ionic liquids for the extraction of metallic ions: a review

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Aim(s) of this review

- Limited to the use of *ILs as liquids* in view of metal extraction
- Results sorted and put in perspective, but not historical one
    - Applied interests
        - Ore mines, production of wastes, end of life of objects
        - Depolluting aqueous fluxes
        - Pre-concentration for element assays
        - REACH regulation
    - Fundamental questions
        - Understanding and describing extraction mechanisms
        - Predicting the behaviour of new systems

Do ILs bring something new ?

So many ideas to use ILs in view of metallic ion extraction

- The basic ways, so many surprises !
  - The good ones…
  - …And the bad ones

- Unconventional uses
  - As solvents replacing both phases
  - As partners for Aqueous Biphasic Systems (ABS)
  - As partners for DES (provided they exist)

- Conclusion and comments

Notations

All uses but ABS

$$Me(x) \ / \ H_2O \ / \ H^+X^- \ // \ Cat^+Ani^- \ / \ E$$

meniscus

in ABS

$$Me(x) + H_2O + H^+X^- + Cat^+Ani^-$$

Chemicals are indicated as they have been used from the bottle

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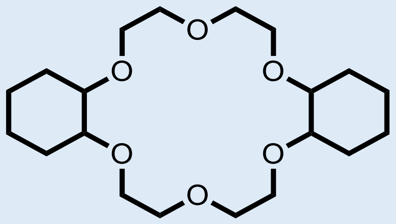
ILs can replace the organic phase

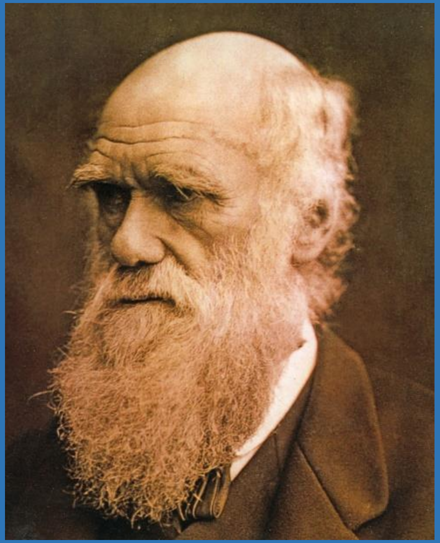
Sr(II) / H_2O pH = 4.1 // Cat^+Ani^- / DCH18C6

solvent	D without CE	D with CE
$C_4C_1C_1im^+PF_6^-$	0.67	4.2
$C_4C_1im^+PF_6^-$	0.89	24
$C_2C_1C_1im^+Tf_2N^-$	0.81	4500
$C_2C_1im^+Tf_2N^-$	0.64	11000
$C_3C_1C_1im^+Tf_2N^-$	0.47	1800
$C_3C_1im^+Tf_2N^-$	0.35	5400
$C_6H_5CH_3$	0	0.76
$CHCl_3$	0	0.77



DCH18C6

Artificial selection effect: only efficient ILs are published !

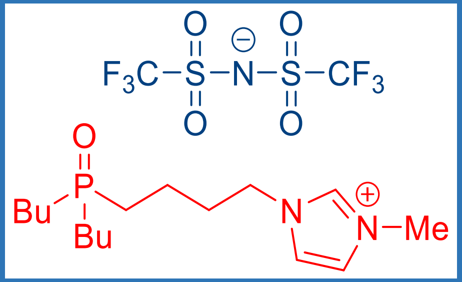


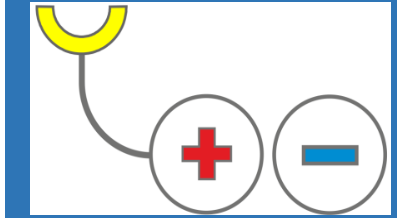
Dai et al., J. Chem. Soc. Dalton Trans, (1999)1201;

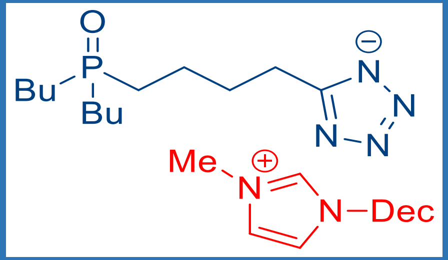
S. Dourdain talk; poster #55

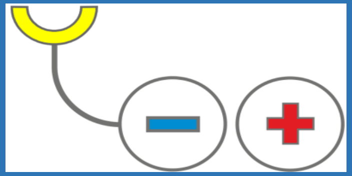
Changing the extractant for a Task Specific IL (TSIL)

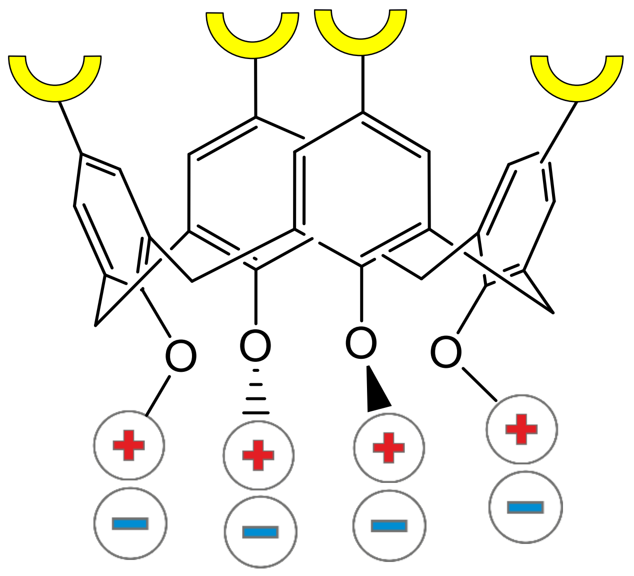
A complexing pattern is grafted onto the IL skeleton. The new compound is dissolved in a 'classical' IL or, more rarely, in a molecular solvent

