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Separation of REE with ionic liquids

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Outline

- Ionic liquids
- Extraction and leaching
  - Non-fluorinated ILs
  - Fluorinated ILs
- IL future and possibilities

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Ionic liquid

- Definition: ionic liquids (ILs) are organic salts that consist entirely out of ions and have traditionally a melting point below 100 °C
- Properties
  - Broad liquidus range
  - Large electrochemical window
- Beneficial properties for extraction systems
  - Negligible vapor pressure
  - Low flammable
  - High metal loadings possible
  - Tunable structures (acidic groups for leaching)

➔ Often called “greener solvents”

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Ionic liquid


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Ionic liquids win Great British Innovation Vote

28 March 2013 Emma Stoye

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Ionic liquids have been voted the UK innovation most likely to shape the 21st century in a nationwide poll run by science museums and learned societies.

The Great British Innovation Vote called upon members of the public to vote for their favourite past and future UK innovations. The potential green applications of ionic liquids as solvents to dissolve almost any chemical saw them triumph over a shortlist of 11 other innovations, including graphene, gene therapy and the Raspberry Pi computer, which came second.

The vote ran for 10 days during the UK's National Science and Engineering week in March. It was publicised through social media by celebrities such as Brian Cox and Stephen Fry, and attracted more than 50,000 votes. While ionic liquids won the future innovations category, Turing's Universal Machine was voted the greatest UK innovation of the past 100 years, beating the Mini and x-ray crystallography into second and third place, respectively.

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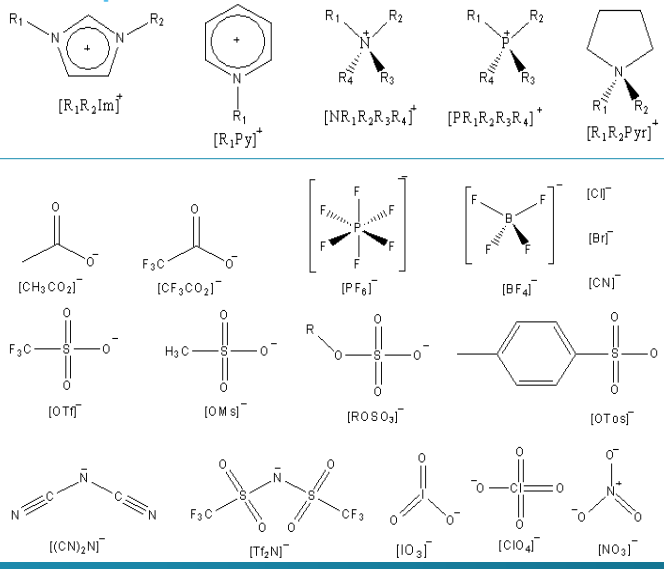
Ionic liquid



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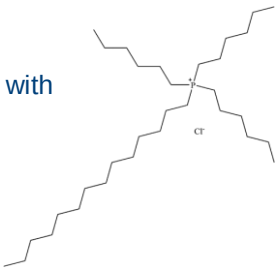
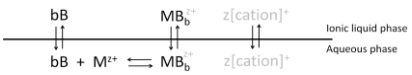
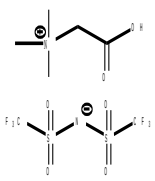
Extraction

- Solvent extraction: limited to hydrophobic ILs with
  - Long alkyl chains
    - High viscosity
  - Fluorinated anions
    - More expensive
    - Ion exchange possible
    - Often no coordinating groups ➔ extractant or functionality required







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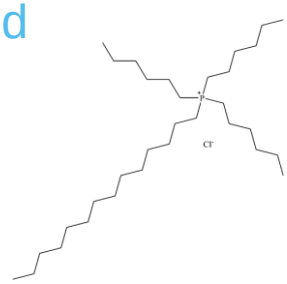
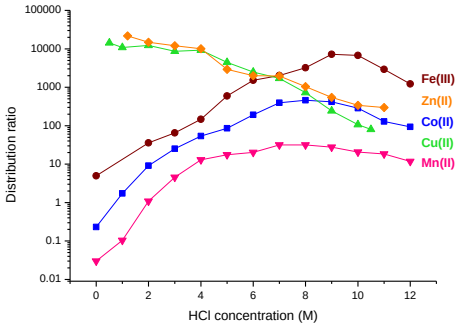
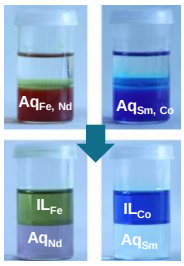
Extraction – non-fluorinated

