Valorization of Bauxite Residue (red mud): in pursuit of a technologically realistic and financially viable process

Yiannis Pontikes
March 2016
Summary of what will follow

I. Who we are

II. Bauxite residue: progress in 10y

III. 100% use in a metallo-centric process

IV. 100% use in a (building) material-centric process
I. Who we are
Vision

Transform local supply of residues towards new materials
Contribute to circular economy

Metal Valley

ArcelorMittal, Gent
- steel: 4000 kt/year*
- BOF slag: 450 kt/year*

Aperam, Châtelet
- stainless steel: 700 kt/year*
- slag: 200 kt/year*

Metallo-Chimique, Beerse
- slag: depends

Umicore, Hoboken
- slag: 150 kt/year*

Group Machiels, Houthalen
- slag: depends

Bring the science to make it happen:
in a robust and analytical way,
develop the processes and the materials
Expertise

Additives

Granulation

New slag for inorganic polymers and new cements

+Na,K-silicate

Additives
A note from morning’s discussion

Is linear
A large constant supply of raw materials is required
This system is unsustainable

Is partially cyclic
Reduced materials and energy required
Reduced waste produced
Characterises most present day industrial systems

Is highly integrated and closed
All by-products constantly used and recycled > apart from re-cycle think also of out-cycle!
Represents a sustainable state
Is the ideal goal of Industrial Ecology

Yes, it can!
See Kalundborg, Denmark

I see that as (one of the) possibilities for European competitiveness (and there is precedence!)
II. Bauxite residue: progress in 10y
25 April 2006

“A Success Story”.

Red mud is now filter-pressed to a cake in many sites in order to progressively cease sea disposal for Red Mud. The overall cost exceeded 2 million euros. In the near future a second Filter Press is expected to be installed and then the whole quantity of produced Red Mud will be processed in this manner.

The resulting semi-dry product is named “Ferro-alumina” and there are concrete hopes for its marketing.
Example 1
Red mud is used industrially

From 2007 onwards, Ferroalumina is used in cement production in Greece and the same applies for many other countries. Other applications are in heavy clay ceramics, filler in plastics, roads etc. Yes, indeed, the total volume is still low…
Red mud can find high added value applications

High purity multi-wall carbon nanotubes (MWCNTs), diam. 20nm to 55nm were produced via Chemical Vapour Deposition at 700°C, in 30% C₂H₄/He.

Alkaline & non-magnetic, sodicity: 51.4 mg/g
Pyrolysis bio-oil from ligno-cellulosic biomass

Pressure, temp

Non-alkaline & magnetic
33 % carbon content, sodicity: 28.9 mg/g
Stabilized, non-acidic high-energy density oil

Example 4

Some of these applications can be up-scaled indeed!

AoG pilot plant facility for pig iron production and mineral wool in Greece during the FP7 ENEXAL project.
Example 5

There is substantial research going on...

NOVEL TECHNOLOGIES FOR ENHANCED ENERGY AND EXERGY EFFICIENCIES IN PRIMARY ALUMINIUM PRODUCTION INDUSTRY

2 x DBOF scholarships

"EURARE: Development of a sustainable exploitation scheme for Europe’s REE ore deposits"

15 PhD thesis all over Europe
Example 5

There is substantial research going on

15 PhD thesis all over Europe
Partners: KU Leuven, UHelsinki, RWTH Aachen, KTH, NTUA, UTartu, MEAB, Aluminium of Greece, Titan
Partner Organisations: UPatras, UAveiro, Bay Zoltan, Tasman Metals
Funding: 3,7 M EURO
Example 6

If you organise a conference people will come!

~ 140 participants from
  28 countries
  27 universities
  40 industries
  and 2 associations

Many ideas on the table, we did not recycle or repeat history: revegetation that works, catalysis, geopolymers, ionic liquids and chitosan…with industry supporting
The message to take home is that there is work being done and that reality is region/plant specific.

Some claim red mud is a residue that waits (who? what?) to be used, others develop processes for recovering Na (and the rest?) or use a fraction as an aggregate (the rest? Is that financially sound?), others develop processes that will be upscaled (maybe) in the next decades.

In the meantime, the major red mud producer is China and by the time “something that works” is developed, (some?) alumina refineries in Europe (US? Australia?) will be only dealing with legacy sites.