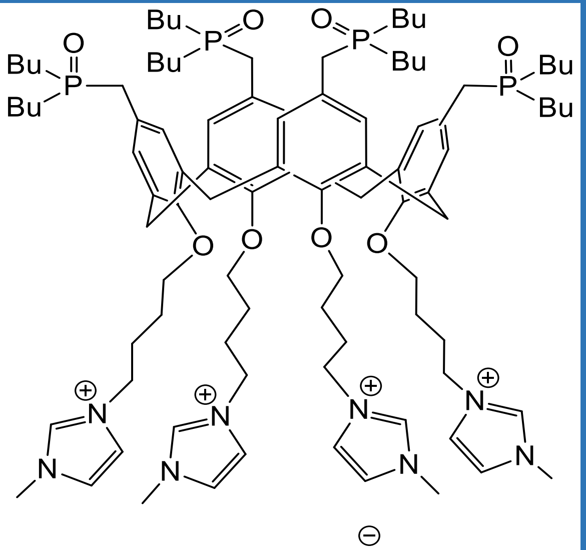


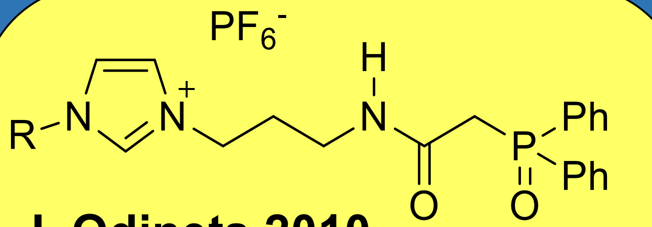




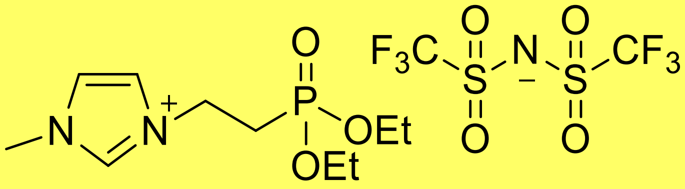








I. Odinets 2010

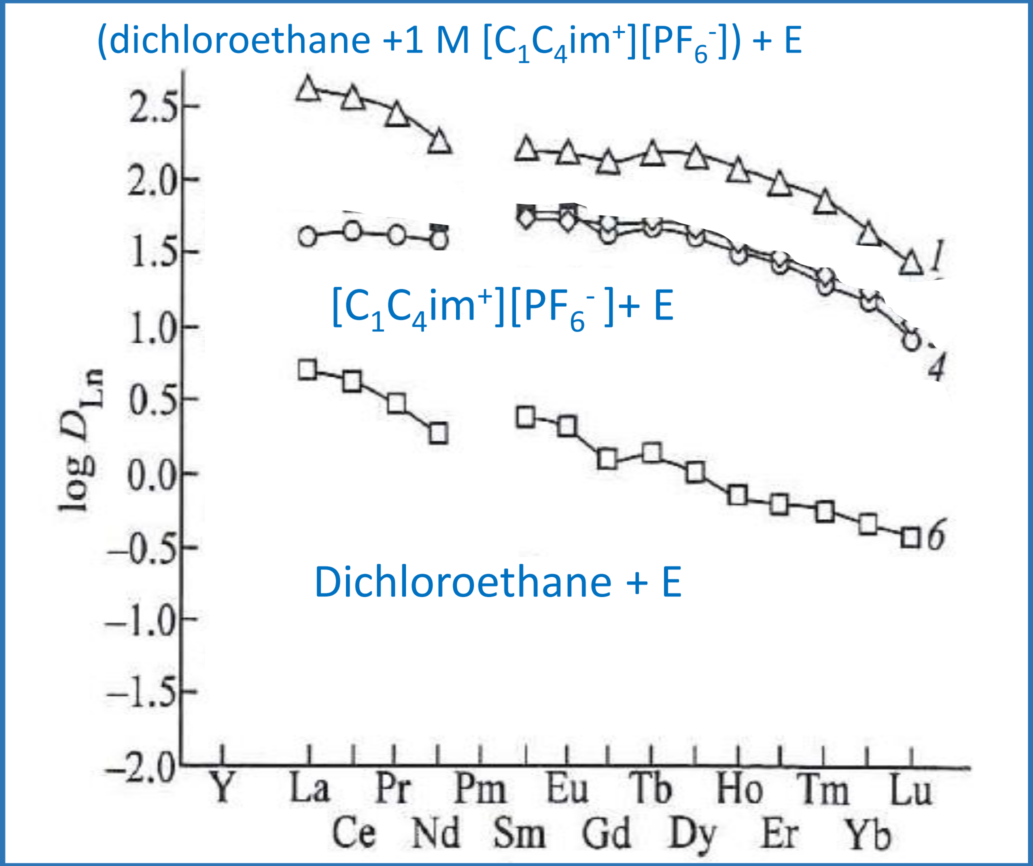


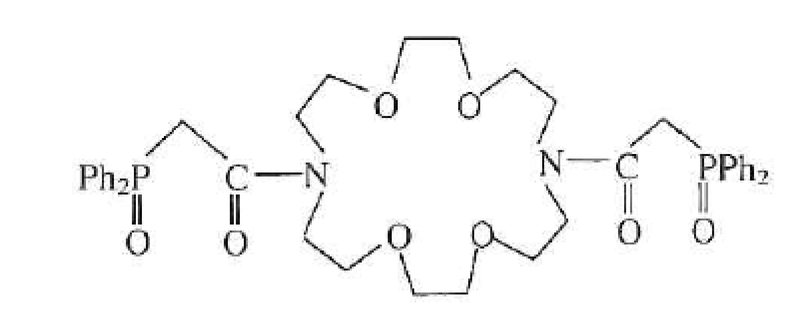
A.Rout 2012

D. Ternova, Ph-D thesis, 2014; S. Miroshnichenko et al., Phosphorus, Sulfur and Silicon and their related elements, 186(2011)903-905 ; Odinets et al., Dalton Trans, 39(2010)4170; Rout et al., Sep. Pur. Technol., 97(2012)164

ILs as additives to VOC + E

Ln(III) / H_2O / $H^+NO_3^-$ // ($E+C_1C_4im^+PF_6^-$) / molecular solvent





Adding an IL to the classical system with VOC increases extraction.
However, there is an optimum concentration for the IL

Little coverage

Turanov et al., Radiochem. 50(2008)266; Turanov et al., Solv. Ext. Ion Exch., 30(2012)244

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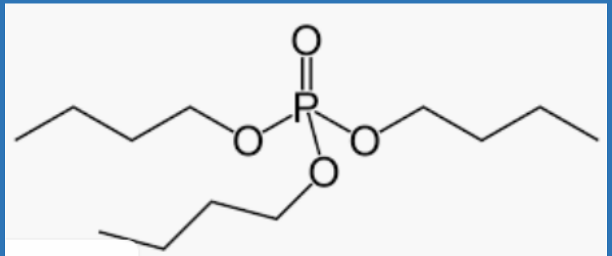
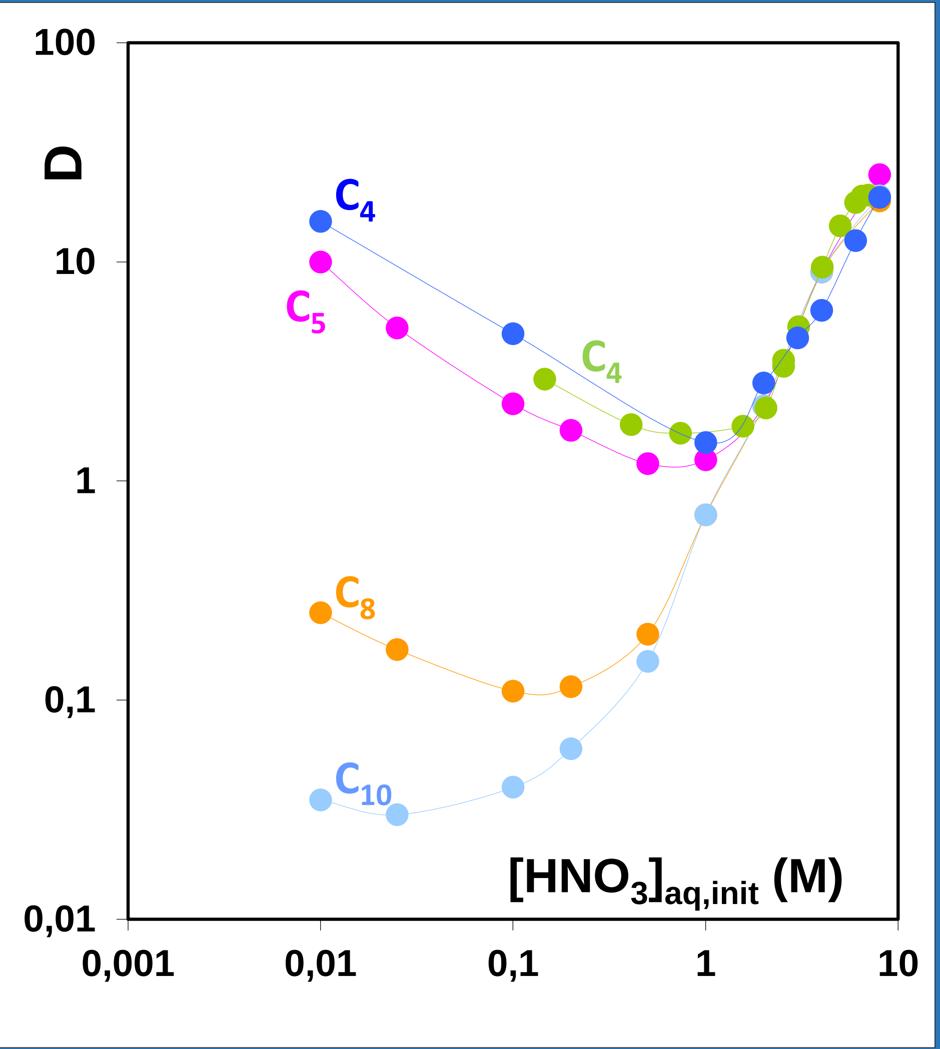
A rather complicated extraction mechanism



