mg oxides from furnace refractories: 18.20 kg
Carbothermic Smelting of red mud

- The pig iron produced was used to substitute 16% scrap in white iron production (high Cr content)

By changing the furnace refractories to Magnesia carbon bricks, a chrome-free pig iron will be produced.

- The Chrome free pig iron could be uses as feedstock in the secondary steel production industry, substituting up to 20% of steel scrap.

<table>
<thead>
<tr>
<th>Pig iron</th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>98.95</td>
<td>0.19</td>
<td>0.19</td>
<td>0.64</td>
<td>0.012</td>
<td>0.017</td>
<td>0.00</td>
</tr>
<tr>
<td>5%</td>
<td>98.92</td>
<td>0.21</td>
<td>0.22</td>
<td>0.62</td>
<td>0.015</td>
<td>0.017</td>
<td>0.00</td>
</tr>
<tr>
<td>10%</td>
<td>98.89</td>
<td>0.23</td>
<td>0.24</td>
<td>0.61</td>
<td>0.018</td>
<td>0.017</td>
<td>0.00</td>
</tr>
<tr>
<td>15%</td>
<td>98.86</td>
<td>0.25</td>
<td>0.27</td>
<td>0.59</td>
<td>0.021</td>
<td>0.018</td>
<td>0.00</td>
</tr>
<tr>
<td>20%</td>
<td>98.82</td>
<td>0.27</td>
<td>0.29</td>
<td>0.58</td>
<td>0.024</td>
<td>0.018</td>
<td>0.00</td>
</tr>
<tr>
<td>25%</td>
<td>98.79</td>
<td>0.29</td>
<td>0.32</td>
<td>0.56</td>
<td>0.027</td>
<td>0.018</td>
<td>0.00</td>
</tr>
<tr>
<td>30%</td>
<td>98.76</td>
<td>0.31</td>
<td>0.34</td>
<td>0.55</td>
<td>0.030</td>
<td>0.019</td>
<td>0.00</td>
</tr>
</tbody>
</table>
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.
Preliminary Economic Evaluation

- Extrapolation for a 5.0 MVA EAF treating 1300 tons of bauxite residues and producing 442 tons of pig iron and 931 tons of mineral wool per month

- Pig Iron revenues (calculated at a market price of 415€/t) amount to 25% of operational costs

- Mineral wool revenues depend on market price (depends on product quality and market demand)
Case Study with Bauxite Residues

Next Step: Industrial Demonstration

- Tests on the 1MW AMRT EAF in Aluminion of Greece
- A year long campaign is foreseen under ENEXAL

The industrial demonstration of the process is expected to prove its industrial applicability
Case Study with Fe-Ni slag

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

<table>
<thead>
<tr>
<th>Pig Iron (wt%)</th>
<th>Model</th>
<th>Slag (wt%)</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Fe</td>
<td>89.49</td>
<td>Al₂O₃</td>
<td>29.65</td>
</tr>
<tr>
<td>%C</td>
<td>1.98</td>
<td>CaO</td>
<td>32.64</td>
</tr>
<tr>
<td>%Cr</td>
<td>5.11</td>
<td>SiO₂</td>
<td>24.23</td>
</tr>
<tr>
<td>%Ni</td>
<td>0.25</td>
<td>MgO</td>
<td>6.78</td>
</tr>
<tr>
<td>%Si</td>
<td>3.17</td>
<td>FeO</td>
<td>4.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr₂O₃</td>
<td>1.89</td>
</tr>
<tr>
<td>Total weight</td>
<td>31.03 kg</td>
<td>Total weight</td>
<td>84.63</td>
</tr>
<tr>
<td>Fe Recovery</td>
<td>99.79%</td>
<td>Slag basicity</td>
<td>1.07</td>
</tr>
</tbody>
</table>
Market Barriers

- Pig iron product: No market barrier
- Mineral wool product: Mineral wool is produced at 2:1 mass ratio to pig iron and including fluxes may weight 70-80% of the initial by-product – hence large amounts of mineral wool would be produced if all by-products were converted in the process
- Mineral wool transportation costs limit its potential markets to nearby regions

Other complimentary methods have to be consider for complete by-product treatment
Bauxite Residue Geopolymeric Tiles/Bricks

Bauxite Residues 85% - Metakaolin 15%
S/L=2.9g/mL [NaOH]=8M [SiO₂]=3.5M
Curing: 60°C – 3 days – RH70%

- Compression Strength: 20.5 MPa - MW
  (Moderate Weathering Conditions)

- Bending strength : 600 N (good for tiles)

- Water Absorption 1.28%

- Negligible water permeability

- 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%
S/L=4g/mL [NaOH]=7M [SiO₂]=4M
Curing: 60°C – 6h – RH70%

- 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
Fe-Ni Slag Fire Resistant Geopolymers

Material / Properties

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Strength (28 days) MPa</th>
<th>Flexural Strength (28 days) MPa</th>
<th>Density (kg/m³)</th>
<th>Water absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>14</td>
<td>4</td>
<td>2090</td>
<td>3</td>
</tr>
<tr>
<td>B</td>
<td>9</td>
<td>1.7</td>
<td>1900</td>
<td>6.65</td>
</tr>
<tr>
<td>C</td>
<td>8.6</td>
<td>2.1</td>
<td>1805</td>
<td>17.3</td>
</tr>
</tbody>
</table>

Before Fire Testing

After Fire Testing

Concrete

RWS Curve

Requirement: 380 °C
Both by-products can be treated with the same pyrometallurgical technology for the production of pig-iron and mineral wool.

Additional technological solutions like Geopolymerization can provide the necessary products diversity which will allow complete valorization of these by-products.

Now, a critical mass of alternative treatment technologies for the Greek metallurgical by-products exists offering viable solutions to the Greek Metallurgical Industry and improving substantially its environmental performance.
Thank you for your attention

Efthymios Balomenos, Dimitrios Panias

Part of the research leading to these results has received funding from the European Union Seventh Framework Programme ([FP7/2007-2013]) under grant agreement n° ENER/FP7EN/249710/ENEXAL