- Nd/Fe and Sm/Co separation (magnets)
- Separation factors up to 10^6







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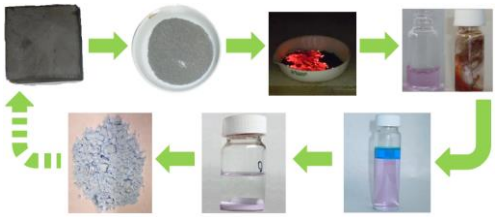
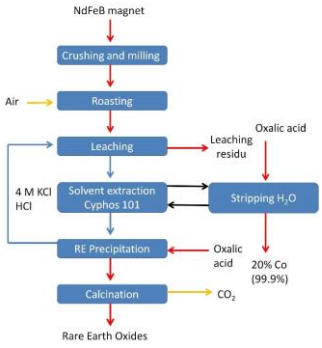
Vander Hoogerstraete, T., Wellens, S., Verachtert, K., Binnemans, K., 2013, *Green Chemistry*, *15* (4), 919-927.

Extraction – non-fluorinated

- Recovery of REs from NdFeB magnet





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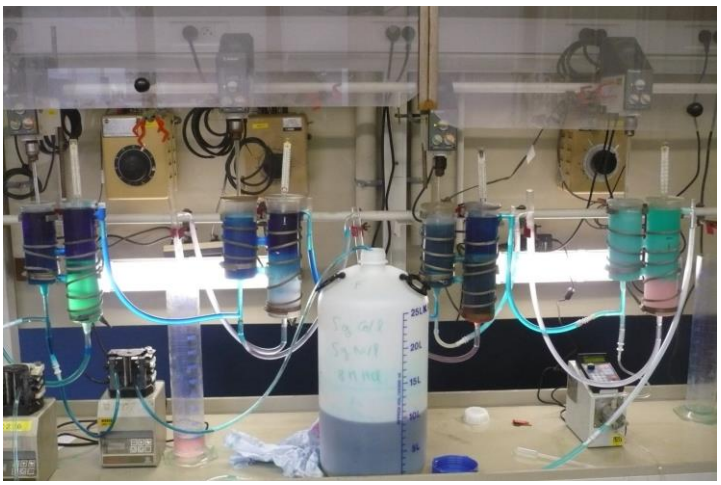
Vander Hoogerstraete, T., Blanpain, B., Van Gerven, T., Binnemans, K., 2014, *RSC Advances*, *4* (109), 64099-64111.

Extraction – non-fluorinated

- Pilot scale test of a Ni/Co separation at umicore with this ionic liquid



umicore
materials for a better life

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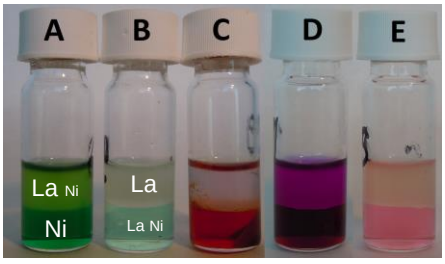
S. Wellens, B. Thijs and K. Binnemans, *Green Chem.*, 2012, 14, 1657-1665.