U(VI) / H_2O / $H^+NO_3^-$ // $C_nC_1im^+Tf_2N^-$ / TBP



Two mechanisms are in competition:

- Low [H^+]: cation exchange: UO_2^{2+} vs $C_1C_nim^+$
- High [H^+]: anion and/or neutral compound extraction

Ionic exchange occurs,
aqueous phase is polluted,
waste of costly IL

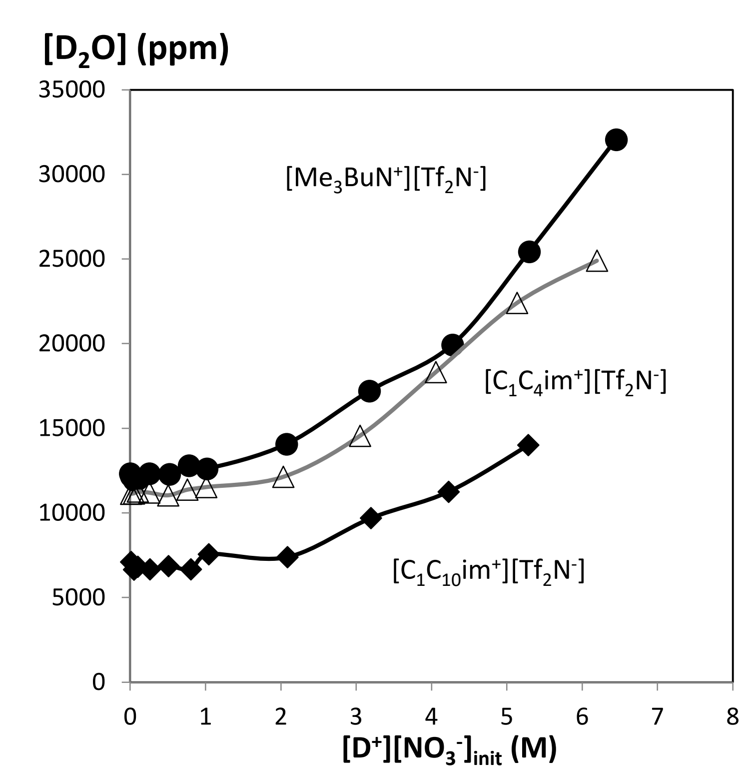
Data: Giridhar et al., JALCOM, 448(2008)104 ; Dietz et al., Talanta, 75(2008)598; Billard et al., ChemPhysChem, 16(2015)2653;

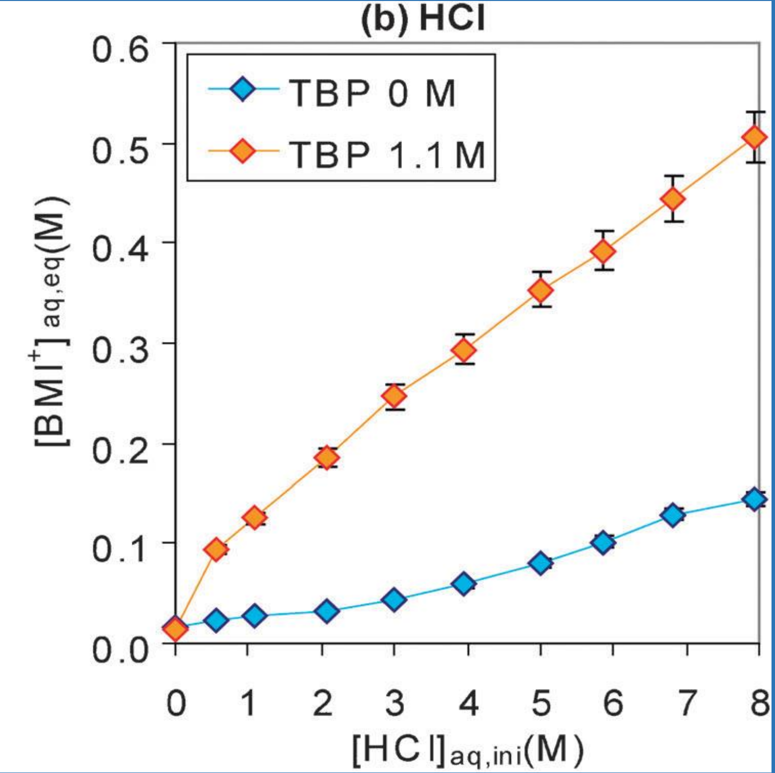
Mechanism : Papaiconomou et al., Chem. Sel. 1(2016)3892

Also cf: A. Masmoudi talk

Other bad news

- Water and acid are soluble in the IL phase
- IL cations and anions are soluble in the (acidic) aqueous phase
- The extracting agent strongly influences these solubilities
- One has to consider *individual* solubilities of all components





Losses of IL ions in the absence of metallic ions are much more important than losses due to ion exchange mechanisms !

Mazan et al., RSC Advances, 4(2014)13371; Gaillard et al., PCCP, 14(2012)5187-5199; Fagnant et al., Inorg. Chem. 52(2013)549; Rickert et al., Talanta, 72(2007)315. Atanassova et al., Chem. Phys. Chem. 16(2015)1703
A. Masmoudi talk

TSILs do not solve these problems

- Using TSILs in classical ILs does not solve the problem of undesired solubilities of IL-diluent components

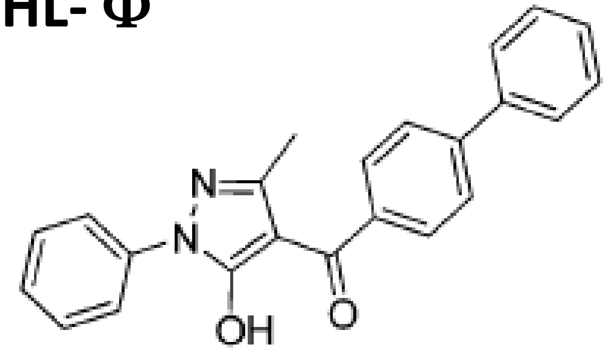
- In addition, TSILs are often *very* viscous, even more expensive, with poor synthetic yields

TSILs are fundamental objects,
for the challenge and their beauty,
but
they hardly have any industrial future

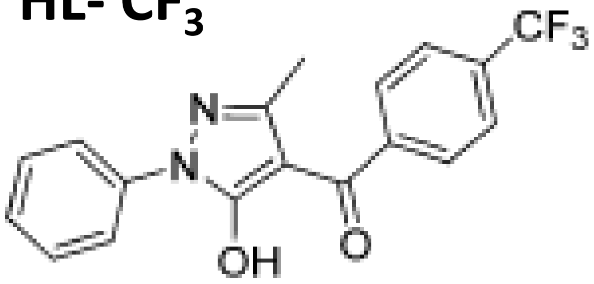
Are there fancy ligands in ILs ?