Can we develop something in the next decade?
III. 100% use in a metallo-centric process
A metallo-centric process

Industrial symbiosis

Mud2Metal H2020 proposal contact Balomenos, Panias et al.
Mud2Metal, in detail

Alumina Refinery → Alumina → Alumina Smelter → Al

Bauxite Ore

Bauxite Residue

Aluminium Industry

Selective Leaching/ Separation → REE oxides → Sc Metal production → Al-Sc Alloy

NORM disposal

EAF Carbothermic Smelting

Fe (Cr, V, Ni)

Slag Processing

Mineral Fibers

Aluminate Cement

Geopolymerization

Geopolymers

Mud2Metal
### Mud2Metal, the metal + REE

<table>
<thead>
<tr>
<th>Element (%)</th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>V</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENEXAL BR Pig iron</td>
<td>92.30</td>
<td>4.25</td>
<td>0.09</td>
<td>1.89</td>
<td>0.22</td>
<td>0.05</td>
<td>0.21</td>
<td>0.57</td>
<td>0.41</td>
<td>-</td>
</tr>
<tr>
<td>Average Steel scrap</td>
<td>98.56</td>
<td>0.09</td>
<td>0.06</td>
<td>0.01</td>
<td>0.02</td>
<td>0.06</td>
<td>0.12</td>
<td>0.11</td>
<td>0.01</td>
<td>0.37</td>
</tr>
<tr>
<td>Grey cast iron alloy</td>
<td>92.78</td>
<td>3.40</td>
<td>0.5</td>
<td>1.80</td>
<td>0.20</td>
<td>0.07</td>
<td>-</td>
<td>0.35</td>
<td>0.15</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>REE Oxide</th>
<th>Greek BR</th>
<th>Price in 2016</th>
<th>Value in 1000 kg of BR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/kg</td>
<td>$/kg</td>
<td>$</td>
</tr>
<tr>
<td>Sc₂O₃</td>
<td>0.21</td>
<td>1,500</td>
<td>309,045</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>0.15</td>
<td>4</td>
<td>582</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>0.18</td>
<td>2</td>
<td>326</td>
</tr>
<tr>
<td>CeO₂</td>
<td>0.59</td>
<td>2</td>
<td>991</td>
</tr>
<tr>
<td>Pr₂O₃</td>
<td>0.04</td>
<td>48</td>
<td>1,792</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>0.15</td>
<td>41</td>
<td>5,984</td>
</tr>
<tr>
<td>Sm₂O₃</td>
<td>0.03</td>
<td>2</td>
<td>59</td>
</tr>
<tr>
<td>Eu₂O₃</td>
<td>0.01</td>
<td>85</td>
<td>523</td>
</tr>
<tr>
<td>Gd₂O₃</td>
<td>0.03</td>
<td>50</td>
<td>1,296</td>
</tr>
<tr>
<td>Dy₂O₃</td>
<td>0.03</td>
<td>210</td>
<td>5,831</td>
</tr>
<tr>
<td>Er₂O₃</td>
<td>0.02</td>
<td>160</td>
<td>2,501</td>
</tr>
<tr>
<td>TOTAL</td>
<td>1.42</td>
<td></td>
<td>328,930</td>
</tr>
</tbody>
</table>

There are quite a few processes on Sc extraction.
Mud2Metal, the slag

<table>
<thead>
<tr>
<th>%wt</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>FeO</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expected BR Slag (400 kg/t of BR)</td>
<td>37.0</td>
<td>29.0</td>
<td>0.7</td>
<td>25.0</td>
<td>8.0</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Typical Blast Furnace Slag</td>
<td>7-16</td>
<td>32-45</td>
<td>5-15</td>
<td>32-42</td>
<td>-</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Calcium Aluminate Cement</td>
<td>36-42</td>
<td>36-42</td>
<td>0.1</td>
<td>3-8</td>
<td>&lt;2</td>
<td>12-20</td>
<td>0.1</td>
</tr>
<tr>
<td>Typical slag wool products</td>
<td>5-16</td>
<td>20-43</td>
<td>4-14</td>
<td>38-52</td>
<td>0.3-1</td>
<td>0-5</td>
<td>0-1</td>
</tr>
<tr>
<td>Refractory ceramic fibers</td>
<td>35-51</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>47-54</td>
<td>0-20</td>
<td>0-1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

A new Al-rich cement or slag wool seems the most obvious choice
Only minor slag engineering required
Mud2Metal, overview

--- | --- | --- | ---
Iron Product | 209,000 | 300 - 1000 | 210
BR Mineral Wool | 60,000 | 600 - 800 | 
BR Aluminate Cements | 50,000 | 300 - 600 | 
BR Geopolymers | 80,000 | 100 - 200 | 14
BR Slag Cement / raw material for industry | 110,000 | 0 - 20 | 
Sc₂O₃ 99% | 136 | 500 - 1000 | 140
Mixed REO concentrate | 902 | 6 - 8 | 

Mud2Metal H2020 proposal contact Balomenos, Panias et al.
III. 100% use in a (building) material-centric process
Focus on binders

Binders are used as an inorganic “glue” to keep together aggregates and form a monolith. The use of the monolith can be from a surface coating finish to a bulk, voluminous wall structure.

