PROMETIA

3rd Scientific Seminar

MINERAL PROCESSING AND EXTRACTIVE METALLURGY FOR MINING AND RECYCLING INNOVATION ASSOCIATION

rare3

KU Leuven Research Platform focusing on the Advanced Recycling and Reuse of Rare Earths and other Critical Metals

Main outputs of the RARE³ project

Joris ROOSEN

(KU Leuven, Belgium)

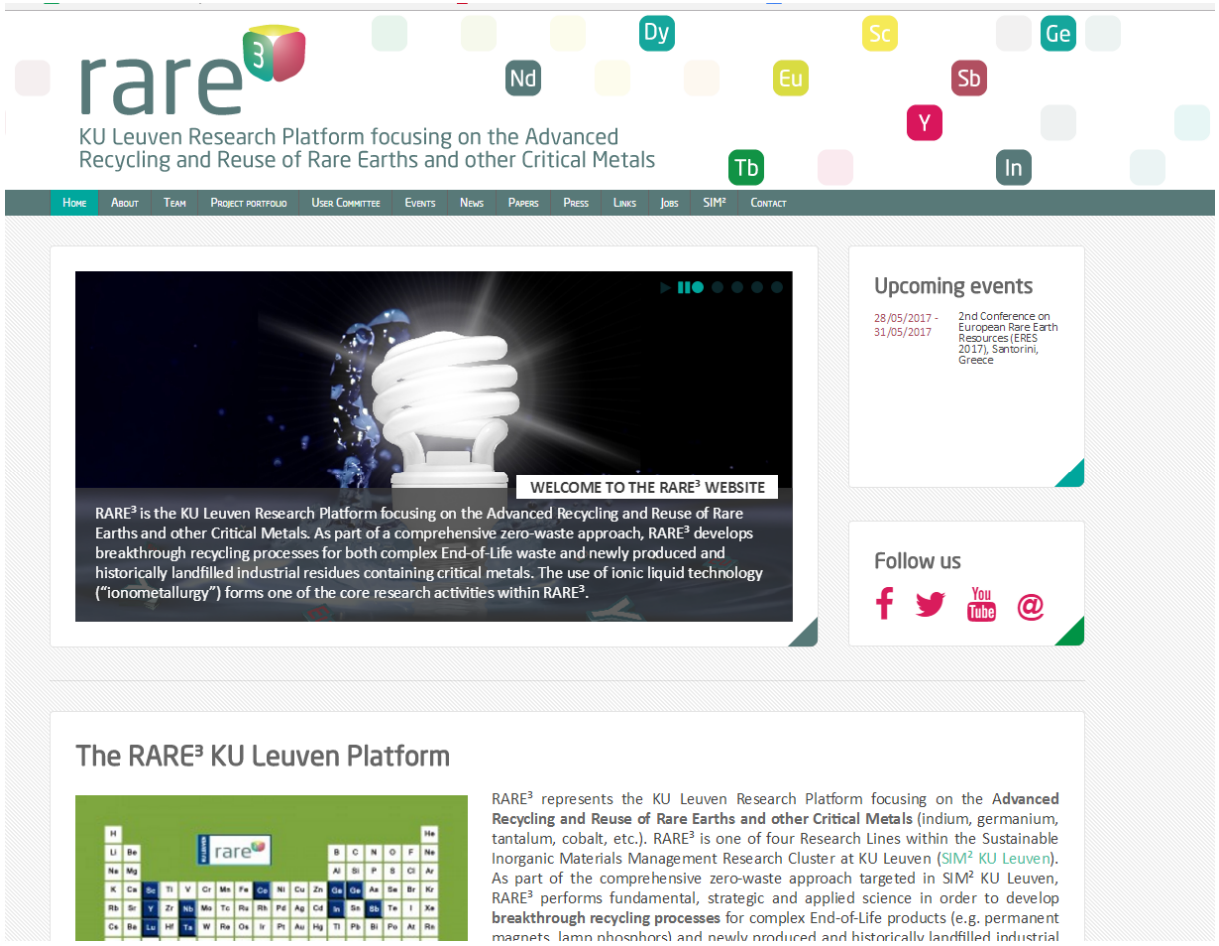
15-12-2016

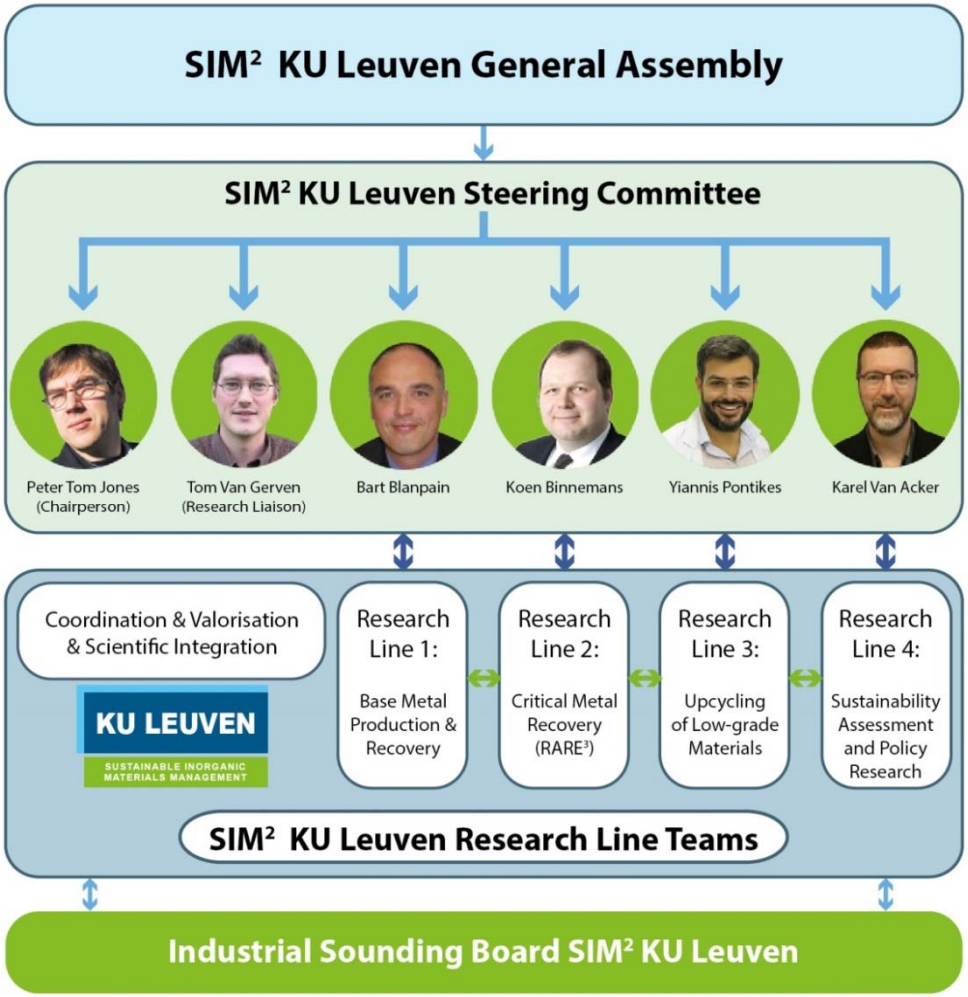
- RARE³ = KU Leuven Research Platform focusing on the Advanced **Re**cycling and **Re**use of **Rare Earths** and other Critical Metals
- RARE³ = one of four Research Lines within the KU Leuven Sustainable Inorganic Materials Management Research Cluster (**SIM² KU Leuven**)
- RARE³ = **fundamental, strategic and applied** science
- RARE³ = development of **breakthrough recycling processes**
  - ➢ Complex End-of-Life products
  - ➢ Industrial process residues containing critical metals
    - ✓ Newly produced and historically landfilled
    - ✓ Examples: bauxite residue (red mud), goethite, phosphogypsum, metallurgical slags, flotation tailings, …
- RARE³ = targeting a comprehensive **zero-waste** approach
- RARE³ = corroboration of **environmental benefits** of recycling processes by development and implementation of novel Life Cycle Assessment (**LCA**) methodologies

1. **About the RARE³ platform**
2. Solvometallurgical leaching
3. Solvent extraction by ILs
4. Adsorption by biopolymers

- **Introduction**
- A broad (international) network
- The bigger picture
- Flagship research domains

A snapshot of the website: http://www.kuleuven.rare3.eu/





RARE³

=

flagship research program within the **interdisciplinary** & **interdepartmental** SIM² KU Leuven consortium

- RARE³ is embedded in an **(inter)national effort** to develop zero-waste solutions

Academic partners

RWTH AACHEN UNIVERSITY

TU Delft Delft University of Technology

CHALMERS UNIVERSITY OF TECHNOLOGY

UNIVERSITY OF BIRMINGHAM

UNIVERSITY OF HELSINKI

National Technical University of Athens

universitätbonn

TECHNISCHE UNIVERSITÄT BERGAKADEMIE FREIBERG
Die Ressourcenuniversität. Seit 1765.

