Selective recovery of scandium(III) from bauxite residue leachates by solvent extraction with a carboxyl-functionalized ionic liquid

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Content

- Recovery of scandium from red mud
- Introduction to solvent extraction with ionic liquids
- Results and discussion of experimental work
- Future prospects
Recovery of Sc from bauxite residue (red mud)

Applications of scandium
Scandium-aluminium alloy

Solid oxide fuel cells

Price in USD/kg (2013)
(source: USGS)

<table>
<thead>
<tr>
<th>Product</th>
<th>Price (USD/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc oxide 99.99%</td>
<td>5000</td>
</tr>
<tr>
<td>Sc metal (ingot)</td>
<td>175 000</td>
</tr>
</tbody>
</table>

Bauxite residue contains 0.02 wt% Sc

- 3 billion tons BR stockpiled
- = 0.6 million tons Sc stockpiled
- 120 million tons BR/year
- = 24 000 ton Sc/year
- = 4 200 billion USD/year worth of Sc

+ ceramics, electronics, lasers, lighting, radioactive isotopes
Direct leaching of bauxite residue


Selective dissolution of valuable REEs from red mud

Example: HCl leaching, 0.2 N, 50:1 L/S, 24 h, 25 °C

<table>
<thead>
<tr>
<th>Composition red mud sample (Aluminium of Greece)</th>
<th>HCl leachate (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$ 44.6 wt%</td>
<td>Fe(III) 109</td>
</tr>
<tr>
<td>Al$_2$O$_3$ 23.6 wt%</td>
<td>Al(III) 520</td>
</tr>
<tr>
<td>CaO 11.2 wt%</td>
<td>Ca(II) 1040</td>
</tr>
<tr>
<td>SiO$_2$ 10.2wt%</td>
<td>Si(IV) 361</td>
</tr>
<tr>
<td>TiO$_2$ 5.7 wt%</td>
<td>Ti(IV) 134</td>
</tr>
<tr>
<td>Na$_2$O 2.5 wt%</td>
<td>Na(I) 396</td>
</tr>
<tr>
<td>Nd</td>
<td>ΣREE(III) (incl. Y) ~ 4</td>
</tr>
<tr>
<td>Sc</td>
<td>Sc(III) ~ 1</td>
</tr>
</tbody>
</table>
Recovery of Sc(III) from bauxite residue by selective extraction and purification of bauxite residue leachates using solvent extraction (liquid-liquid extraction) with an ionic liquid as the extracting phase.
Solvent extraction

**SOLVENT EXTRACTION:**
preferential distribution of a solute between two mutually immiscible phases

\[
D = \frac{[M]_{IL}}{[M]_{aq}}
\]

\[
\%E = \frac{n_{IL}}{n_{IL} + n_{aq}} \cdot 100\%
\]

\[
\alpha_B^A = \frac{D_A}{D_B}
\]
 Ionic liquids (ILs) in solvent extraction

**IONIC LIQUID** = liquid that consists entirely of ions + low melting point (< 100 °C)

<table>
<thead>
<tr>
<th>Cations</th>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Cation Structure" /></td>
<td><img src="image" alt="Anion Structures" /></td>
</tr>
</tbody>
</table>

**Properties:** low flammability, low volatility, broad liquidus range, tunable depending on structure (hydrophobic/hydrophilic), ...

**Use in solvent extraction as replacement for volatile solvents (e.g. kerosene):**

- more environmentally friendly
- safer
- higher metal loading
- different mechanism

- generally high viscosity
- high price
Results and discussion of experimental work

Recovery of Sc(III) from red mud leachates with the ionic liquid [Hbet][Tf$_2$N]
Betainium bis(trifluoromethylsulfonyl)imide [Hbet][Tf₂N]

cation = natural product, commercially available

hydrophobic anion

Properties:
- hydrophobic
- high solubility in water (14 wt%), high uptake of water (13 wt%)
- thermomorphic behavior in water (UCST = 55 °C)
- pH dependent phase behavior
- carboxyl function on cation
- acidic extractant: extraction is pH dependent
- betaine coordinates to metal ions
Conceptual flow sheet