$Ln(III) / H_2O // C_1C_4im^+Tf_2N^- / E$

HL- Φ



HL- CF_3

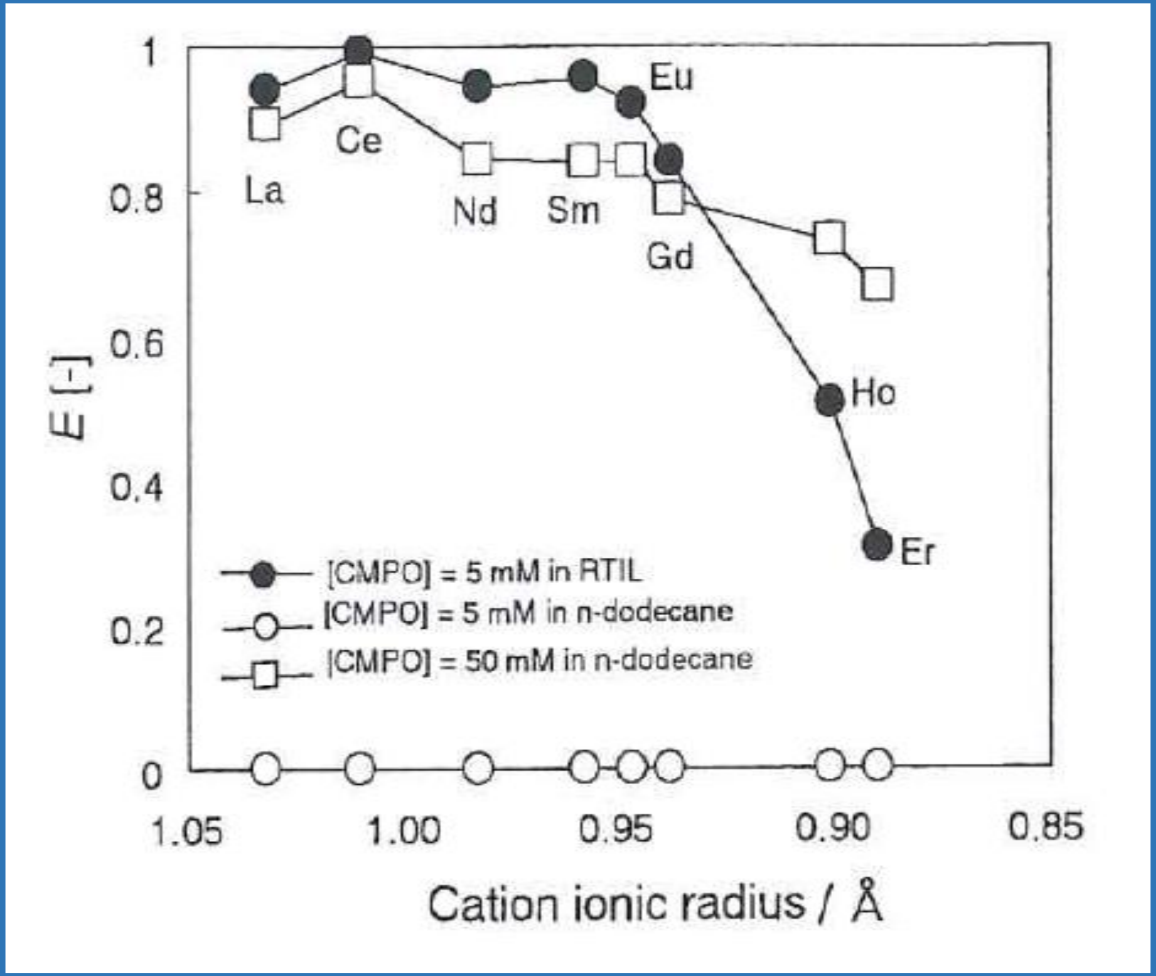


ILs induce a levelling of extracting properties.
All extracting agents become 'very good' ones in ILs.

System	$CHCl_3$ log K_L	$[C_1C_4im^+][Tf_2N^-]$ log K_L
HL- Φ	−6.31	−2.2
HL- CF_3	−3.24	−2.33

Atanassova et al., NJC, 39(2015)7932;
Atanassova, RSC Adv., 4(2014)38820

By the way, what is the gain using an extractant in IL ?



Nakashima et al., Anal. Sci. 19(2003)1097

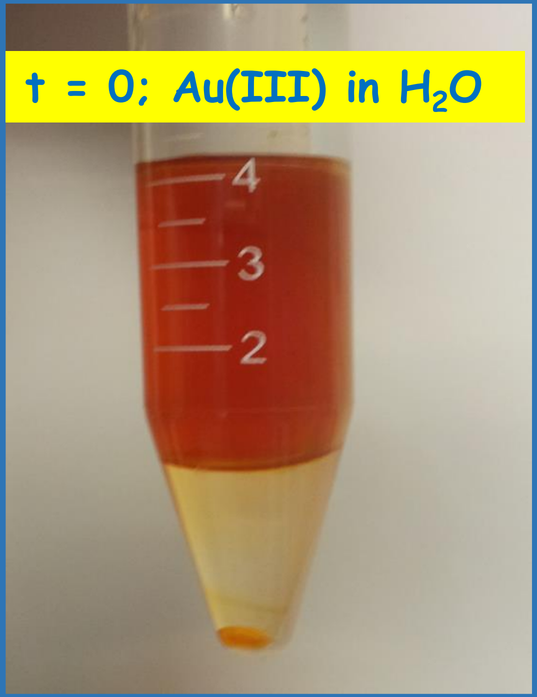
CMPO in $C_1C_4im^+PF_6^-$ is ca. 10 times more efficient than in dodecane

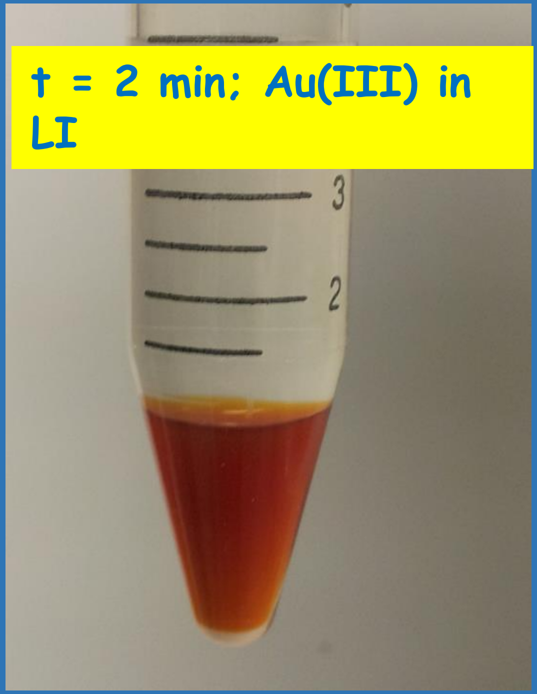
Costly extracting agents can be saved by using costly solvents

ILs do not necessarily need extracting agents !