University of Leicester

Industrial partners

PRAYON

LCM less common metals

SOLVAY asking more from chemistry®

YARA

TOYOTA

Molycorp THE RARE EARTHS COMPANY

ALUMINIUM OF GREECE

JGI HYDROMETAL

umicore materials for a better life

INDAVER

MEAB

campine committed and competent

TREIBACHER INDUSTRIE AG

KU LEUVEN rare³

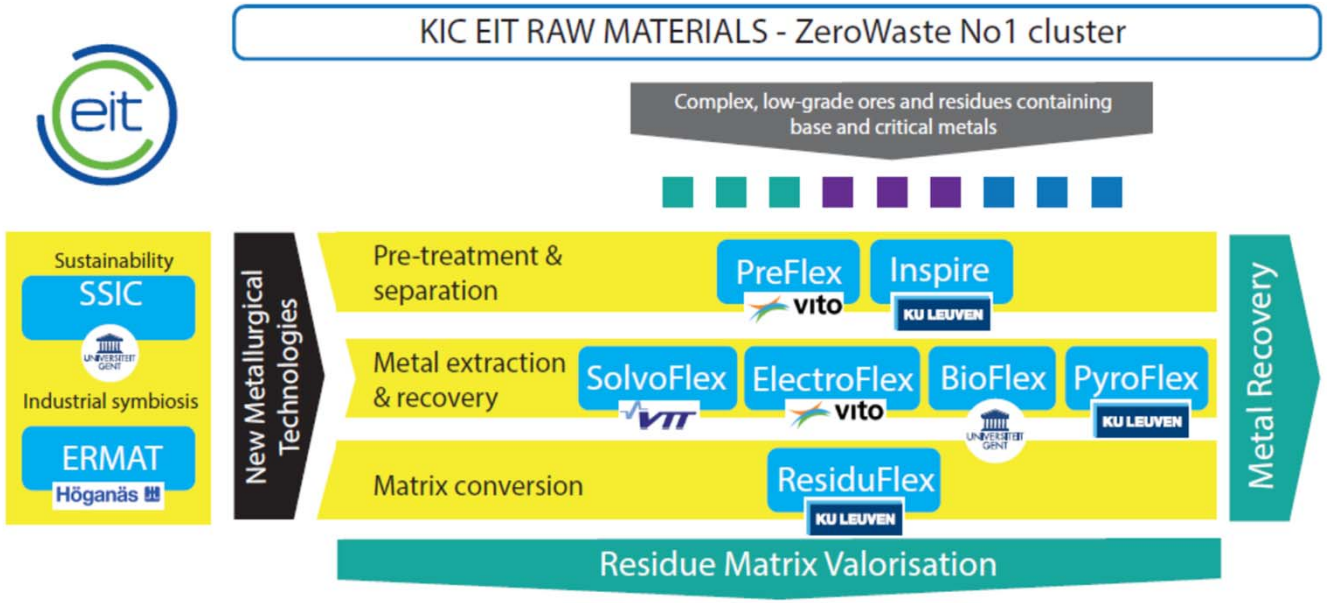
- RARE³ is embedded in an **(inter)national effort** to develop zero-waste solutions

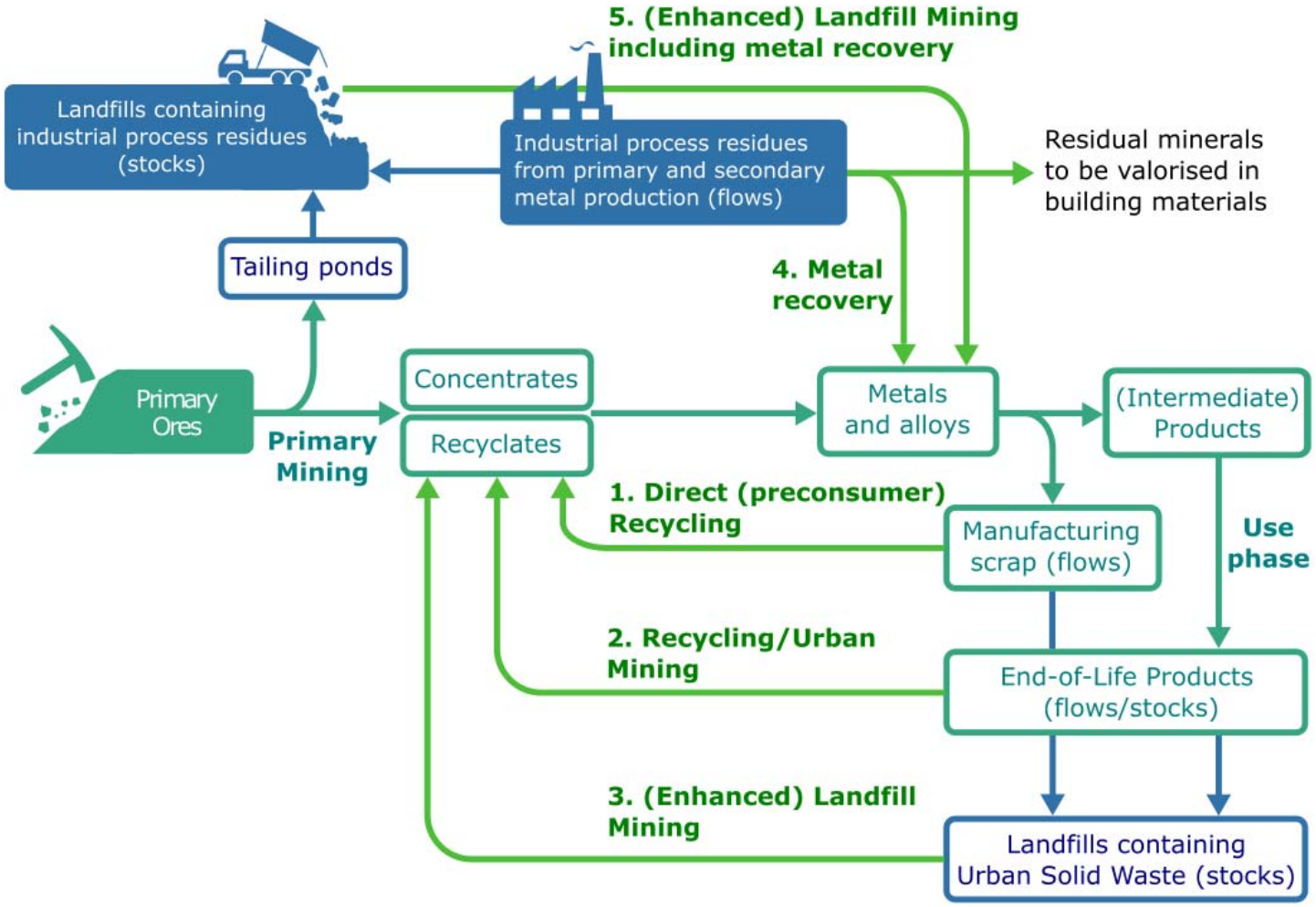
KU LEUVEN
SUSTAINABLE INORGANIC MATERIALS MANAGEMENT

SIM
innovating together

MaRes

eit RawMaterials




5. (Enhanced) Landfill Mining including metal recovery
Landfills containing industrial process residues (stocks)
Industrial process residues from primary and secondary metal production (flows)
Residual minerals to be valorised in building materials
Tailing ponds
4. Metal recovery
Primary Ores
Primary Mining
Concentrates
Recyclates
Metals and alloys
(Intermediate) Products
1. Direct (preconsumer) Recycling
Manufacturing scrap (flows)
Use phase
2. Recycling/Urban Mining
End-of-Life Products (flows/stocks)
3. (Enhanced) Landfill Mining
Landfills containing Urban Solid Waste (stocks)

1. **About the RARE³ platform**
2. Solvometallurgical leaching
3. Solvent extraction by ILs
4. Adsorption by biopolymers

- Introduction
- A broad (international) network
- The bigger picture
- **Flagship research domains**

SYNTHESIS

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

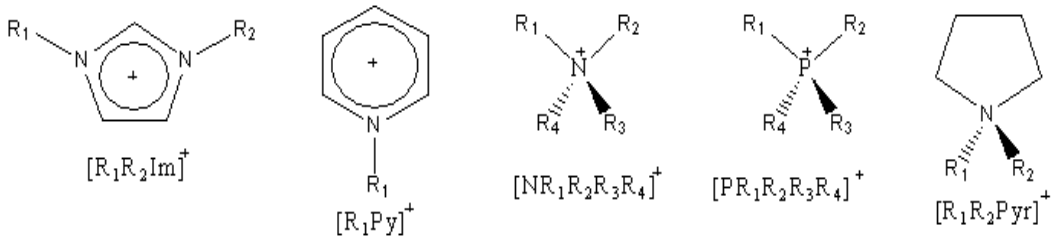
Development of more selective processes through a deeper understanding of the mechanism of solvent extraction processes

