RECOVERY OF SCANDIUM AND OTHER RARE EARTHS FROM GREEK BAUXITE RESIDUE

Dženita Avdibegović

KU Leuven, Belgium

27 November 2018, Berlin Germany
Who we are?

SIM² KU Leuven is a leading, interdisciplinary research cluster at KU Leuven uniting the research groups working on **Sustainable Inorganic Materials Management**.

https://kuleuven.sim2.be
1. About the SIM² KU Leuven
2. Bauxite residue
3. Solvent extraction by ionic liquids (IL)
4. Sorption by supported ionic liquids (SILPs) and biopolymers
About the SIM² KU Leuven

1. **Bauxite residue**
2. **Solvent extraction by ionic liquids (IL)**
3. **Sorption by supported ionic liquids (SILPs) and biopolymers**
SOLVOMET is KU Leuven’s Centre set up to industrially valorise the expertise in solvometallurgy (incl. hydrometallurgy) that has been and is being developed in Prof. Koen Binnemans’ research group (Department of Chemistry, KU Leuven, Belgium).

https://solvomet.eu/
Synthesis of new mining chemicals (extractants, diluents, adsorbents, collectors, flotation agents) for base and critical metal recovery and purification

**CONCENTRATION & SEPARATION**
- Solvometallurgical leaching
- Solvent extraction for separation and purification of base and critical metals
- Metal recovery from dilute aqueous waste streams by adsorption and ion flotation

**SPECIATION**
Development of more selective processes through a deeper understanding of the mechanism of solvent extraction processes

**PROCESSES**
Chemical engineering and mini-pilot-scale testing (upscaling) of developed processes and mining chemicals
About the SIM² KU Leuven

Bauxite residue

Solvent extraction by ionic liquids (IL)

Sorption by supported ionic liquids (SILPs) and biopolymers

Bauxite residue = waste from the production of alumina by the Bayer process

- Estimated global production 150 millions of tonnes/year
- Bauxite residue is only rarely used in bulk quantities
- Presence of Sc(III) comprises more than 90% of its economic value of rare earth elements (REEs)

Greek bauxite residue = 120 g/tonne of Sc

<table>
<thead>
<tr>
<th>Compound</th>
<th>wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>44.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>23.6</td>
</tr>
<tr>
<td>CaO</td>
<td>11.2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>10.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>5.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.5</td>
</tr>
</tbody>
</table>

- The recovery of REEs with or without other metals from bauxite residue, and utilization of the left-over residue in other applications like building materials = contribution to a solution of the management problem of the bauxite residue.

Compounds consisted exclusively of ions. They can be organic or inorganic salts, with low melting temperature.

The most important properties:
✓ negligible vapor pressure,
✓ broad electrochemical window,
✓ low flammability,
✓ broad liquidus range, 
✓ tunable structures (acidic groups for leaching)

• Designer solvents.

Ionic liquid process for Co/Ni separation (SOLVOMET)
Betainium bis(trifluoromethylsulfonyl)imide [Hbet][Tf₂N]

Used for recovery of scandium from sulfation-roasted leachates of Greek bauxite residue by solvent extraction.
1. **About the SIM² KU Leuven**

2. Bauxite residue

3. **Solvent extraction by ionic liquids (IL)**

4. Sorption by supported ionic liquids (SILPs) and biopolymers

---

**L**: sulfate leachate after 5-stage leaching,  
**EX**: ionic liquid phase after extraction  
**SC1**: IL phase after scrubbing step 1  
**SC2**: ionic liquid phase after scrubbing step 2  
**SC3**: ionic liquid phase after scrubbing step 3  
**ST**: aqueous phase after stripping  
**PR**: precipitate after precipitation with NaOH (pH 12.5).