Pure ILs can extract metals, without being structurally complex (cf Dai et al.)

$$AuCl_4^- / H^+Cl^- / H_2O // C_8C_1im^+Tf_2N^-$$





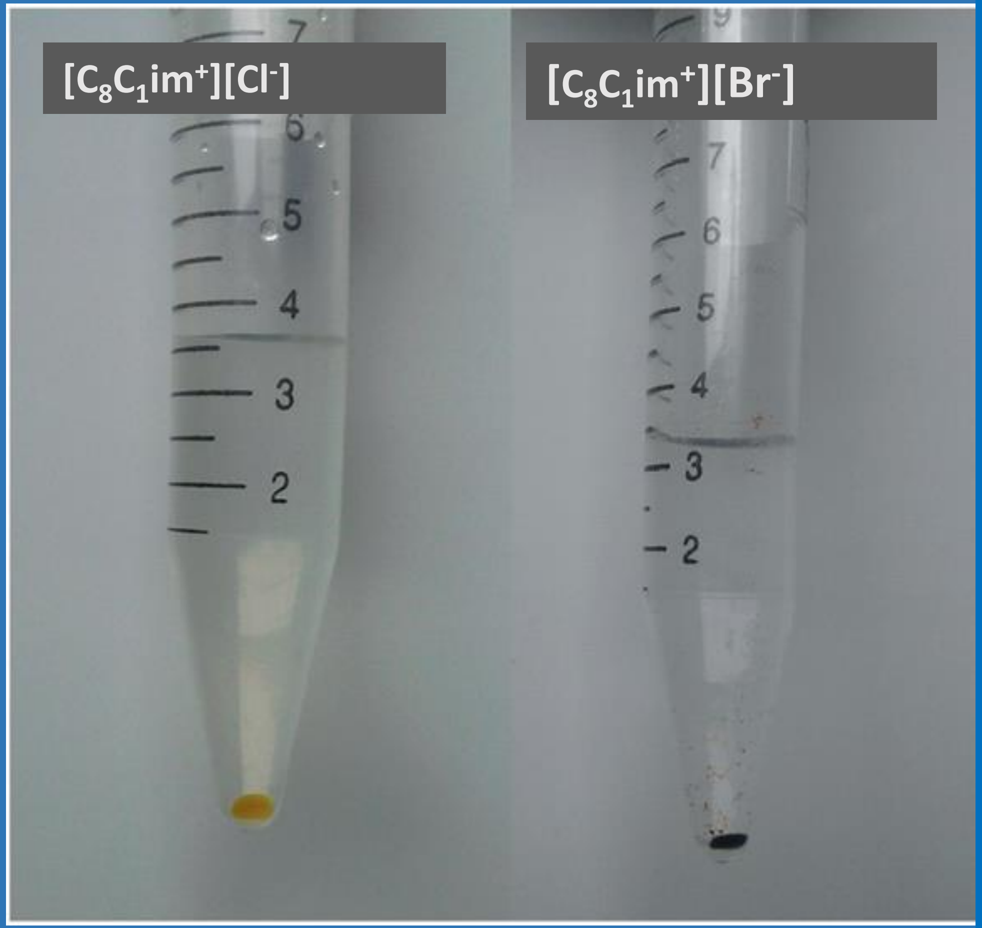
Other examples with Pt(IV), Ir(IV), Pd(II), Rh(III).

N. Papaiconomou et al., *Green Chem.* 14(2012)2050; Papaiconomou et al., RSC Advances, 4(2014)48260-48266; Talk by L. Svecova.

The most expensive IL in the world ?

$Au(III)$ / H^+Cl^- / H_2O / Cat^+Ani^-

$[Cat^+][AuX_4^-]$ precipitates under a solid or liquid form



Papaiconomou et al., Green Chem. 14(2012)2050

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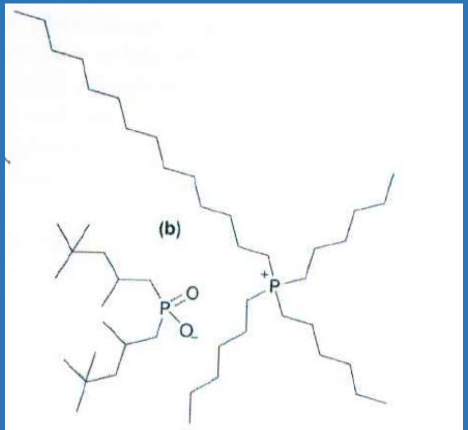
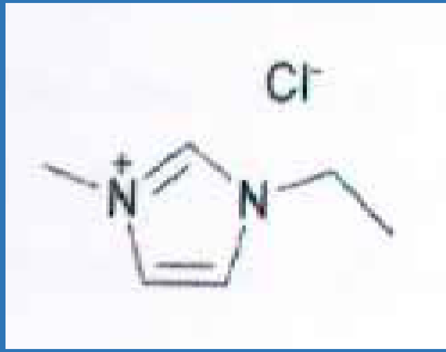
Two mutually immiscible ILs

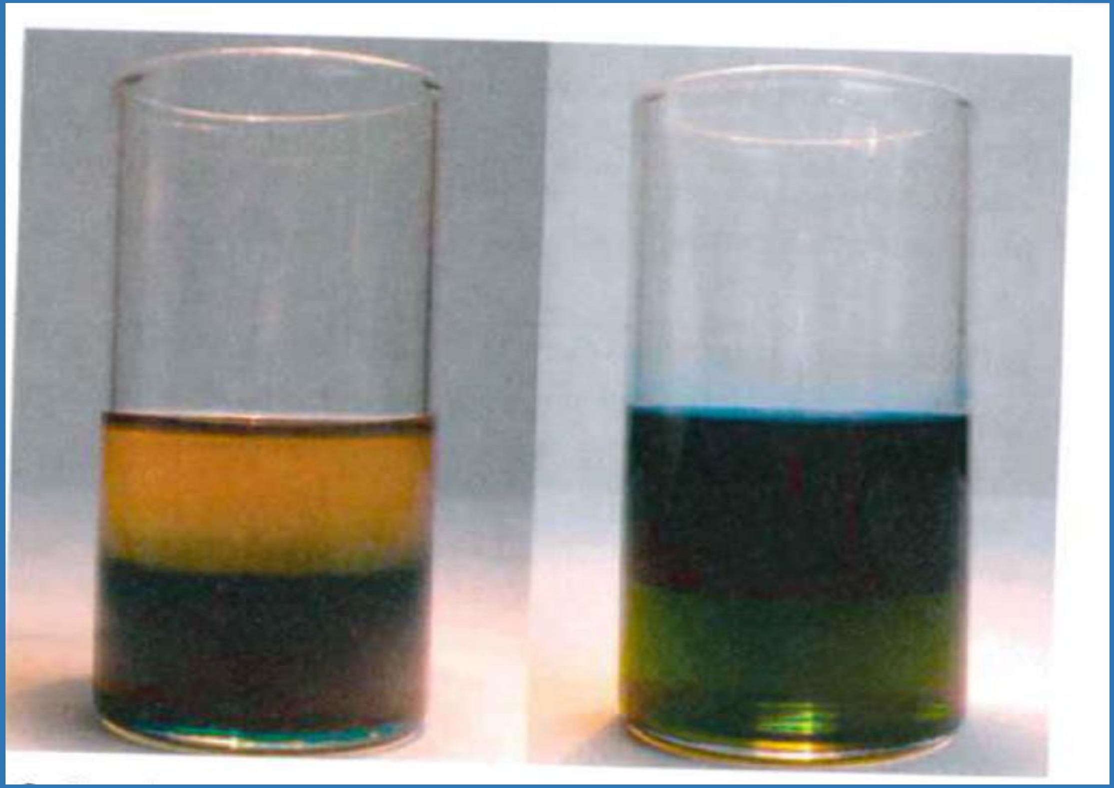
Co(II),Ni(II) / $C_1C_2im^+Cl^-$ // $P_{66614}^+R_2POO^-$ T = 95°C

Upper phase





Bottom phase



Before extraction:
Co and Ni are down

After extraction:
Co is up, Ni is down
D_{Co} = 44; D_{Ni} = 0,06

Solvometallurgy.