PROCESSES

Chemical engineering and mini-pilot-scale testing (upscaling) of developed processes and mining chemicals

KU LEUVEN rare³

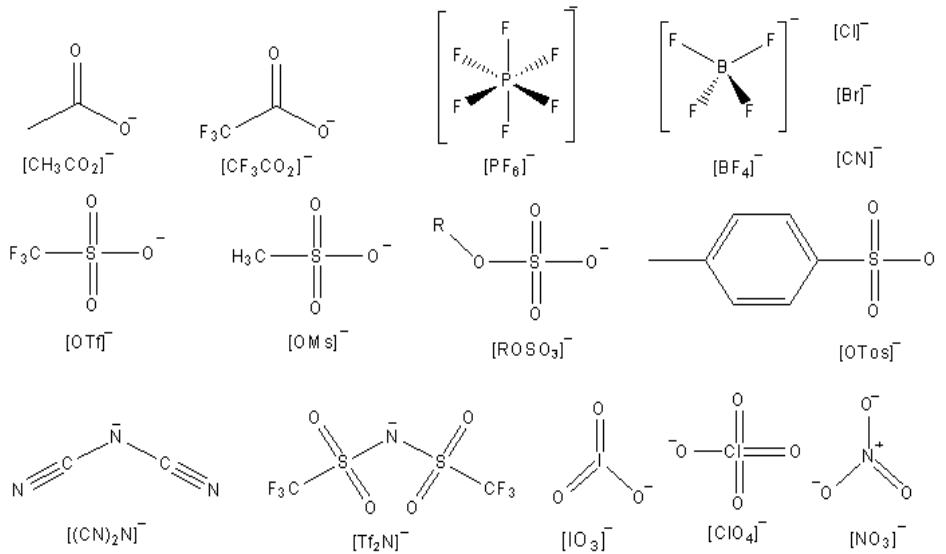
- **Definition**: ionic liquids (ILs) are organic salts that consist entirely of ions and have traditionally a melting point below 100 °C



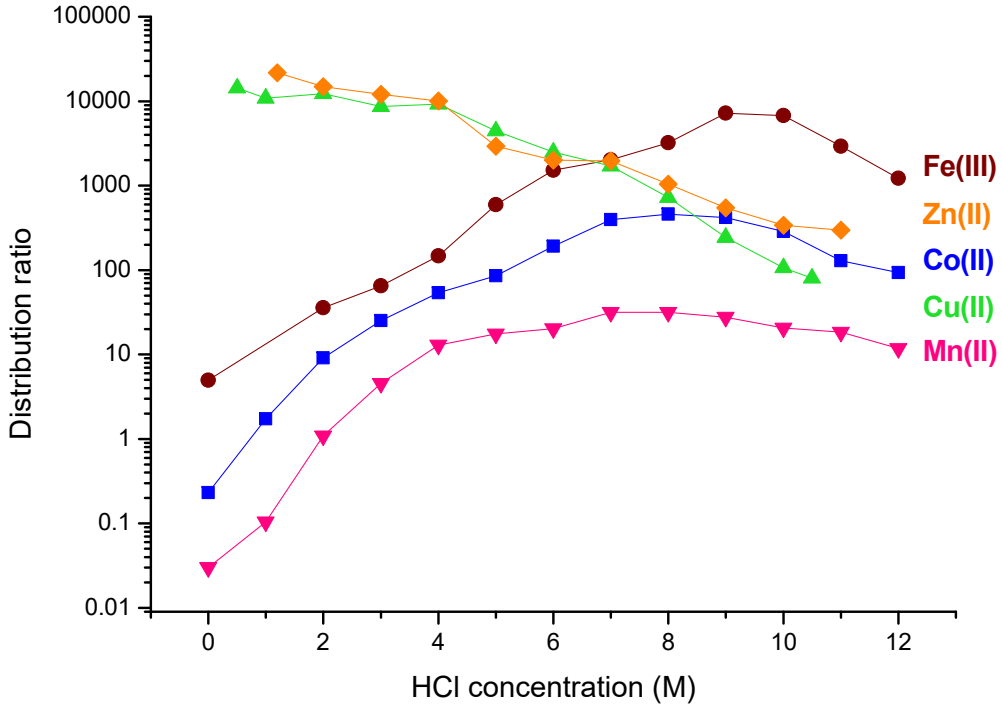
- **Properties**
  - ✓ Broad liquidus range
  - ✓ Large electrochemical window

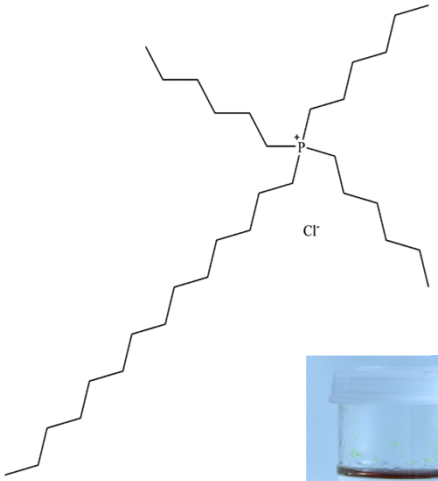
- **Beneficial for extraction systems**
  - ✓ Negligible vapor pressure
  - ✓ Low flammability
  - ✓ High metal loadings possible
  - ✓ Tunable structures
    (acidic groups for leaching)

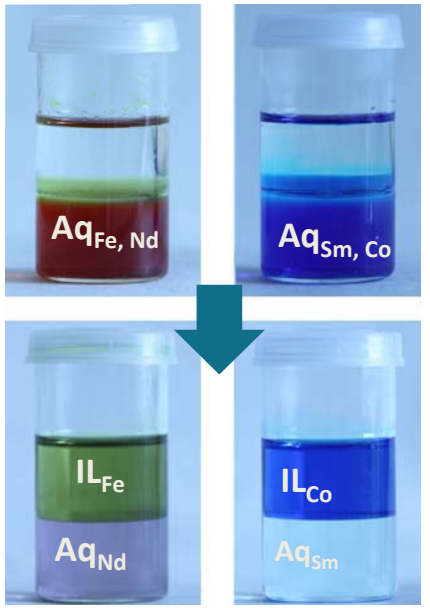
➔ Often called “greener solvents”



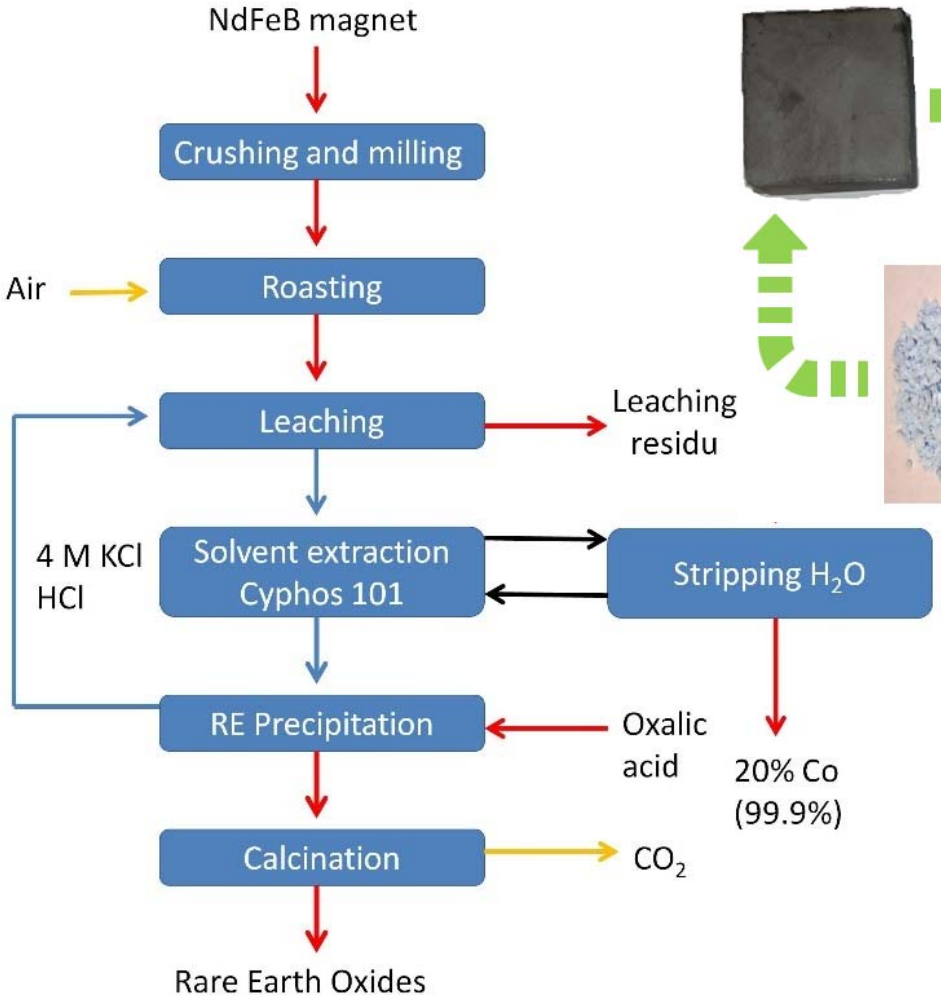
- **Magnet recycling**: Nd/Fe and Sm/Co separations
- **Separation factors** up to 10^6 with Cyphos 101