---

### Multi-stage leaching = increase the Sc concentration (mg L⁻¹) in the leachate.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>1</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.12</td>
<td>3.08</td>
</tr>
<tr>
<td>Sc</td>
<td>14.6±0.2</td>
<td>47.7±0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>59±1</td>
<td>271±1</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;0.5</td>
<td>0.42±0.01</td>
</tr>
<tr>
<td>Ca</td>
<td>540±10</td>
<td>585±7</td>
</tr>
<tr>
<td>Na</td>
<td>3850±30</td>
<td>16100±6</td>
</tr>
<tr>
<td>Al</td>
<td>1078±1</td>
<td>4360±60</td>
</tr>
<tr>
<td>Y</td>
<td>12.7±0.2</td>
<td>25.1±0.1</td>
</tr>
<tr>
<td>La</td>
<td>16.0±0.2</td>
<td>25.1±0.1</td>
</tr>
<tr>
<td>Ce</td>
<td>44.4±0.8</td>
<td>53.8±0.3</td>
</tr>
<tr>
<td>Nd</td>
<td>11.0±0.1</td>
<td>11.5±0.1</td>
</tr>
<tr>
<td>Dy</td>
<td>2.09±0.01</td>
<td>2.65±0.01</td>
</tr>
</tbody>
</table>
• The **viscosity** of ionic liquids is generally higher than that of common organic solvents.

• Supported ionic liquids (SILPs) were introduced to avoid the disadvantage of high viscosity of ionic liquids. SILPs include combination of ionic liquids and porous solid supports.

SILP betainium sulfonyl(trifluoromethanesulfonylimide) poly(styrene-co-divinylbenzene)

[Hbet-STFSI-PS-DVB]
1. About the SIM² KU Leuven
2. Bauxite residue
3. Solvent extraction by ionic liquids (IL)
4. Sorption by supported ionic liquids (SILPs) and biopolymers

(1) = bauxite residue leachate
(2) = solution for removal of ions (e.g. nitric acid)
(3) = column filled with sorbent (e.g. SILP or biopolymers)
(4) = fraction collector

✓ High purification/preconcentration factors.

Optimised pH gradient elution with $\text{H}_3\text{PO}_4$ and $\text{HNO}_3$ as a function of the bed volume (BV).

Feed 2 mL of BR leachate with HCl prepared from a BR slag performed after smelting reduction for Fe recovery.

$pH_{ini}=1.5$. Flow rate 0.5 mL min$^{-1}$. Bed volume = 10.8 mL

**SILP**

<table>
<thead>
<tr>
<th>Ca</th>
<th>Al</th>
<th>Fe</th>
<th>Si</th>
<th>Ti</th>
<th>Nd</th>
<th>Sc</th>
<th>Y</th>
<th>Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>4209</td>
<td>1972</td>
<td>518</td>
<td>49</td>
<td>3.3</td>
<td>7.7</td>
<td>1.0</td>
<td>7.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Recovery by the SILP (%)

<table>
<thead>
<tr>
<th>Ca</th>
<th>Al</th>
<th>Fe</th>
<th>Si</th>
<th>Ti</th>
<th>Nd</th>
<th>Sc</th>
<th>Y</th>
<th>Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>49.8</td>
<td>71.7</td>
<td>34.3</td>
<td>0.00</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>97.7</td>
<td>100</td>
</tr>
</tbody>
</table>

Elution sequence: Sc(III) > Fe(III) > Ca(II) > Al(III) ≈ Dy(III) ≈ Y(III) ≈ Nd(III).
Recovery of \textbf{Sc(III)} from leachate of Greek bauxite residue by functionalization of chitosan-silica with \textbf{EGTA}

Biopolymers

Optimised pH gradient elution with HNO₃ as a function of the elution volume.

Feed 10 mL of BR leachate with HNO₃.

pH$_{\text{ini}}$=1.5. Flow rate 40 mL h$^{-1}$. Bed volume = 8.3 mL.

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Ca</th>
<th>Al</th>
<th>Fe</th>
<th>Si</th>
<th>Ti</th>
<th>Sc</th>
<th>ΣLn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration in the HNO₃ feed (mg L$^{-1}$)</td>
<td>1104</td>
<td>939</td>
<td>670</td>
<td>106</td>
<td>558</td>
<td>106</td>
<td>2</td>
<td>6</td>
</tr>
</tbody>
</table>

Acknowledgement

Prof. Koen Binnemans (KU Leuven, Belgium)

Members of the ETN REDMUD Project
http://redmud.org/
https://etn.redmud.org/

Members of the SOLVOMET group
https://solvomet.eu/
Thank you!