Need for waste leaching without water (and acid).
Under development

Wellens et al., PCCP, 15(2013)9663; Binnemans J. Sus Metall. 3(2017)570

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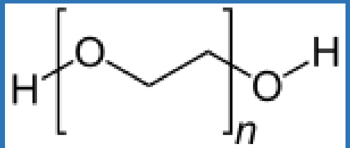
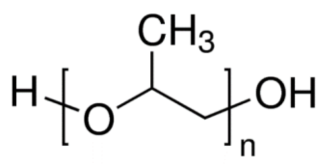
A (r)evolution in two steps

Before 2003, ABS were either one of two kinds of ternary mixtures :

- H_2O + polymer + inorganic salt
- H_2O + polymer1 + polymer2



PEG



PPG

$NaCl$, Na_2SO_4, Na_3PO_4, $LiCl$, $Al_2(SO_4)_3$, Na_2CO_3, $MgCl_2$…

In 2003: polymers are replaced by ILs

imidazolium, piperidinium, pyrrolidinium, Cl^-, $CF_3SO_3^-$, BF_4^-, etc.

In 2016: inorganic salts are replaced by mineral acids

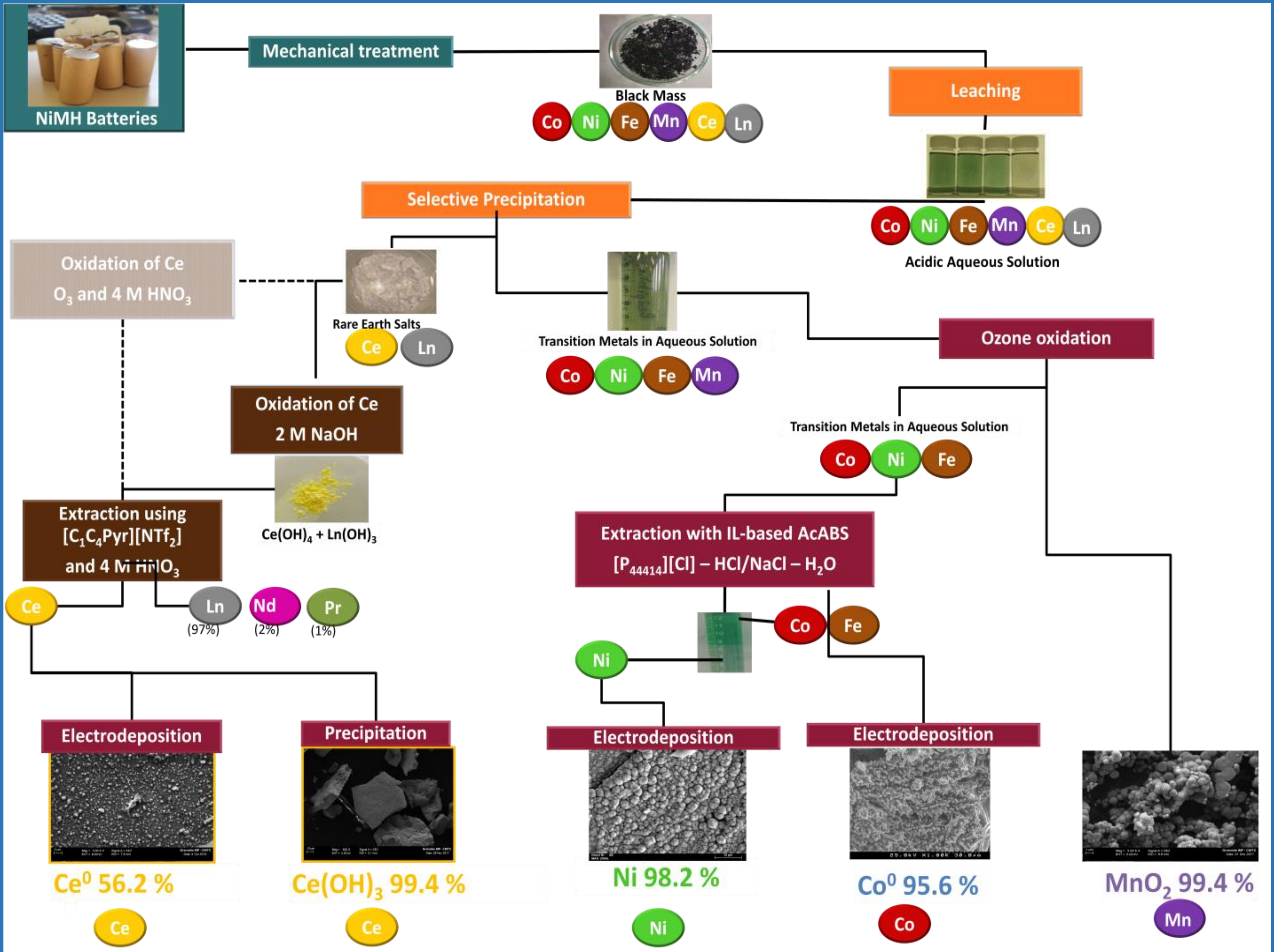
HCl, HNO_3, H_2SO_4, H_2SO_3

J. Am. Chem. Soc., 125(2003)6632; Chem Soc. Rev, 41(2012)4966; Trends Anal. Chem., 29(2010)1336; Angew. Chem., Int Ed. 57(2018)1563; patent; Eris Sinoimeri talk on Tuesday

What does it change ?

- From biological compound-compatible to metal-compatible
- 'One pot' leaching + extraction from powders is feasible
- Direct application to industrial problems by finding the 'good' IL
- **Just another mean of separation, not the solution to all problems**

Application :
Separating metals from NiMH batteries


NiMH Batteries
Mechanical treatment
Black Mass
Co Ni Fe Mn Ce Ln
Leaching
Co Ni Fe Mn Ce Ln
Acidic Aqueous Solution
Selective Precipitation
Oxidation of Ce
O_3 and 4 M HNO_3
Rare Earth Salts
Ce Ln
Transition Metals in Aqueous Solution
Co Ni Fe Mn
Ozone oxidation
Oxidation of Ce
2 M NaOH
$Ce(OH)_4$ + $Ln(OH)_3$
Transition Metals in Aqueous Solution
Co Ni Fe
Extraction using
$[C_1C_4Pyr][NTf_2]$
and 4 M HNO_3
Extraction with IL-based AcABS
$[P_{44414}][Cl]$ – HCl/NaCl – H_2O
Ce
Ln (97%)
Nd (2%)
Pr (1%)
Co Fe
Ni
Electrodeposition
Precipitation
Electrodeposition
Electrodeposition
Ce^0 56.2 %
Ce
$Ce(OH)_3$ 99.4 %
Ce
Ni 98.2 %
Ni
Co^0 95.6 %
Co
MnO_2 99.4 %
Mn

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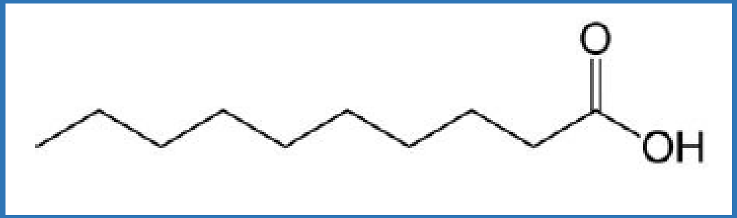
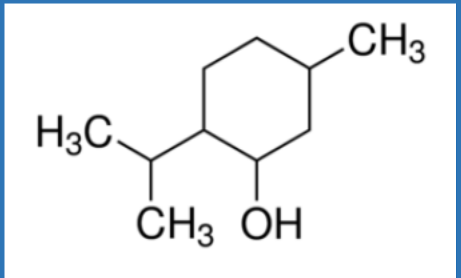
Deeply Exotic Solvents;