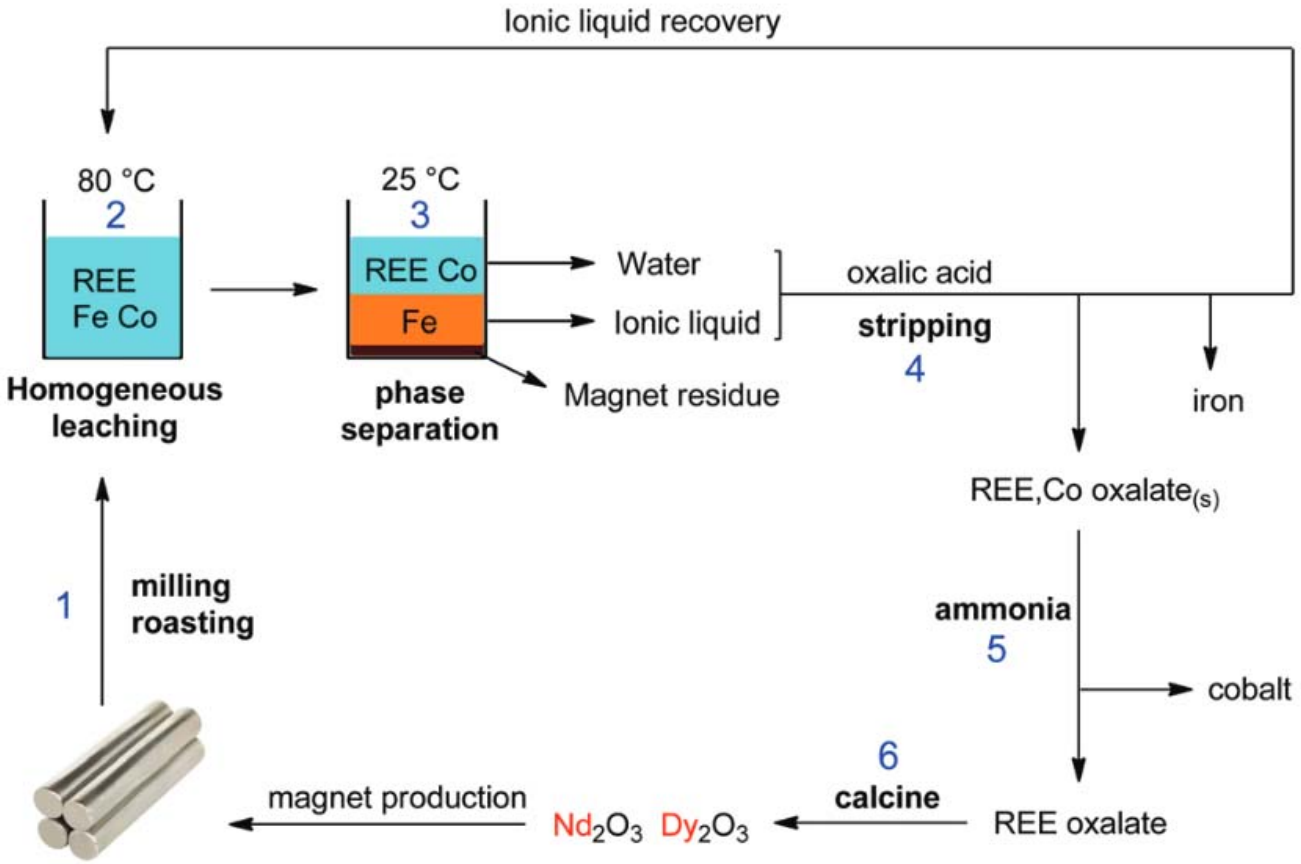
Vander Hoogerstraete, T., Wellens, S., Verachtert, K., Binnemans, K., 2013, *Green Chemistry, 15* (4), 919-927.



Recovery of REs from NdFeB magnet

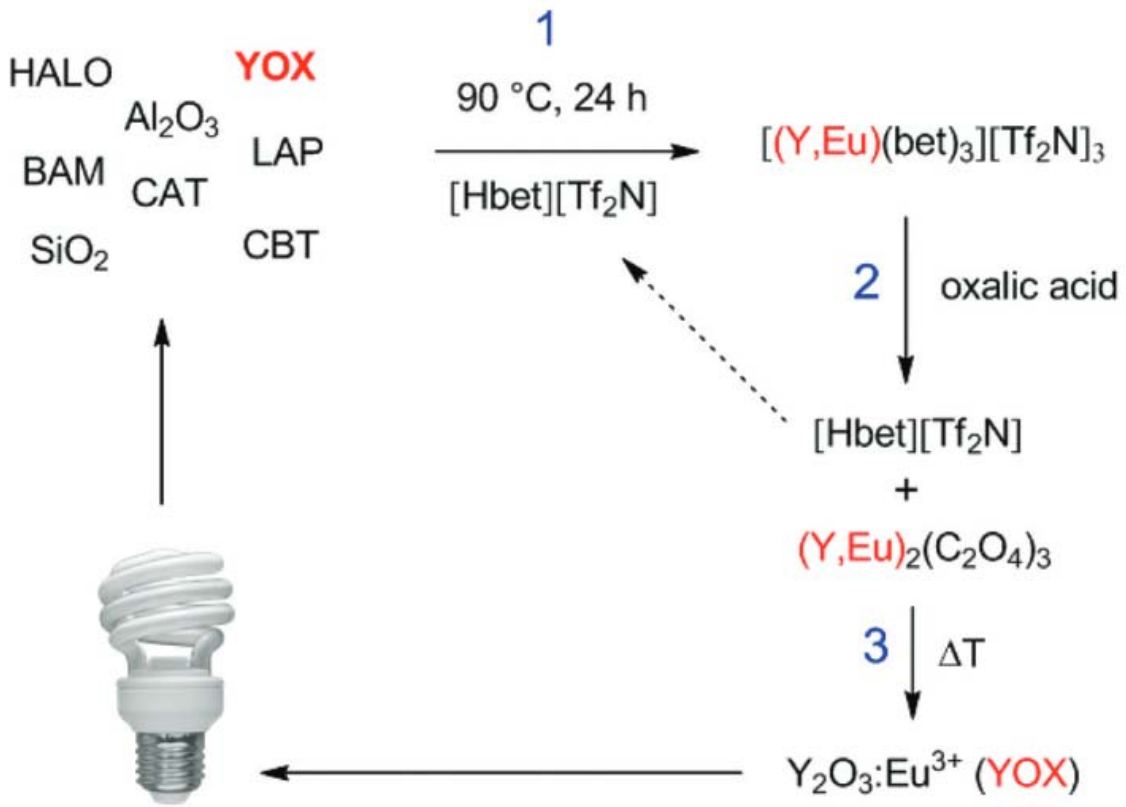
Vander Hoogerstraete, T., Blanpain, B., Van Gerven, T., Binnemans, K., 2014, *RSC Advances, 4* (109), 64099-64111.

- **[Hbet][Tf_2N],** a functionalized fluorinated IL suitable for **NdFeB magnet recycling**

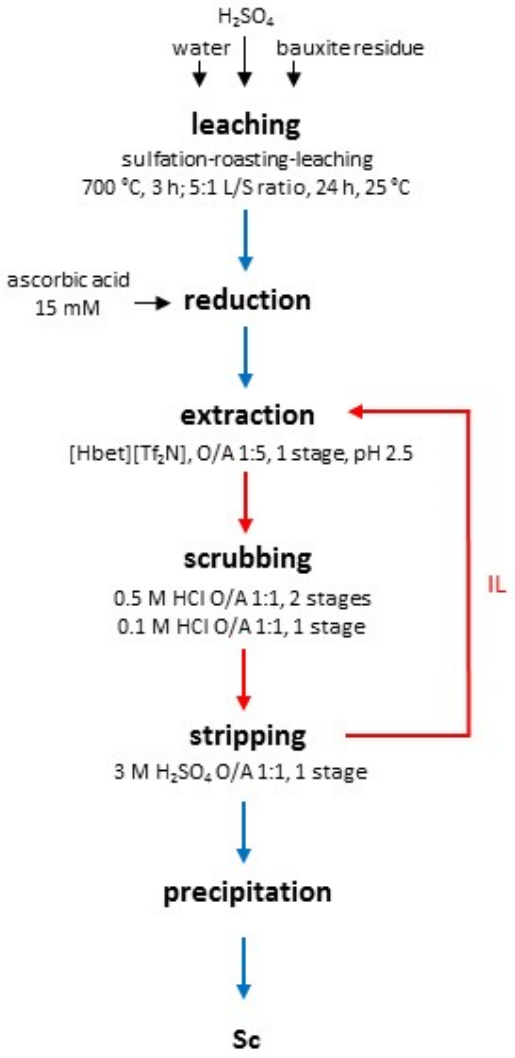


Dupont, D., Binnemans, K., *Green Chem.*, 2015, 17 (4), 2150-2163.