Although they are “low value” stream compared to metal production, they can accommodate substantial volumes of BR.

Two areas are explored:

- cementitious binders (work in progress)
- inorganic polymers (slides follow)
Why binders?

High added value

High volumes produced

Focus on cements

Table with compositions

Chemical compositions of calcium sulfoaluminate based clinkers available in literature with BR or possibly with BR (in the patent by Gartner and Li, 2010).

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>31.1–47.0</td>
<td>44.8–60.7</td>
<td>47.2–50.8</td>
<td>48.2–57.3</td>
<td>50–61</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.6–5.9</td>
<td>14–27–26.2</td>
<td>9.3–13.4</td>
<td>9.5–21.3</td>
<td>15–25</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10.7–32.8</td>
<td>7.2–16.7</td>
<td>10.6–24.8</td>
<td>12.5–28.7</td>
<td>9–22</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>10.4–21.5</td>
<td>5.9–12.3</td>
<td>9.9–20.7</td>
<td>4.2–4.6</td>
<td>3–11</td>
</tr>
<tr>
<td>MgO</td>
<td>n.r.</td>
<td>n.r.</td>
<td>1.6–1.8</td>
<td>n.r.</td>
<td>≤5</td>
</tr>
<tr>
<td>TiO₂</td>
<td>5.2–12.4</td>
<td>n.r.</td>
<td>n.r.</td>
<td>0.9–1.0</td>
<td>n.r.</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0–3.3</td>
<td>n.r.</td>
<td>0.4–0.9</td>
<td>0.6</td>
<td>≤5</td>
</tr>
<tr>
<td>K₂O</td>
<td>n.r.</td>
<td>n.r.</td>
<td>0.2–0.4</td>
<td>0.01</td>
<td>≤5</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
<td>≤3</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
<td>≤7</td>
</tr>
<tr>
<td>ZnO + MnO + TiO₂</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
<td>≤5</td>
</tr>
<tr>
<td>CaF₂ + CaCl₂</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
<td>n.r.</td>
<td>≤3</td>
</tr>
<tr>
<td>SO₃</td>
<td>5.4–8.7</td>
<td>0–11.6</td>
<td>4.2–6.5</td>
<td>5.0–7.4</td>
<td>3–10</td>
</tr>
</tbody>
</table>

Work on-going, results go public early 2017
Focus on inorganic polymers

Ways to make IP from BR

- With additives (e.g. fly ash, silica fume etc)
- After heating (at 500-800 deg. C)
- After melting > our process under development at SREMat; there is a second process also explored
...and we produce results; focus on IP.

How to increase liquid phase formation?

1083 °C

1093 °C

SiO₂

CaO

FeO

Al₂O₃

FeO
...and we produce results; focus on IP

FactSage calculation 1100 °C – Carbon + silica
...and we produce results; focus on IP

- K-silicate activation solution, SiO₂/K₂O = 1.6, H₂O/K₂O = 16
- activation solution/solid ratio = 0.25
- Curing: 60 °C, 72 h

<table>
<thead>
<tr>
<th>Test Type</th>
<th>100BR</th>
<th>98.4BR_1.6C</th>
<th>88.6BR_1.4C_10S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive</td>
<td>13 MPa</td>
<td>20 MPa</td>
<td>44 MPa</td>
</tr>
<tr>
<td>Flexural</td>
<td>4 MPa</td>
<td>6 MPa</td>
<td>10 MPa</td>
</tr>
</tbody>
</table>
...and we produce results; focus on IP

- **BR slurry** → **Filterpressing**
  - **BR “dry”**
  - **Optional addition of <15wt% SiO₂/CaO/C**
  - **Firing in rotary kiln at 1100-1200 °C**
  - **Boiling/additives for alkalinity increase**

- **Alkali solution** → **Mixing and casting** → **New product!**
...and we produce results; focus on IP

BR slurry → Filterpressing

BR “dry”

- Addition of >20wt% Na$_2$CO$_3$
- Firing in rotary kiln at 1100-1200 °C or sinterbed…
- Recovery of water-leached Al, Na
- Magnetic recovery of Fe

Alkali solution

- Boiling/additives for alkalinity increase

Mixing and casting

New product!
Instead of conclusions

• Reality is a convention, a photograph in time.
• We have moved within few years only, from sea disposal creating an azoic zone, to filter-presesses and valorisation of a fraction of BR. And I think we are also moving from sustainability to resilience.
• It seems that there is momentum and some solutions will be implemented in the next decade, leading to less disposal and more products with BR.
• Stewardship from industrial partners will accelerate the transition.
• All is left, is for us to demonstrate the process, focus on building the ladder to this new reality…and things will happen!
Thank you!
More information