**Recovery of Sc(III) from red mud leachates with the ionic liquid [Hbet][Tf₂N]**

**RM leachate**
HCl or HNO₃

**EX1**
Ti, Al, Ca, Si, Na, ...

**IL**
Sc, Fe, (REEs)

**SCR1**
0.01 M HCl
Sc, Fe, (REEs)

**SCR2**
0.01 M HCl
Sc, Fe, (REEs)

**SCR3**
0.01 M HCl
Sc, Fe

**STR1**
oxalic acid
REEs

Fe(III) oxalate (aq)
Sc(III) oxalate solid

Sc₂O₃
Extraction of Sc(III) with [Hbet][Tf₂N]

- **pH**
  - %E vs. initial pH
  - Initial pH range: 0 to 4

- **[Sc]_{aq,in}**
  - %E vs. [Sc]_{aq,in} (mmol·kg⁻¹)
  - [Sc]_{aq,in} range: 0.01 to 150

- **time**
  - %E vs. shaking time (min)
  - Shaking time range: 0 to 35 min
  - Temperature: 25 °C, 30 °C, 40 °C

- **phase ratio**
  - [Sc]_{IL} (mol·kg⁻¹) vs. Θ
  - [Sc]_{IL} range: 0.01 to 1
  - Θ range: 0 to 1
Separation of Sc(III) from synthetic solutions

- Initial concentration: 10 mmol/g for each metal ion
- pH adjusted with HCl
- 15 min shaken, 25 °C

- Initial concentration: 10 mmol/g for each metal ion
- pH adjusted with HCl
- 15 min shaken, 15 °C
Improving the Sc-Fe separation

Addition of chloride to aqueous phase during extraction
Improving the Sc-Fe separation

Addition of chloride to aqueous phase during extraction

Precipitation stripping with oxalic acid

![Graph showing the effect of chloride addition on extraction efficiency](image1.png)

![Graph showing precipitation stripping with oxalic acid](image2.png)
Sc/Fe separation from real RM leachates

**Addition of base**

The leachates have a pH of around 1, which is not within the optimal range of extraction.

Addition of base may increase the pH and increase extraction.
Sc/Fe separation from real RM leachates

Influence of phase ratio A/O

In principle, by lowering the phase ratio, the metal concentration in the IL phase will increase.
Scrubbing and stripping

1. Scrubbing with mineral acid (HCl/HNO₃) to remove coextracted REE
2. Oxalic acid precipitation stripping to strip Fe and Sc and selectively precipitate Sc
Application of process to real RM leachates

RM leachate
HCl or HNO₃

IL

EX1

Ti, Al, Ca, Si, Na, ...

Sc, Fe, (REEs)

RM leachate HCl or HNO₃

SCR1
0.01 M HCl

Sc, Fe, (REEs)

SCR2
0.01 M HCl

Sc, Fe, (REEs)

SCR3
0.01 M HCl

Sc, Fe

REEs

Fe(III) oxalate (aq)

Sc(III) oxalate solid

STR1
oxalic acid

Sc₂O₃

Precipitation of Sc oxalate
concentration Sc₂(ox)₃ > 1.5 g/L
maximum solubility Sc₂(ox)₃ = 0.1 g/L
Application of process to real RM leachates

+ • No extraction of Ca, Al, Na, Ti, Si
  • Good separation of Sc and REE
  • Easy stripping
  • Fast kinetics
  • ...

- • Low concentrations in leachates:
  o oxalic acid stripping = problematic
  o SX less suitable for metal recovery
• Only moderate %E of Sc(III) with [Hbet][Tf₂N]
• Bad Sc/Fe separation
• No pH adjustment possible
• Loss of IL to aqueous phase
• ...

Bauxite Residue Valorization and Best Practices Conference - Leuven 2015
Future prospects

• Increasing the Sc(III) concentration in the leachate → better solvent extraction
• Less consumption of acid by trying to avoid leaching of Al-Na-Ca-Si-matrix
• Implementation of Sc recovery in bigger picture
• Trying other IL systems to improve Sc/Fe separation
Acknowledgments

Laboratory of Inorganic Chemistry, KU Leuven
Prof. Koen Binnemans
Chenna R. Borra and Prof. Tom Van Gerven (Chemical Engineering, KU Leuven)

IWT, FWO and KU Leuven for funding

For more info, check:
http://www.kuleuven.rare3.eu/