Extraction – non-fluorinated

- Similar ionic liquid with nitrate anion
- Also possible to separate La/Ni => NiMH batteries



Ni/La Fe/Nd Co/Sm

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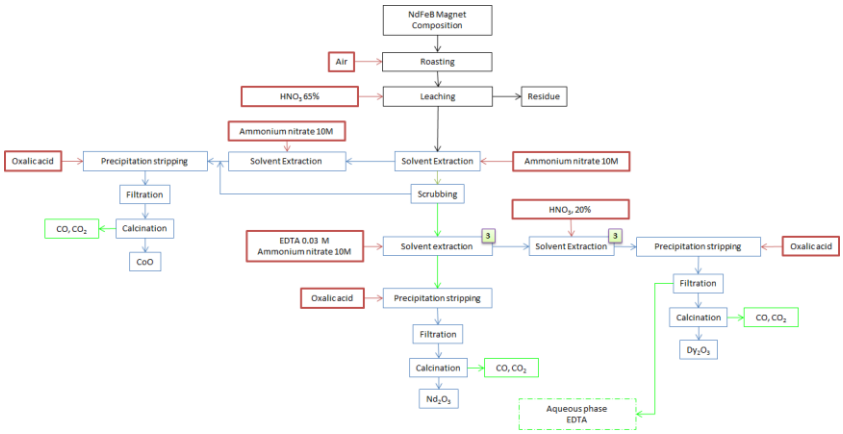
T. Vander Hoogerstraete and K. Binnemans, Green Chemistry, 2014, 16, 1594-1606.

Extraction – non-fluorinated

- Recovery of REs from NdFeB magnet



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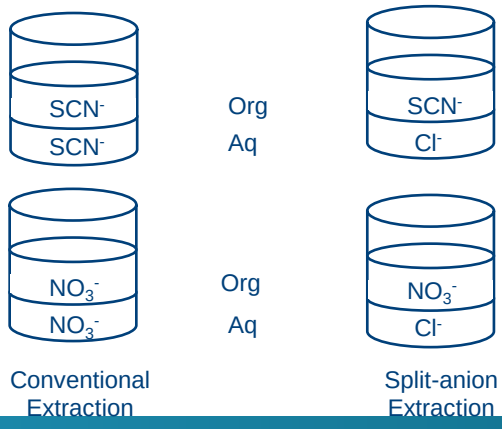
Riaño, S., Binnemans, K. 2015, *Green Chemistry, 17* (5), 2931-2942.

Extraction – non-fluorinated

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



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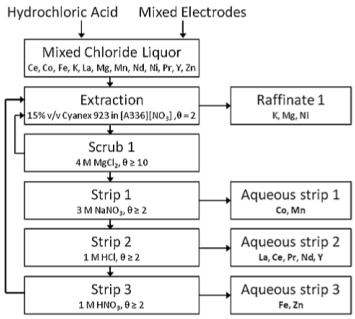
Larsson, K., Binnemans, K., 2015, *Hydrometallurgy, 156*, 206-214.

Extraction – non-fluorinated

- Non-fluorinated ILs + extractants for recycling NiMH battery recycling



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Larsson, K., Binnemans, K., 2015, *Journal of Sustainable Metallurgy, 1* (2), 161-167.

Extraction – non-fluorinated

- Fluorinated ILs + extractants (e.g. TBP) for recycling NdFeB magnets

N. Sasaya, M. Matsumiya, and K. Tsunashima, *Polyhedron*, 2015, **85**, 888-893.

M. Matsumiya, Y. Kickuchi, T. Yamada, and S. Kawakami, *Separation and Purification Technology*, 2014, **130**, 91-101.

Y. Kikucki, M. Matsumiya, and S. Kawakami, *Solvent Extraction Research and Development, Japan*, 2014, **21**, 137-145.

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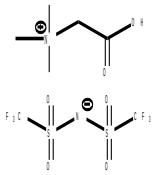
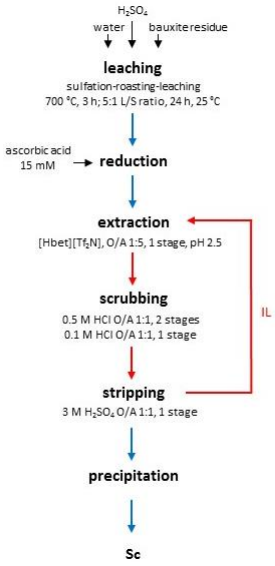
Extraction - fluorinated

- Functionalized fluorinated ILs
- E.g. [Hbet][Tf_2N]
- Recovery Sc from bauxite residue





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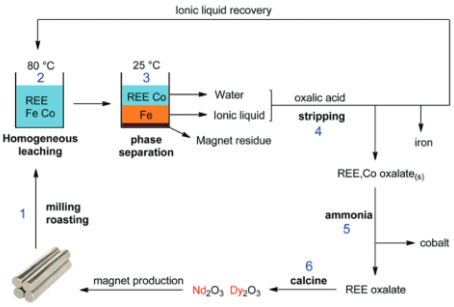
Onghena, B., Borra, C., Van Gerven, T., Binnemans, K. (2017). *Separation and Purification Technology, 176*, 208-2019.

