Transformation of the Hematite Ultramicroparticles from Red Mud into Other Forms of Iron Oxides

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This presentation is part of the dissemination for the project:

RIS-RESTORE

Evaluation of Red Mud Tailings in the ESEE region
Why doesn’t Europe dig anymore?

• Large problem with raw materials sustainability
• High dependance on the Asian supply
• Recycle rates differing in different regions of Europe
• Prefering environmental protection over mining investments has its cost
Bosnia is digging as never before! In the heart of mining investments

- Sase (zinc)
- Milići, Jajce, Srebrenica (bauxite)
- Omarska, Ljubija (iron)
- Carmeus (lime)
- Bentoproduct (bentonite)
- Lukavac (cement)
- Srebrenica (copper coming soon)
- Vareš (barite, copper) ...
It is not only the classical mining that we should do! The tailings hold a large potential too!

- What was wasted a century ago is now a valuable resource
Our approach to raw materials for nanotechnology

1. Sampling the waste sludge from Bosnian mines (case study shown here: iron mine Omarska)
2. Acidic digestion for removal of organic matter and rendering the metals soluble (oxidation)
3. Synthesis of the nanomaterials from the digested sludge
Usual ingredients for nanosynthesis

Various P.A. Grade chemicals obtained from scrap metals (oxides, hydroxides, nitrates, sulfates ...) combined with surfactants, oils etc

!!! Lots of energy used only for ingredients production !!!
Basic process on the lab scale

1. Sludge separation
2. Gentle acid digestion (slow)
3. Oxidation finished
4. Water dissolution
5. Filtration: pure ionic metal solution
Synthesis of the nanomaterials

Supported by:

NaOH

Metal ions

Surfactant micelle

Nanoreactor
Collection of the nanomaterials obtained from iron mine sludge

Highly porous iron oxide

Highly crystalline hematite with carbon shell

Highly crystalline cubic maghemite
State of this invention:

Patent obtained in Sept 2021

We are offering to Arcelor Mital company the patent rights in exchange for employing our students
Hypothesis: is it possible to do something similar with the sludge from bauxite processing ("red mud")?
European red mud: where can we find it?

https://etn.redmud.org/where-is-all-of-the-red-mud/
## European red mud: some disposal data

<table>
<thead>
<tr>
<th>Refinery</th>
<th>Disposal Period</th>
<th>Disposal Method</th>
<th>Rate (kt/year) *</th>
<th>BRDA Surface (ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stade</td>
<td>1973</td>
<td>Lagooning</td>
<td>1500</td>
<td>150</td>
</tr>
<tr>
<td>Gardanne</td>
<td>1893–2012</td>
<td>Sea discharge</td>
<td>690</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2012–2014</td>
<td>Sea discharge/Dry stacking</td>
<td>n.d.</td>
<td>29.4</td>
</tr>
<tr>
<td>San Ciprian</td>
<td>1981–2014</td>
<td>Dry stacking</td>
<td>2175</td>
<td>84</td>
</tr>
<tr>
<td>Aughinish</td>
<td>1983</td>
<td>Dry stacking</td>
<td>3000</td>
<td>121</td>
</tr>
<tr>
<td>Aluminium of Greece</td>
<td>1966–2012</td>
<td>Sea discharge/ Dry stacking</td>
<td>1200</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>2012–2014</td>
<td>Dry stacking</td>
<td>749**</td>
<td></td>
</tr>
<tr>
<td>Eurallumina</td>
<td>1977–2009</td>
<td>Lagooning</td>
<td>1200</td>
<td>120</td>
</tr>
</tbody>
</table>

*Calculated as 1.5 times of the production rate of alumina

**Mytilineos Holdings Sustainability report 2014

[https://etn.redmud.org/where-is-all-of-the-red-mud/](https://etn.redmud.org/where-is-all-of-the-red-mud/)
Why the Bosnian red mud?