- **[Hbet][Tf_2N],** a functionalized fluorinated IL suitable for **lamp phosphor recycling** (*WO 2016065433 A1)*



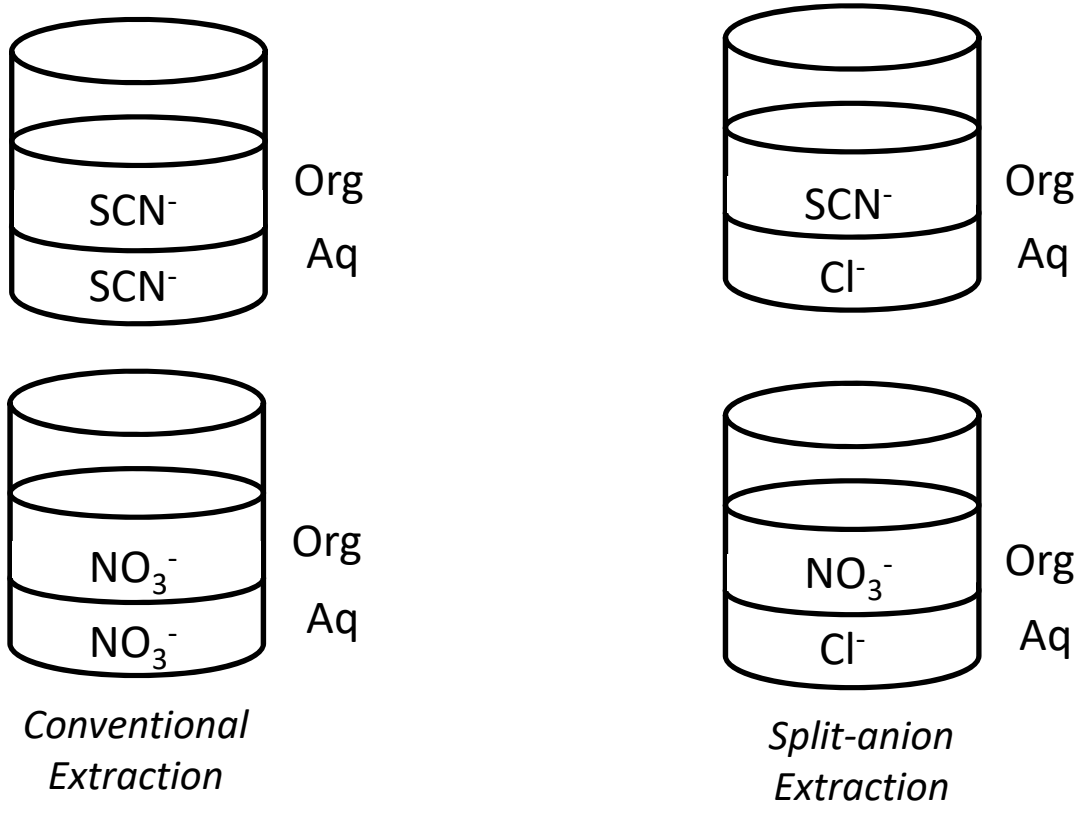
Dupont, D., Binnemans, K., *Green Chem.,* 2015, 17 (2), 856-868.



- **Bauxite residue** = waste stream resulting from the production of alumina by the Bayer process
  - ✓ Global production = 120 millions of tonnes/year
  - ✓ No large-scale industrial application yet
  - ✓ Presence of **Sc(III)** comprises 90% of its economic value
- **[Hbet][Tf_2N],** a functionalized fluorinated IL suitable for **the recovery of Sc(III) from bauxite residue**

Onghena, B., Borra, C.R., Van Gerven, T., Binnemans, K.. *Proceedings of the Bauxite Residue Valorisation and Best Practices Conference* 2015, Leuven (Belgium), pp. 331-337

- Challenge in REE separation by ionic liquids: **efficient extraction of REE from Cl^- media by neutral or basic extractants**
- Solution: **split-anion extraction** (WO2015106324, 2015)



Conventional Extraction

Split-anion Extraction

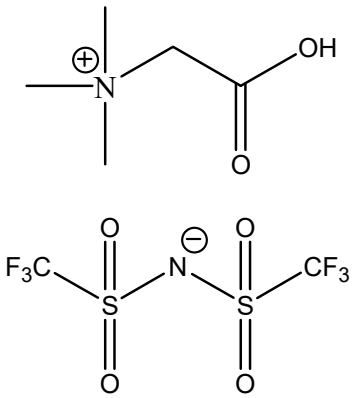
Larsson, K., Binnemans, K., 2015, *Hydrometallurgy, 156*, 206-214.

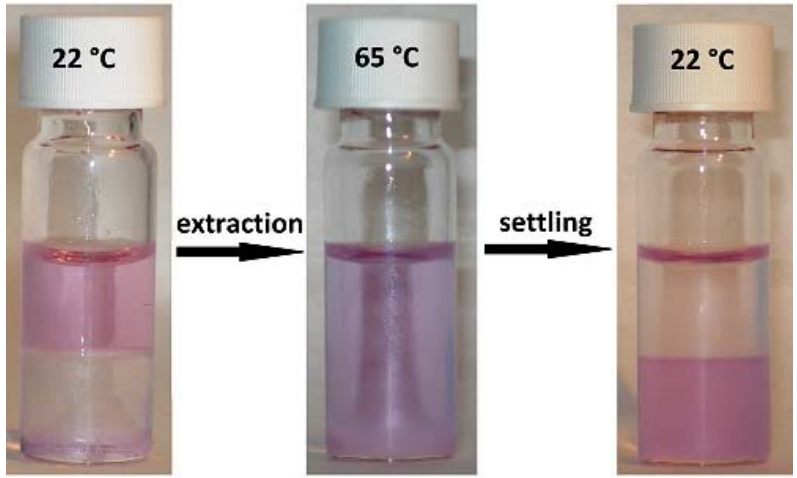
- **Homogeneous liquid-liquid extraction**
- Main drawback of ionic liquids = high viscosity:
  - × Slow extraction processes
  - × Slow mass transport

  } ➔ time and energy consuming

➔ New innovative technique = *homogeneous liquid-liquid extraction*

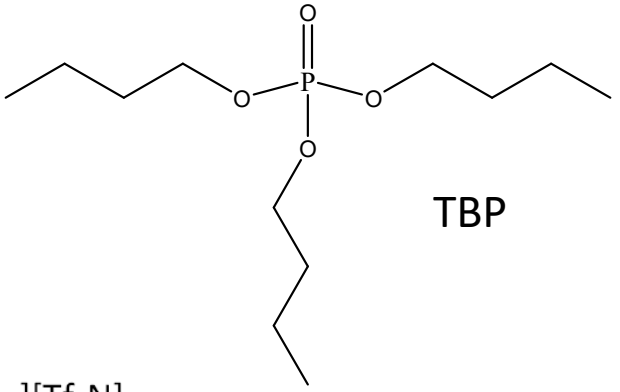
➔ One homogeneous liquid phase above UCST or below LCST