Deeply Exotic Solvents; Disappointing Evolved Solvents; Demanding Explanation Solvents, Dummy Experimental Samples

- Typical DES mixture: decanoïc acid + DL-Menthol





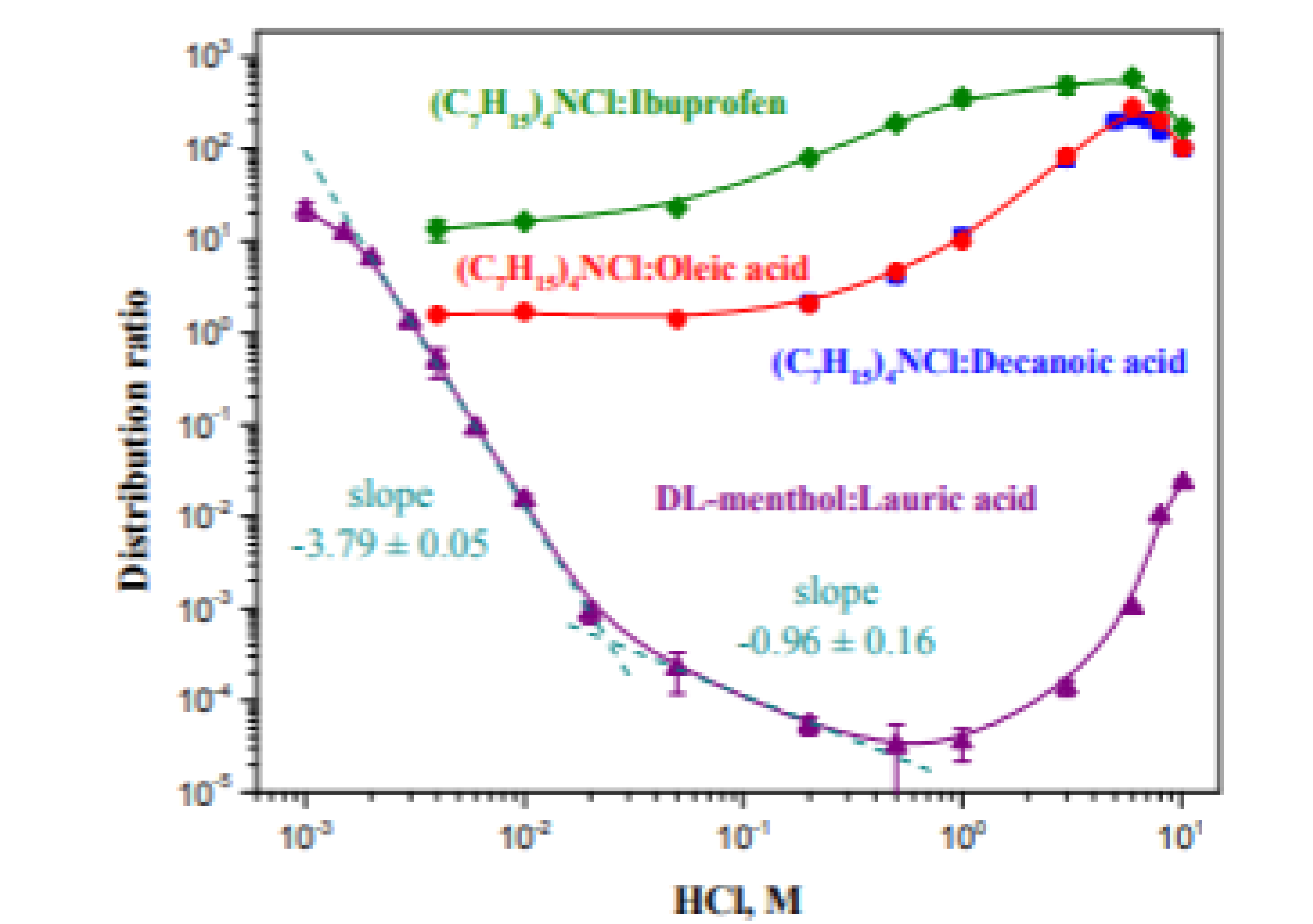
- ILs can be used for 'DES', as H bond acceptors
- Some of these mixtures are hydrophobic ones

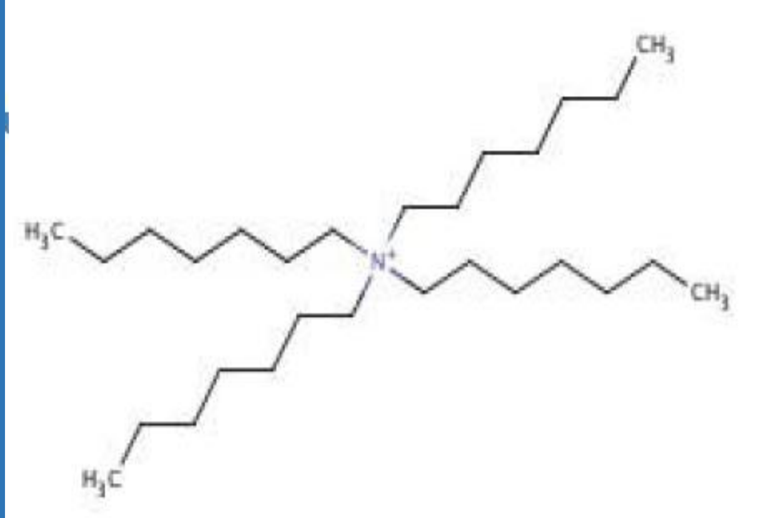
Any chloride based IL might be suitable

J. Coutinho 's talk on Monday;

A new playground

In(III) + H_2O + X-oïc acid + $(C_7H_{15})_4N^+Cl^-$





A very limited number of publications so far.

Boltoeva et al., Green Chem 18(2016)4616

Conclusion and comments

- **ILs are so versatile !**
  - Solvents, extracting agents, both of these roles, ABS and DES partners
  - No need for: water, or extracting agent, or organic solvent
- **Are these categories meaningful ???**
  - In particular, all ILs are TSILs
- **ILs are neither 'tunable', nor 'designer solvents'**
  - Because we are working on a trial/error way, we hardly understand (so far)
- **Many ILs are not 'green'**
- **How much do processes cost ?**
  - Need for Life Cycle Analysis

Billard, Current opinion in green and sustainable chemistry, 18(2019)37

Mother nature is full of biosourced *highly toxic* compounds

Thank you for your attention !

Lenka
Svecova

Eris
Sinoimeri

Nicolas
Papaiconomou

Vijetha
Mogilireddy

Matthieu
Gras

Merci à …

Isabelle Billard

Nadine Commenges-Bernole

Eric Chainet

Jérôme Cognard

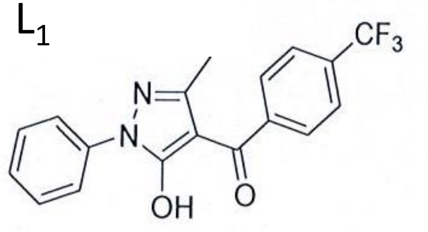
Victor Maia Fernandes

Delphine Yetim

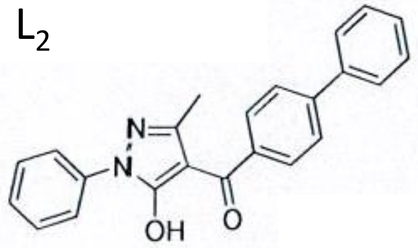
Merci de votre attention

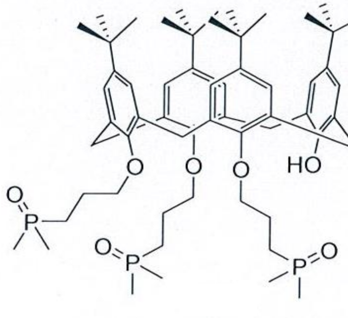
Synergie pour les La(III)

