RECOVERY OF RARE EARTHS FROM INDUSTRIAL WASTE RESIDUES

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## Rare earths in the periodic table

![Periodic Table](image)

**Lanthanides** = series of elements La-Lu  
**Rare earths** = lanthanides + Y + Sc  
**REEs** = rare-earth elements
## Rare earths: names and symbols

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Symbol</th>
<th>Atomic Number (Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scandium</td>
<td>Sc</td>
<td>21</td>
</tr>
<tr>
<td>Yttrium</td>
<td>Y</td>
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<tr>
<td>Lanthanum</td>
<td>La</td>
<td>57</td>
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<tr>
<td>Cerium</td>
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<tr>
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<td>Gadolinium</td>
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<td>Terbium</td>
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<td>Dysprosium</td>
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<td>Ytterbium</td>
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<tr>
<td>Lutetium</td>
<td>Lu</td>
<td>71</td>
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</table>
Rare earths: what do they look like?
Rare earths are not rare!
Rare earths as critical raw materials

Source: report EU commission “Critical raw materials for the EU” (2010)
Supply risk of rare earths

Rare-earth ore minerals

- Bastnäsite: $(\text{Ce,La})(\text{CO}_3)\text{F}$
- Monazite: $(\text{Ce,La,Nd,Th})\text{PO}_4$
- Xenotime: $\text{YPO}_4$
- Ion-adsorption clays

- Eudialyte: $\text{Na}_4(\text{Ca,Ce})_2(\text{Fe}^{2+},\text{Mn,Y})\text{ZrSi}_8\text{O}_{22}(\text{OH,Cl})_2$
- Allanite: $(\text{Ce,Ca,Y})_2(\text{Al,Fe}^{3+})_3(\text{SiO}_4)_3\text{OH}$
- Loparite: $(\text{Ce,La,Na,Ca,Sr})(\text{Ti,Nb})\text{O}_3$
REE production is dominated by China

No problem of resources, but a real supply problem
REE export quota

- China introduced REE expert quota due to sharp increase in domestic demand
- Export quota:
  - 2009: 50145 tonnes
  - 2012: 31130 tonnes
- Quota do not reflect availability of individual REEs
- Balance problem
- Quota cause serious problems for REE users outside of China
How to tackle the REE supply challenge?

- To *substitute* critical rare earths by less critical metals
- To invest in *sustainable primary mining* from old or new REE deposits
- *Technospheric mining*
  - *direct recycling* of pre-consumer manufacturing REE scrap/residues
  - *urban mining* of post-consumer (often complex multi-material) End-of-Life products
  - *landfill mining* of historic (and future) urban and industrial waste residues containing REEs
Technospheric mining

Rare-earth recycling

- Less than 1% of the REEs were being recycled in 2011 due to inefficient collection, technological issues, and lack of incentives.

- Main sources:
  - permanent magnets ($\text{Nd, Pr, Tb, Dy}$)
  - nickel metal hydride batteries ($\text{La, Ce}$)
  - lamp phosphors ($\text{Eu, Tb, Y, Gd, La, Ce}$)

- Advantages:
  - no issues with radioactive thorium
  - composition of the obtained REE concentrate is less complex
  - high concentrations, small volumes

Industrial waste residues

- Much lower concentrations of REEs than the End-of-Life consumer goods considered for recycling (often well below 1% of REOs)
- Volumes of these residues are enormous; total amounts of REEs are large
- Main waste streams:
  - metallurgical slags
  - bauxite residue (red mud)
  - phosphogypsum
  - mine tailings
  - waste water streams
Metallurgical slags (e.g. Umicore)

- REEs lost to oxide slags (low concentration)
- mainly Ce (automobile catalysts)
- Slags used as building material
Slags of battery smelter (Umicore)

Source: Maurits van Camp (Umicore)
Bauxite residue (red mud)

- Bauxite: most important aluminium ore
  Mixture of impure hydrated aluminium oxides
- Alumina purified by Bayer process
  (digestion in hot concentrated NaOH)
- Solid impurities of Bayer process: bauxite residue or red mud
- pH $\approx 12$
- Annual production: 120 million tonnes
Bauxite residue (red mud)

Source: http://jbi.org.jm
Red mud
Rare earths in red mud

- Bauxite contains 30–50% Al$_2$O$_3$, the rest being SiO$_2$, various Fe oxides, TiO$_2$, but also Ca, Na, Zn, Ga, Ni, V, Zr, Nb, Th, U and REEs
- Enrichment of REEs by a factor of 2 compared to bauxite
  - bauxite from Greece: 506 ppm of REEs (on average)
  - red mud from Greek bauxite: 1040 ppm of REEs

Ref.:
Scandium in red mud

- Red mud is rich in scandium
  - Greece: 130 ppm
  - Jamaica: 390 ppm
  - Moengo (Suriname): 1700 ppm
  - average abundance of scandium: 22 ppm

- Scandium represents > 95% of the economic value of rare earths in red mud

Ref.:
Recovery of rare earths from red mud

Hydrometallurgical processes
- to selectively leach minor metals from red mud, leaving behind major components such as iron oxides
- REEs are readily leachable from red mud by diluted mineral acids, other elements not
- Best leachant: dilute HNO₃
  Recovery: Y 96%, Sc 80%, light lanthanides 30-50%
- After leaching, REEs can be recovered from leachate by selective precipitation (oxalate) or solvent extraction

Ref.:
Recovery of rare earths from red mud

- Combination of pyrometallurgical and hydrometallurgical processes
  - to first recover iron from red mud and to subsequently concentrate REEs in an oxide slag
  - red mud is treated in a blast furnace in the presence of a reducing agent, generating pig iron and a titanium-rich slag (containing REEs)
  - problems with high sodium content and water
  - hydrometallurgical step consists of leaching REEs from slag with diluted mineral acid