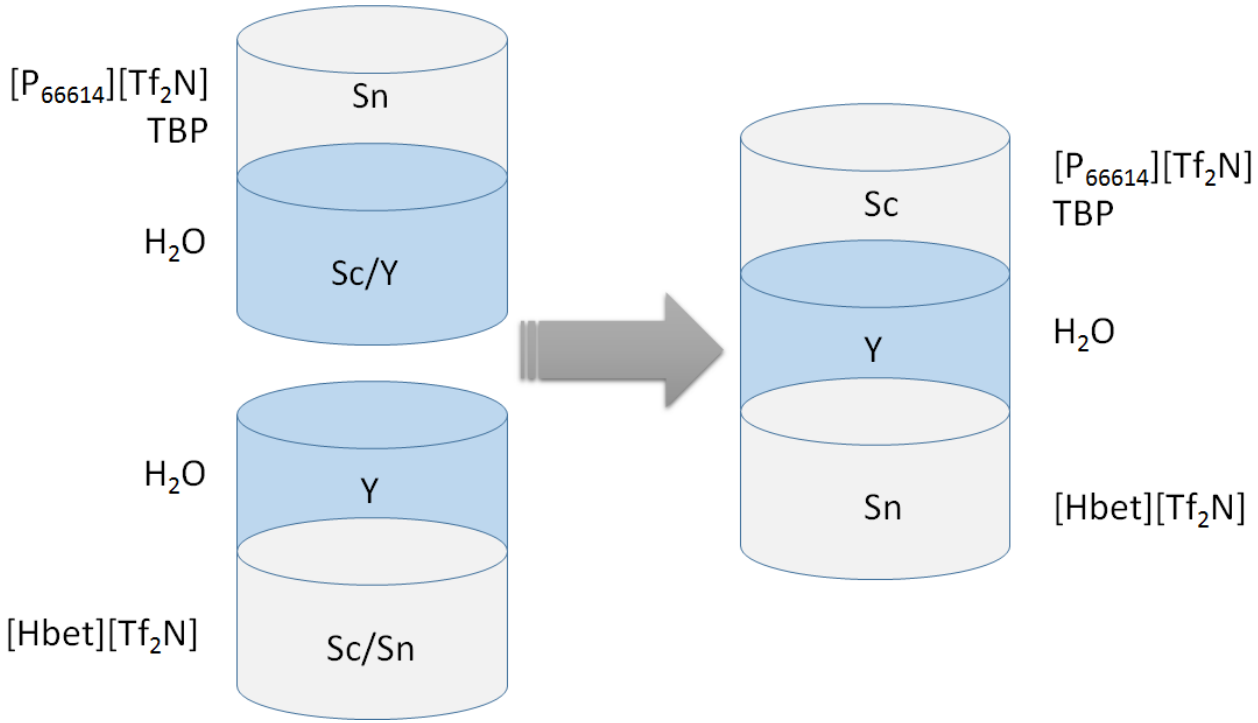


Vander Hoogerstraete, T., Onghena, B., and Binnemans, K., *International journal of molecular sciences*, 2013, 14, 21353-21377.

- **Triphasic IL/H_2O/IL extraction system**
- 1-step separation of a ternary mixture of Sn/Sc/Y

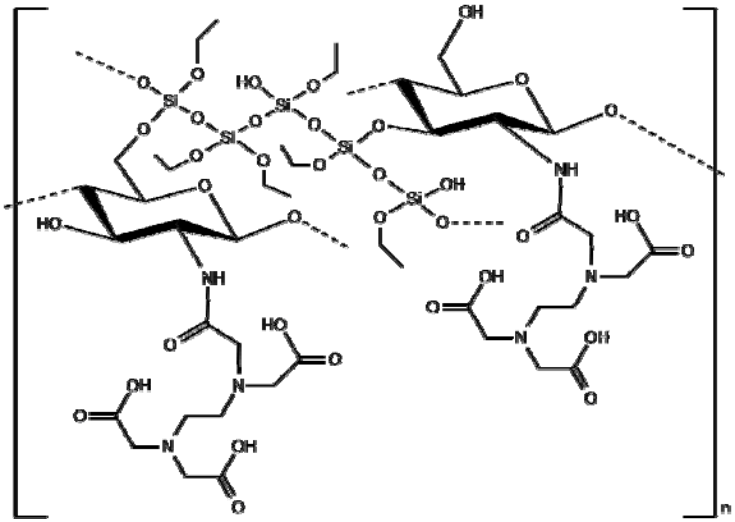


TBP

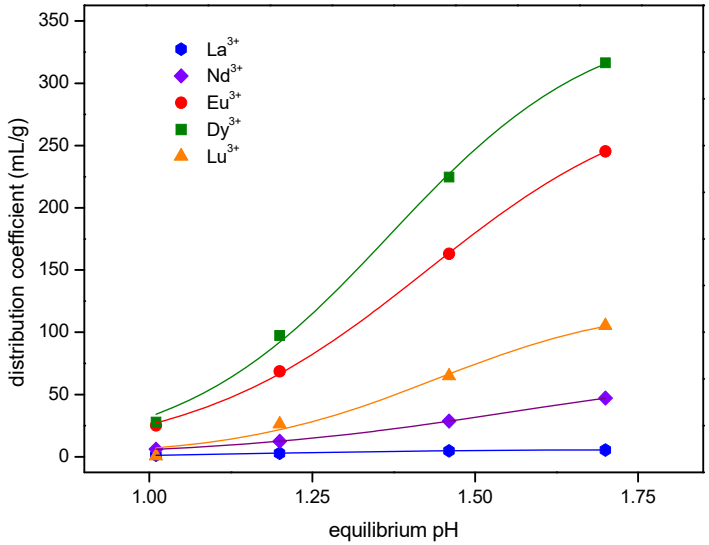


Van der Hoogerstraete, T., Blockx, J., De Coster, H., Binnemans, K., 2015, *Chemistry - a European Journal, 21* (33), 11757-11766.

- Selective recovery of critical metals from **dilute** aqueous waste streams by **adsorption** on functionalized biomaterials, like chitosan and alginate
- Selectivity for (and in between) Ln(III) metal ions in synthetic mixture by functionalization of chitosan-silica with **EDTA** (organic ligand)



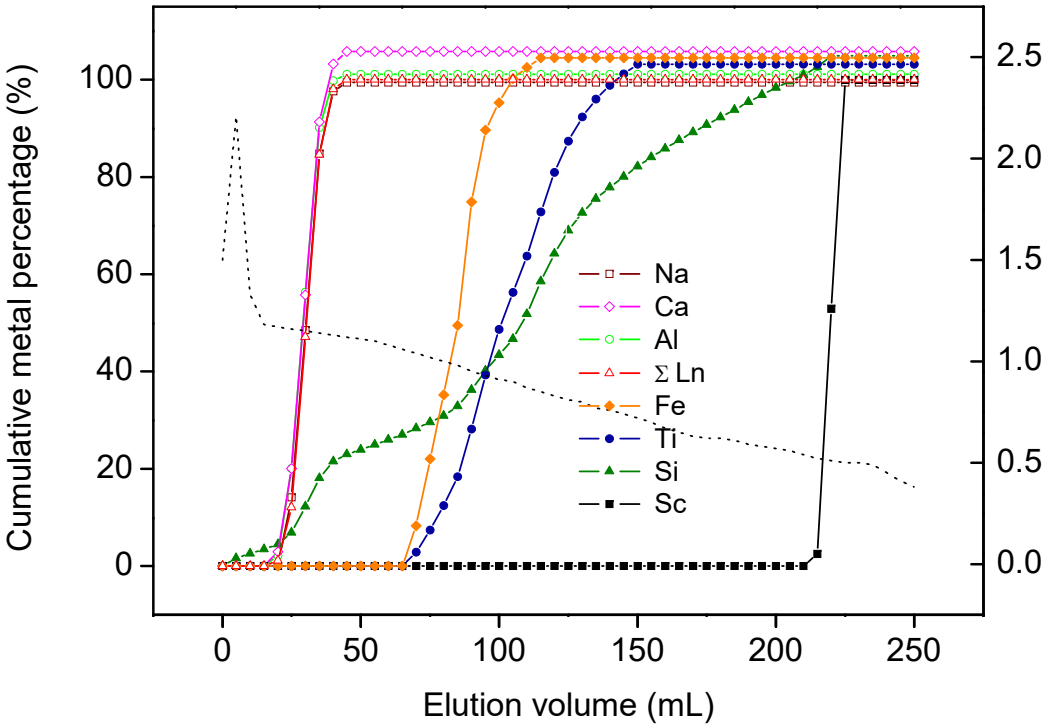
EDTA-functionalized chitosan-silica

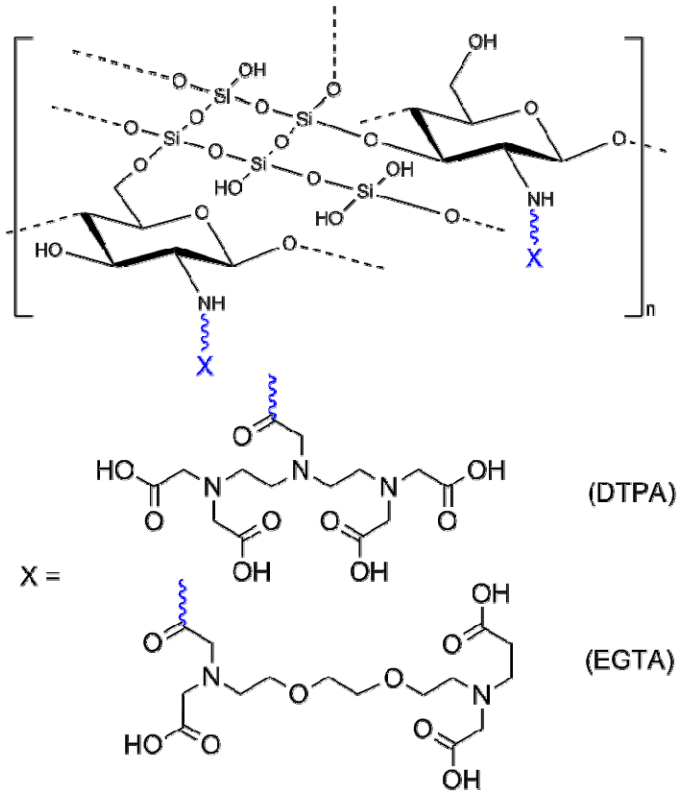


Affinity differences between Ln(III) ions

Roosen, J., Spooren, J., Binnemans, K. (2014). *Journal of Materials Chemistry A, 2* (45), 19415-19426.