Extraction - fluorinated

- Functionalized fluorinated ILs
- E.g. [Hbet][Tf_2N]
- NdFeB magnet recycling



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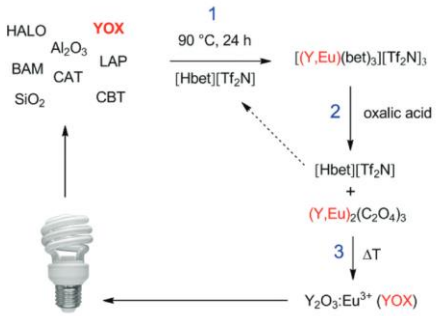
Dupont, D., Binnemans, K.,2015, *Green Chemistry, 17* (4), 2150-2163.

Extraction - fluorinated

- Functionalized fluorinated ILs
- E.g. [Hbet][Tf_2N]
- Lamp phosphor recycling (*WO 2016065433 A1)*



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

IL future

- *A few examples…*

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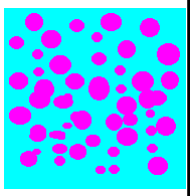
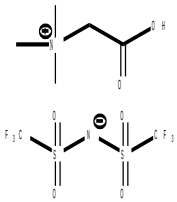
IL future

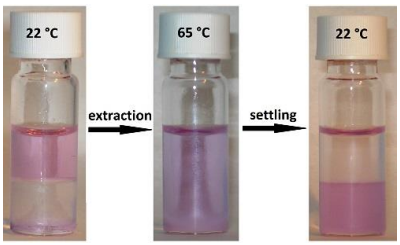
- Homogeneous liquid-liquid extraction
- Main drawback of ionic liquids = high viscosity
  - Slow extraction processes
  - Slow mass transport

➔ time and energy consuming



New innovative technique ➔ *homogeneous liquid-liquid extraction*





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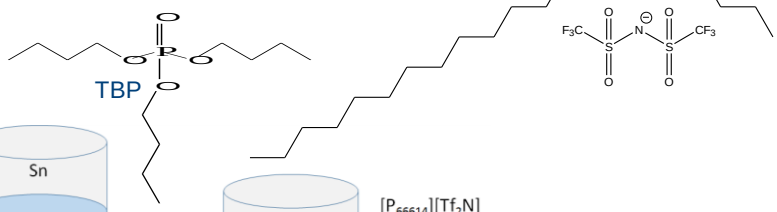
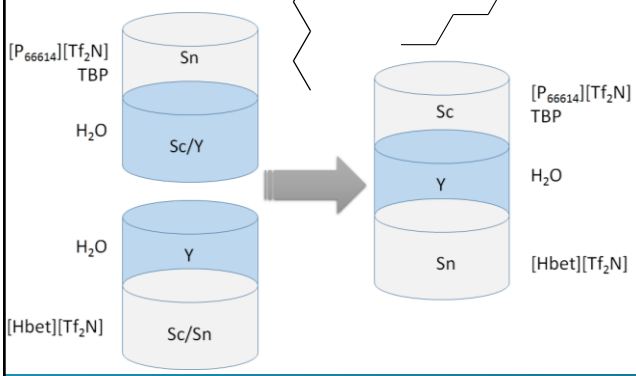
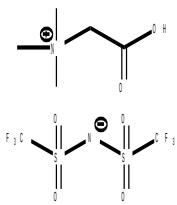
T. Vander Hoogerstraete, B. Onghena, and K. Binnemans, *The Journal of Physical Chemistry Letters*, 2013, 4, 1659-1663.
T. Vander Hoogerstraete, B. Onghena, and K. Binnemans, *International journal of molecular sciences*, 2013, 14, 21353-21377.