We have plenty of bauxite and two major accumulation sites (tailings)

Location: Dobro Selo (5M t)
South of the country

Location: Đulići-Zvornik (>19M t)
East of the country

Supported by:
Even if not using the acidic leaching: ultramicroparticles are already there!
Chemical analysis of Alumina red mud by 2021. months is given in the table:

<table>
<thead>
<tr>
<th></th>
<th>SiO₂ (%)</th>
<th>Al₂O₃ (%)</th>
<th>Fe₂O₃ (%)</th>
<th>TiO₂ (%)</th>
<th>CaO (%)</th>
<th>Na₂Oᵣ (%)</th>
<th>Na₂Oᵤ (%)</th>
<th>LOI (%)</th>
<th>ZnO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>11,19</td>
<td>13,51</td>
<td>45,04</td>
<td>4,94</td>
<td>7,68</td>
<td>4,21</td>
<td>4,46</td>
<td>7,11</td>
<td>0,0195</td>
</tr>
<tr>
<td>February</td>
<td>9,97</td>
<td>12,94</td>
<td>48,94</td>
<td>5,38</td>
<td>7,76</td>
<td>5,11</td>
<td>5,24</td>
<td>6,69</td>
<td>0,0188</td>
</tr>
<tr>
<td>March</td>
<td>11,21</td>
<td>13,91</td>
<td>47,31</td>
<td>5,35</td>
<td>7,47</td>
<td>5,88</td>
<td>5,99</td>
<td>6,41</td>
<td>0,0192</td>
</tr>
<tr>
<td>April</td>
<td>10,87</td>
<td>12,88</td>
<td>44,62</td>
<td>3,82</td>
<td>7,87</td>
<td>5,20</td>
<td>5,44</td>
<td>9,06</td>
<td>0,0179</td>
</tr>
<tr>
<td>May</td>
<td>9,85</td>
<td>13,40</td>
<td>49,79</td>
<td>5,38</td>
<td>5,72</td>
<td>5,81</td>
<td>6,27</td>
<td>6,27</td>
<td>0,0202</td>
</tr>
<tr>
<td>Average value</td>
<td>10,62</td>
<td>13,32</td>
<td>47,14</td>
<td>4,74</td>
<td>7,3</td>
<td>5,24</td>
<td>5,48</td>
<td>7,11</td>
<td>0,0191</td>
</tr>
</tbody>
</table>

The pH of the filtrate of the mud is about 12,5. Filtrate also contains certain amounts of all macro and semi components from bauxite/red mud (Al, Fe, Ti, Ca, Zn..)

Some of the micro components in the filtrate and red mud:

<table>
<thead>
<tr>
<th>Filtrate of red mud</th>
<th>Cd mg/l</th>
<th>Co mg/l</th>
<th>Cu mg/l</th>
<th>Ga mg/l</th>
<th>K mg/l</th>
<th>Li mg/l</th>
<th>Mg mg/l</th>
<th>Mn mg/l</th>
<th>Ni mg/l</th>
<th>Pb mg/l</th>
<th>Zn mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>filtrate of red mud</td>
<td>0,112</td>
<td>&lt; 0.006</td>
<td>0,069</td>
<td>1,928</td>
<td>&gt; 48.179</td>
<td>0,058</td>
<td>0,003</td>
<td>0,009</td>
<td>&lt; 0,010</td>
<td>0,979</td>
<td>&lt; 0,001</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Red mud</th>
<th>%</th>
<th>%</th>
<th>%</th>
<th>%</th>
<th>%</th>
<th>%</th>
<th>%</th>
<th>%</th>
<th>%</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>red mud</td>
<td>0,067</td>
<td>0,095</td>
<td>&lt; 0,002</td>
<td>0,117</td>
<td>0,06</td>
<td>0,006</td>
<td>0,153</td>
<td>0,075</td>
<td>0,018</td>
<td>0,037</td>
</tr>
</tbody>
</table>
What if we remove the iron component???