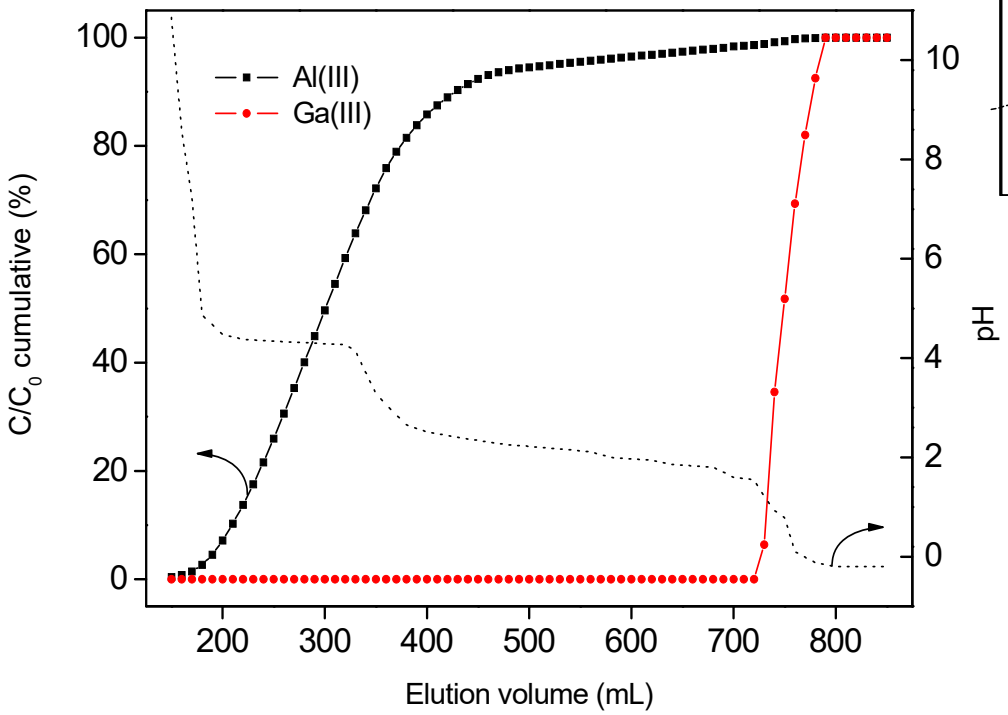
- Recovery of **Sc(III)** from leachate of Greek bauxite residue by functionalization of chitosan-silica with **EGTA**

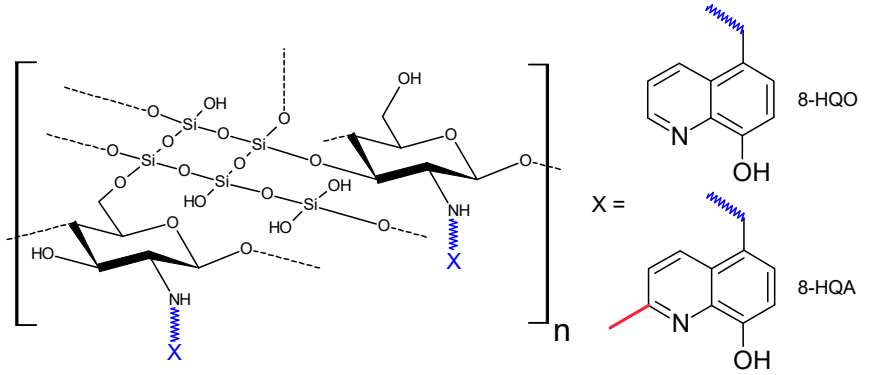




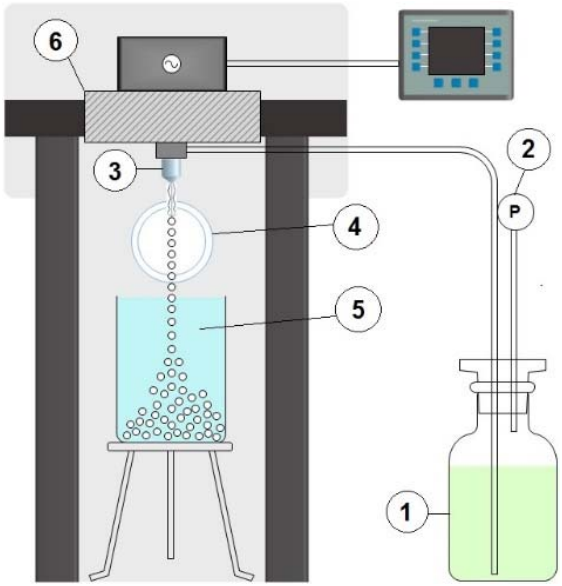
Roosen, J., Van Roosendael, S., Borra, C., Van Gerven, T., Mullens, S., Binnemans, K. (2016). *Green Chemistry, 18* (7), 2005-2013.

- Revovery of **Ga(III)** from highly alkaline Bayer liquor by functionalization of chitosan-silica with **8-hydroxyquinaldine**

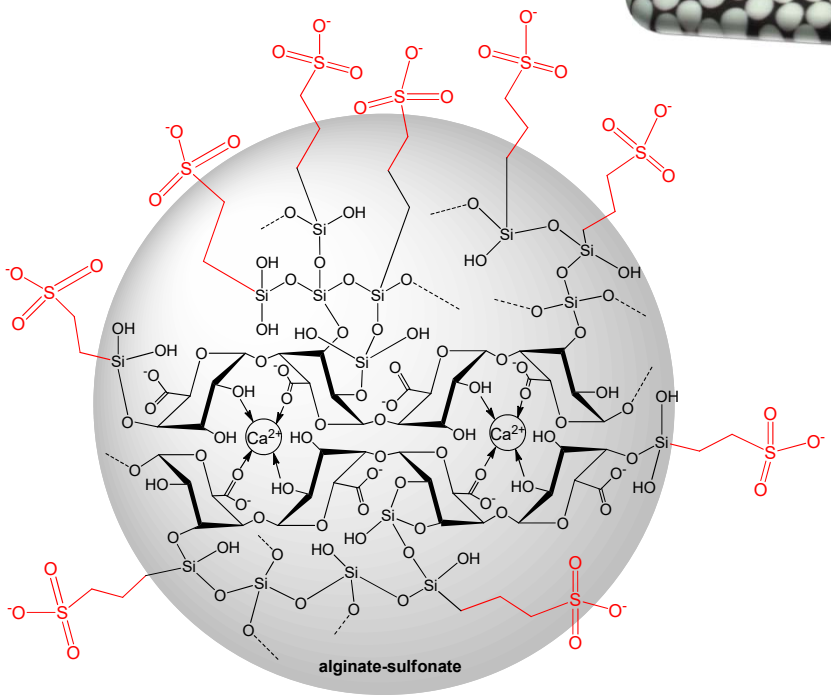




- Design of alginate microspheres by **vibrating-nozzle technology**
- Simple functionalization by **soaking** in organosilane solution