IL future

- Triphasic IL/H_2O/IL extraction system







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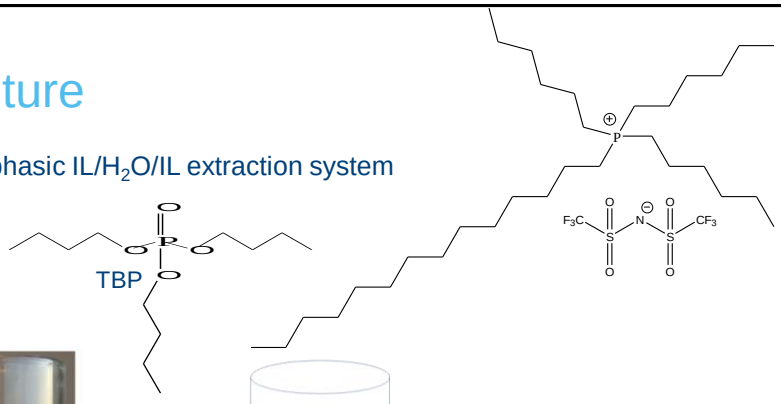
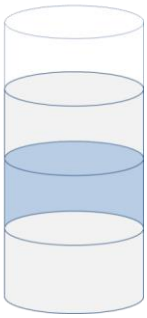
Vander Hoogerstraete, T., Blockx, J., De Coster, H., Binnemans, K., 2015, *Chemistry - a European Journal*, *21* (33), 11757-11766.

IL future

- Triphasic IL/H_2O/IL extraction system

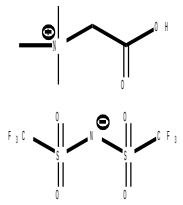




$[P_{66614}][Tf_2N]$
TBP or cyanex 923

H_2O
$MgCl_2$ or $CaCl_2$

$[Hbet][Tf_2N]$



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

IL future

- IL/IL extraction system

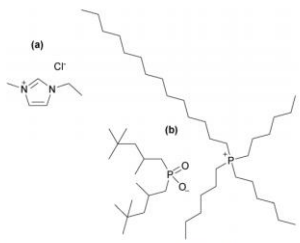

Fig. 1 Chemical structures of (a) 1-ethyl-3-methylimidazolium chloride, $[C_2mim]Cl$, and (b) trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate, $[P_{66614}][R_2POO]$.

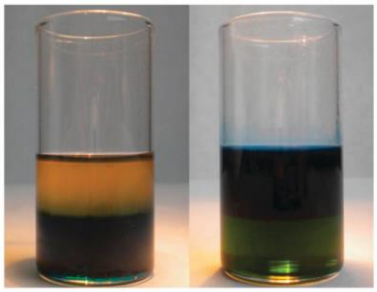

Fig. 2 Sample showing the ionic liquid $[P_{66614}][R_2POO]$ layered on top of the ionic liquid $[C_2mim]Cl$, before (left) and after (right) cobalt(II) extraction.

- **Solvometallurgy** (Organic solvent/organic solvent)

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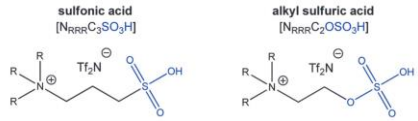
A. Rout, S. Wellens, and K. Binnemans, *RSC Adv.*, 2014, 4, 5753-5758.
S. Wellens, B. Thijs, C. Möller, and K. Binnemans, *Phys. Chem. Chem. Phys.*, 2013, 15, 9663-9669.

IL future

- New type of super acidic ILs (pKa -2 to -4)



- High temperature leaching (e.g. 200 °C)

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Dupont, D., Raiguel, S., Binnemans, K., 2015, *Chemical Communications*, *51* (43), 9006-9009.
Dupont, D., Renders, E., Binnemans, K., 2016, *Chemical Communications*, *52* (25), 4640-4643.

Funding

- LIC: http://chem.kuleuven.be/onderzoek/en/research/mds/lic/
- RARE³: www.kuleuven.rare3.eu

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Questions?

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