Removal of cca 50% Fe₂O₃

Doubling of other components!!!
What are we trying:
Transforming hematite into other forms of iron oxides

hematit + kvarc porijeklom iz piritne rude → magnetit

FeS₂ → FeSₓ + (2 - x)S    x = 1–2    (450-750 °C)

FeS₂ + 4Fe₂O₃ → 3Fe₃O₄ + 2S
2S + 12Fe₂O₃ → 8Fe₃O₄ + 2SO₂

Supported by:

<table>
<thead>
<tr>
<th>Tempereature</th>
<th>600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time at final T</td>
<td>0.5 h</td>
</tr>
<tr>
<td>Heat rate</td>
<td>10 °C/min</td>
</tr>
<tr>
<td>Nitrogen flow</td>
<td>50 L/h</td>
</tr>
<tr>
<td>Cooling</td>
<td>In N₂ flow down to 25 °C</td>
</tr>
</tbody>
</table>

characterisations

- N₂ adsorption
- FTIR
- XRD

Supported by:
XRD

- Raw red mud: hematite species dominant

- Red mud treated with pyrite-dressed quartz: appearance of the magnetite peaks 41°, 73°
XRD

- Red mud treated with pyrite-dressed quartz: appearance of the magnetaite peaks 41°, 73°

- Different treatments appearance of (TiO₂): 32°, 43°, 64°, 83°
XRD

- Again magnetite: 42°, 48°, 58°, 74°

- Other forms of titanium dioxide (rutile and titanite):
  41.5°, 74°, 32°, 42°, 28°, 40°
Plan: to make use of the domestic abandoned pyrite mine in Ključ

Sjeverozapadno od Ključa, u području Muhammedbegove Prisjeke, nalazi se praon oruđenje, koje je još početak ovog stoljeća istraživano, a prije II svjetskog rata i odlazano. Detaljnim istražim radovima samo su djelomično obuhvaćene lokalnosti Šišman i Osoje, čija međusobna udaljenost iznosi oko 600 m, vazdušne linije.

Ležište Šišman izgrađeno je od tri rudna tijela međusobno spojena Vjerovatno čine cjelinu, ali zbog pomanjkanja istražnih radova to nije utvrđeno. Može se, ležišta je veoma nepravilna. Ležište Osoje ima oblik izduženog nepravilnog sočiva. Jedinica osa mu je orijentirana u pravcu sjeverozapad—jugostok. Zalijevanje mu je vertikalno, a izgrađena dužina iznosi 36 m, dobljina je neuvedena i kreće se od 1—5 m.

Na osnovu postojećih podataka može se zaključiti da oruđenje pirita kod Muhammedbegove Prisjeke po genetskim karakteristikama pripada metamorfnom tipu ležišta, koja su nastala dinamometamorfozom sedimentnih stezarinoko-eshalacionih tvorevina.
Success story: **Alumina company**

- Over 1500 employes
- Absolute European leader

- Customers at 5 continents
- Products reaching 40 countries

Supported by: [EIT](https://www.eit.europa.eu) [RawMaterials](https://www.rawmaterials.eu)
**Maybe titanium?**

- Titanium ores rutile and anatas contain cca 90% of Ti-oxides
- HOWEVER, in „soft“ ores, titanium extraction is economical even at 1%
  - Red mud is very „soft“ !!!

**TiO₂ 6% becomes 12%!**
Conclusions:

• It is important to recognize a need for awakening of the mining in Europe
• The mining can be done in a „green“ manner

• Not only ore deposits, but tailings as well hold a potential for raw material exploitation
• One direction of the tailings application should be in nanotechnologies
• Red mud tailings lead the way as one with a very diverse composition
Supported by:

This activity has received funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under the Horizon 2020, the EU Framework Programme for Research and Innovation.
Thank you for kindly your attention!

Questions & Suggestions?