Ref.:
Scandium-rich minerals are rare

- Thortveitite \((\text{Sc,Y})_2\text{Si}_2\text{O}_7\)
- Bazzite \(\text{Be}_3\text{Sc}_2(\text{Si}_6\text{O}_{18})\)
- Kolbeckite \(\text{ScPO}_4 \cdot 2\text{H}_2\text{O}\)
- Ixiolite-Sc \((\text{Nb,Ta,Ti,Sc,Fe,Mn})_4\text{O}_8\)
- Perrierite-Sc
  \[\text{(Ce,Ca,Th)}_4(\text{Fe}^{2+},\text{Sc})\text{Fe}_2^{3+}(\text{Ti,Fe}^{3+})_2(\text{Si}_2\text{O}_7)_2\text{O}_8\]
- Magbasite \(\text{KBa(Al,Sc)Fe}^{2+}\text{Mg}_5\text{F}_2\text{Si}_6\text{O}_{20}\)

Scandium occurs in many ores in trace amounts, but is not found in sufficient concentrations to be mined for scandium alone.
Applications of scandium

- Al-Sc alloys for minor aerospace industry components (Russian military aircraft, MiG-21 and MiG-29) 0.1% and 0.5% Sc
- Al-Sc high-strength light weight alloy is used in bicycle frames, golf clubs, and baseball bats
- yttrium-scandium-gallium garnet (Er,Cr:YSGG) lasers for use in dentistry
- ScI$_3$ in high-intensity discharge lamps
- Sc(CF$_3$SO$_3$)$_3$: water-stable Lewis acid catalyst for use in organic synthesis
Applications of scandium

[Images of a fighter jet, a bicycle, a baseball bat, and light bulbs]
Main by-product of phosphoric acid production
Formed by acidic digestion of phosphate rock
Phosphate rock (phosphorite) contains mainly apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH,F,Cl})$
Digestion is mainly done by $\text{H}_2\text{SO}_4$, although also $\text{HNO}_3$ can be used.
Depending on the production method, phosphogypsum consists primarily of either $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ (gypsum) or $\text{CaSO}_4\cdot \frac{1}{2}\text{H}_2\text{O}$
4.5 to 5.5 tonnes of phosphogypsum are generated per tonne of $\text{P}_2\text{O}_5$
Phospogypsum
Rare earths in phosphate rock

- On average: 0.01 and 0.1 wt% of REOs
- Phosphate rock of Kola Peninsula (Russia): up to 1.0 wt% of REOs
- Ce, La, Nd: 80% of the total REE content

Ref.:
Rare earths in phosphogypsum

- REEs concentrated in phosphogypsum during phosphoric acid production
- 70 to 85% of REEs originally present in phosphate rock end up in phosphogypsum; rest remains dissolved in leaching solution.
- Average concentration of REEs in phosphogypsum: 0.4 wt%
- Phosphogypsum contains lower concentrations of scandium than red mud

Ref.:
Recovery of REEs from phosphogypsum

- About 50% of rare earths present in phosphogypsum can be recovered by leaching at ambient temperature with 0.1 to 0.5 M H$_2$SO$_4$
- Impossible to quantitatively recover rare earths without destruction of phosphogypsum lattice
- Leaching efficiencies can be increased by gravity flow of H$_2$SO$_4$ solution through column packed with phosphogypsum
- Enhanced leaching after mechanical activation of phosphogypsum by ball-milling
Recovery of REEs from phosphogypsum

- Higher leaching efficiencies by leaching with HNO$_3$ solution instead of H$_2$SO$_4$
- Rare earths recovered from leaching solution by precipitation (sodium rare-earth double sulphates) or solvent extraction
- Possible to leach metals from phosphogypsum with organic extraction agents dissolved in kerosene

Ref.:
• E. P. Lokshin et al., Russian J. Appl. Chem., 84 (9), 1461-1469, 2011.
• D. Todorovsky et al., Hydrometallurgy, 45 (1-2), 13-19, 1997
Mine tailings

- Older processing methods of rare-earth ores were not efficient
- During flotation process of ground rare-earth ores large losses occurred
- Large volumes of solid waste with significant concentrations of rare earths
- Mountain Pass mine tailings still contain between 3 to 5% REOs
- Large amounts of REEs in tailings of uranium mines in Queensland (Australia), Kazakhstan and Kyrgyzstan
Mountain Pass mine (Molycorp)

Source: http://webservices.itcs.umich.edu
Waste water

- Waste water produced during the extraction and separation of rare earths
- Acid mine drainage (AMD)
- Gadolinium from MRI contrast agents in waste water of hospitals

- Low concentrations of REEs
- Recovery by ion-exchange resins and chelating resins to be preferred
- Biosorption
Conclusions

- Waste streams have in common that they contain relatively low REE concentrations (<1% REOs)
- Large volumes are available
- Could become economically attractive secondary sources of rare earths
- Bauxite residue (red mud): source of scandium
- Phosphogypsum: source of light rare earths
- Dilution of rare earths in most types of slags remains a problem
- Recovery of rare earths from mine tailings and waste water is not well investigated
FP7 EURARE project

“Development of a sustainable exploitation scheme for Europe’s Rare Earth ore deposits”

Project coordinator: Prof. Ioannis Paspaliaris (NTUA, Greece)
Start date: 2013-01-01   End date: 2017-12-31
Project Funding: 9,000,000 EURO
Subprogramme Area: New environmentally friendly approaches in minerals processing
Contract type: Large-scale integrating project
Website: www.eurare.eu
www.kuleuven.rare3.eu/

Thank you!