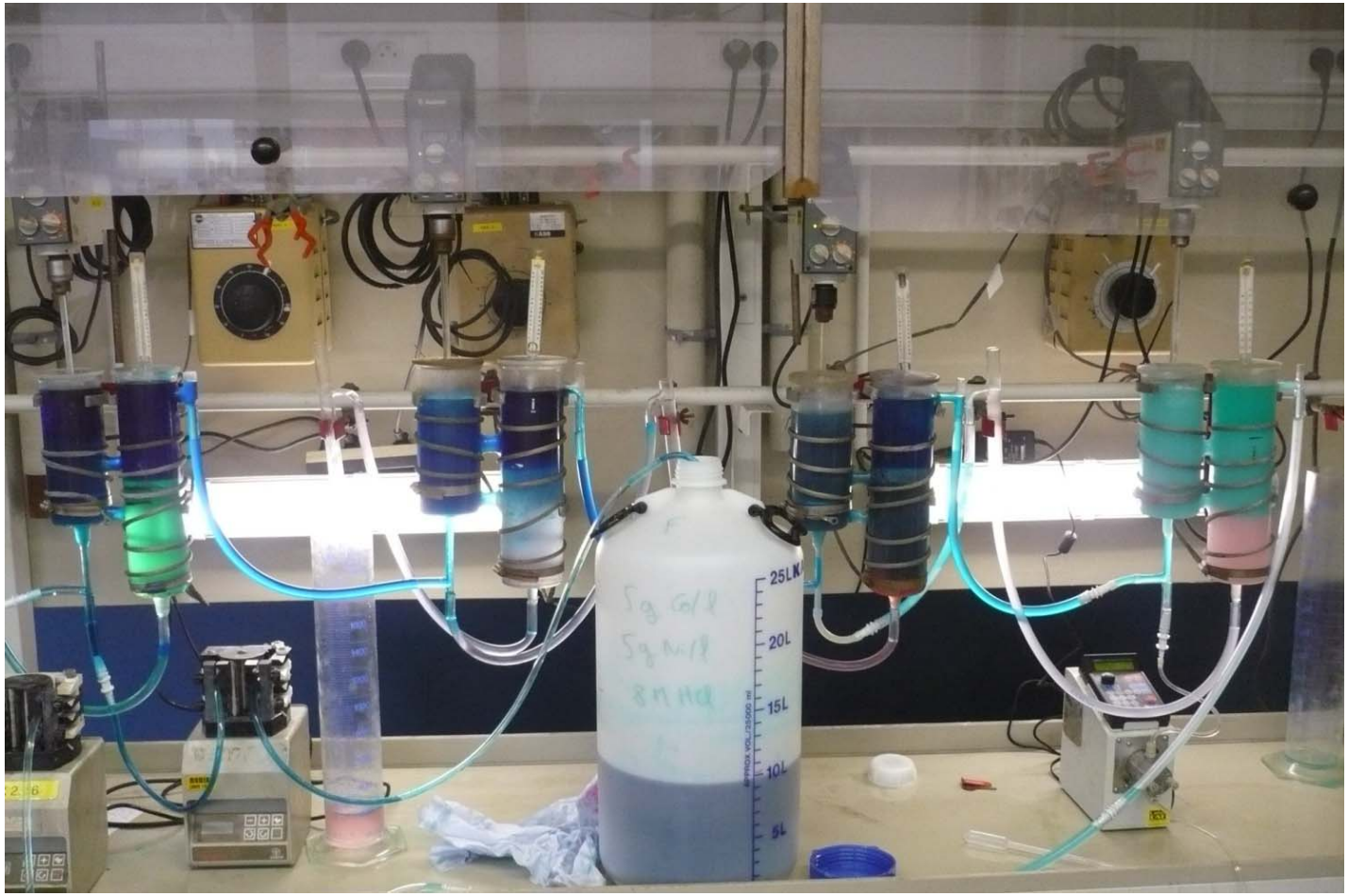


Experimental set-up vibrating nozzle



Roosen, J., Pype, J., Binnemans, K., Mullens, S. (2015). *Industrial & Engineering Chemistry Research, 54* (51), 12836-12846.

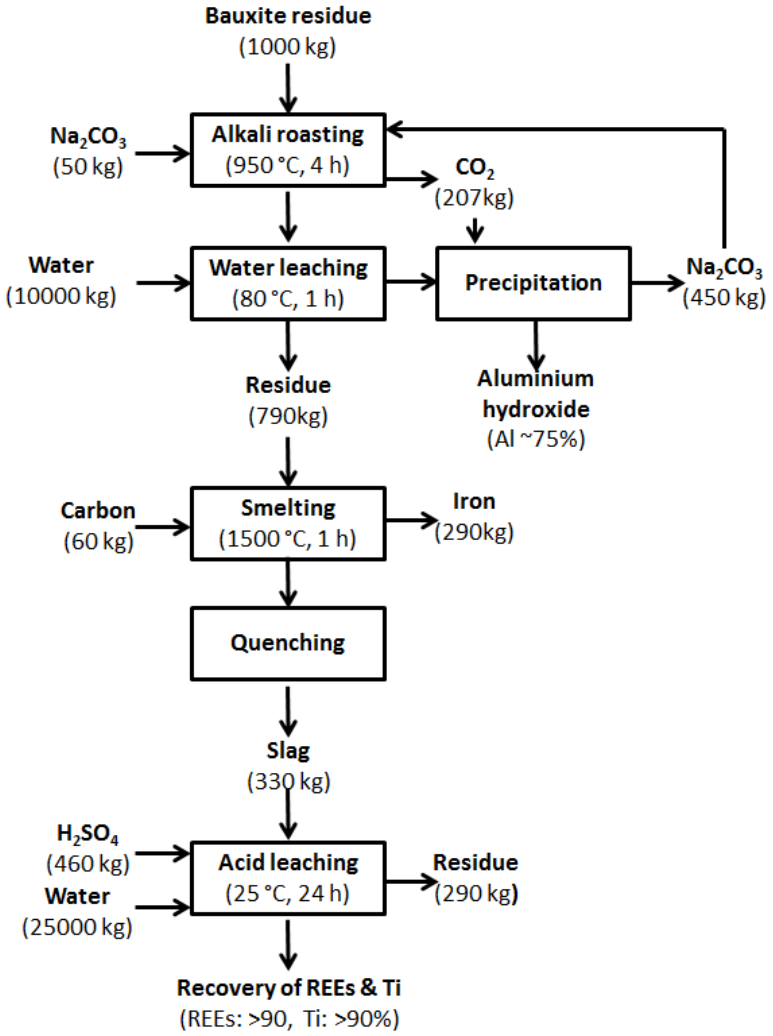
- **Pilot scale mixer-settler set-up** for a Ni/Co separation at Umicore



umicore
materials for a better life

KU LEUVEN rare³

Wellens, S., Thijs, B., and Binnemans, K., *Green Chem.*, 2012, 14, 1657-1665.



- Selective recovery of rare earths from bauxite residue by **combination of sulfation, roasting and leaching**

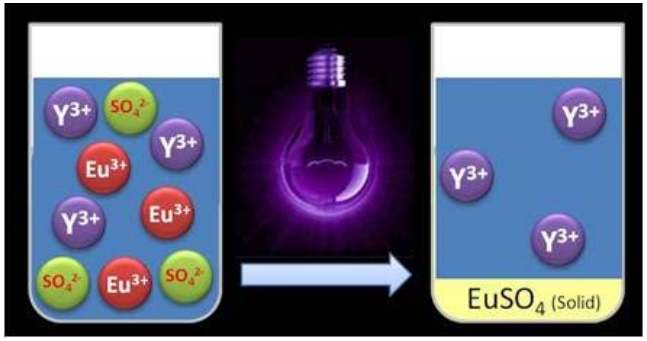
- **Further optimizations**: bauxite residue (high alumina content) requires large amounts of fluxes during smelting:
  - × process cost ↗
  - × energy consumption during smelting ↗
  - × acid consumption during slag leaching ↗

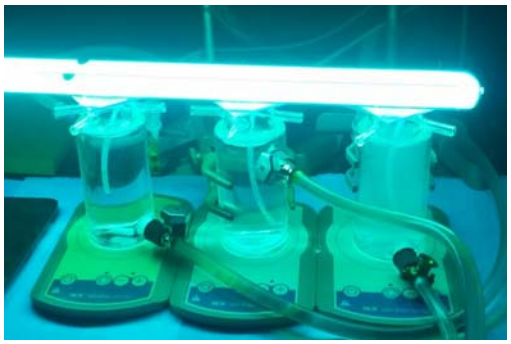
  ➔ Removal of alumina by alkali roasting prior to smelting resulted in clear slag

  ➔ Metal separation without need of any flux

Borra, C.R., Blanpain, B., Pontikes, Y., Binnemans, K., Van Gerven, T., *JOM*, 2016, 68, 2958-2962.

- **Aim: separate Eu/Y (~ red lamp phosphors) by UV light irradation in 2 steps:**
  1. Selective photochemical reduction of Eu(III) to Eu(II)
  2. Precipitation of Eu(II) as $EuSO_4$ (in water) or $EuCl_2$ (in alcohols)
- Y(III) remains unaffected and stays in solution
- High purity (> 98%) and recovery (up to > 95%) of Eu for synthetic Eu/Y mixtures
- Proof-of-principle established for real red lamp phosphor





Advantages of UV light:

✓ No harmful chemicals

✓ High separation efficiency

✓ High purity

Van den Bogaert, B., Havaux, D., Binnemans, K., Van Gerven, T., *Green Chem., 2015,* 17, 2180–2187.

THANK YOU … for your attention!

rare 3

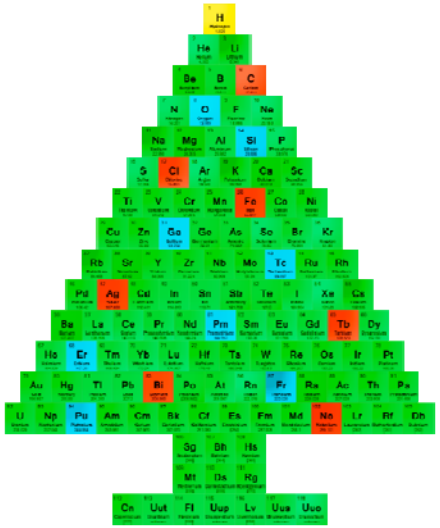
KU Leuven Research Platform focusing on the Advanced Recycling and Reuse of Rare Earths and other Critical Metals

http://www.kuleuven.rare3.eu/

Acknowledgement
(financial support)

KU LEUVEN

Questions



KU LEUVEN rare 3