L1

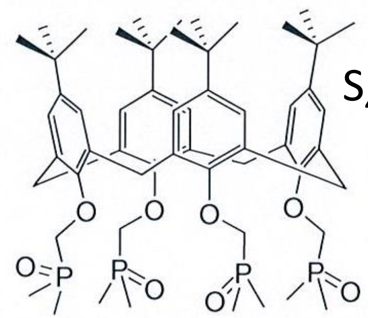


L2





S3



S4

	$logK_L$	$logK_{L+S}$	SC	$logK_L$	$logK_S$	$logK_{L+S}$	SC
L_1+S_4	-6,31	-1,24	3,54	-2,2	3,38	3,38	2,45
L_2+S_3	-3,24	1,22	3,13	-2,33	3,30	3,30	2,52

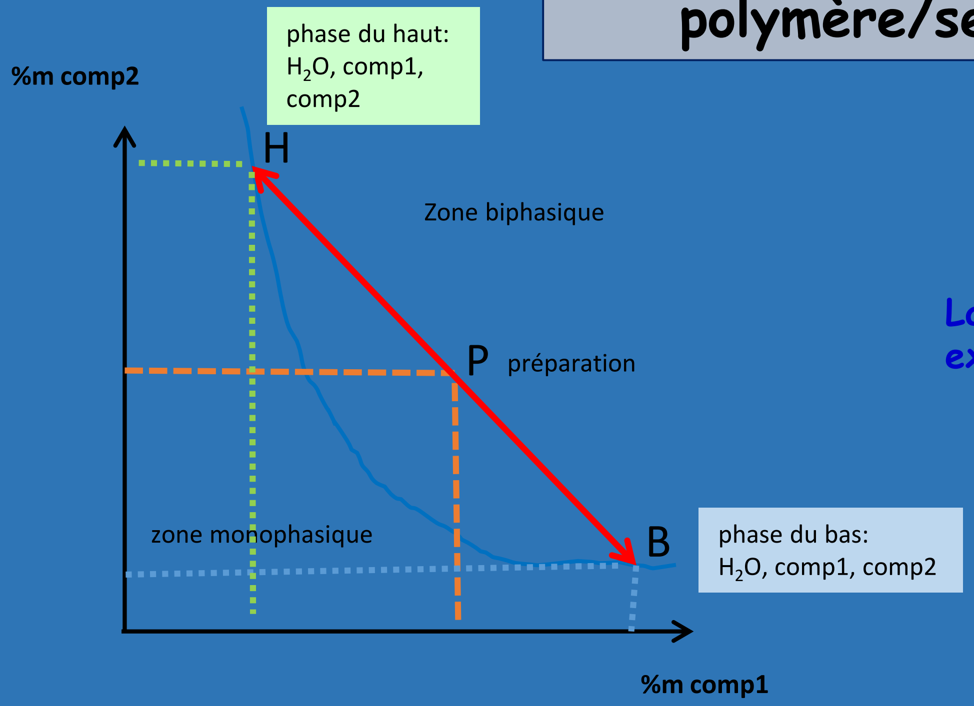
in $CHCl_3$ — in $C_1C_4imTf_2N$

Les LI augmentent tellement l'efficacité d'extraction qu'on observe un phénomène de saturation, dommageable en terme de synergie.

Anatassova et al., NJC, 39(2015)7932

Diagrammes de phase simples (simplifiés?)

polymère/sel inorganique/H_2O



La courbe binodale est obtenue expérimentalement par turbidimétrie.

- Points P, H and B are aligned. The line H-P-B is t la conodale de P.
- La démonstration mathématique s'appuie sur le fait chimique que les deux phases sont électriquement neutres.
- Tous les points d'une conodale donnée correspondent aux mêmes compositions massiques des phases haute et basse, seuls les volumes respectifs des phases haute et basse varient.
- Les conodales ne sont pas exactement parallèles entre elles.

Second exemple: nanoparticules dans les piles à combustible

$+P_{44414}Cl$

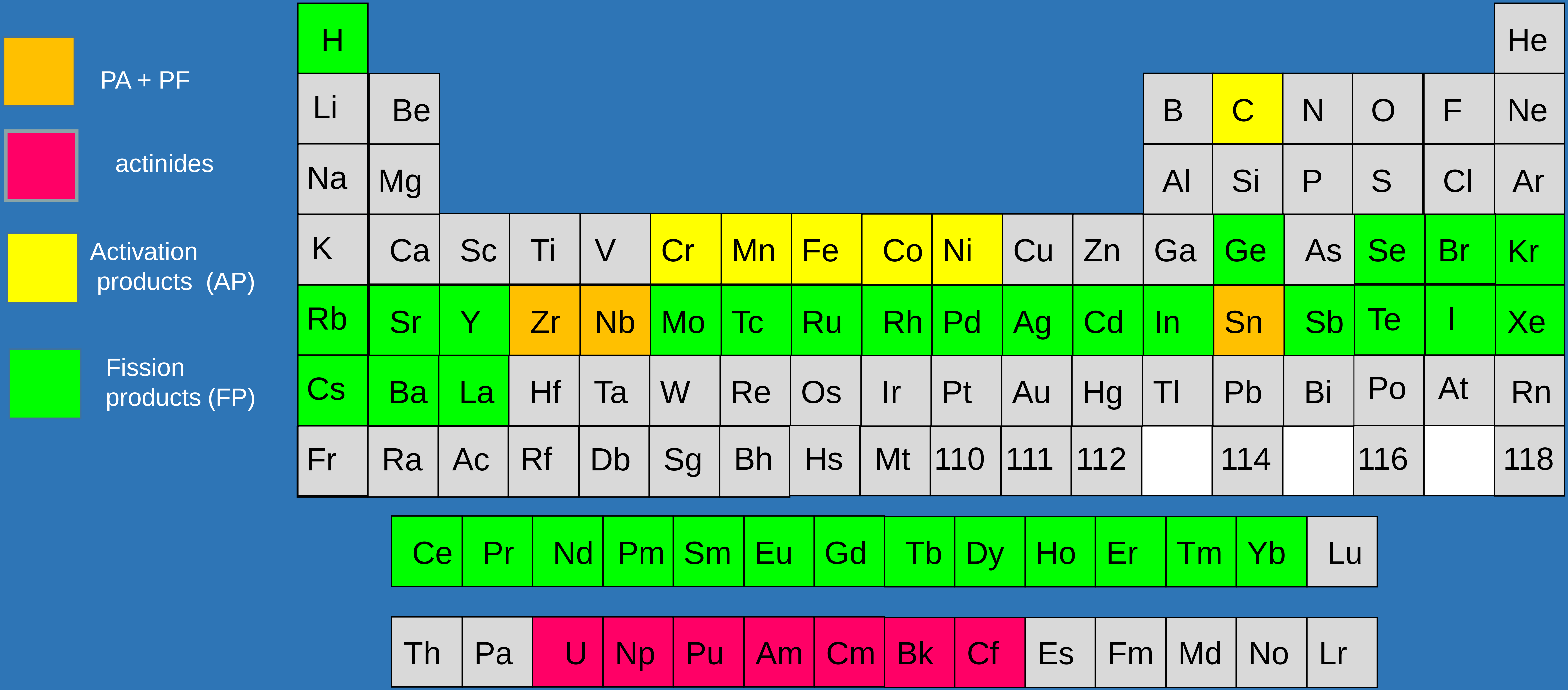
+imidazoliumCl

Lixiviation dans HCl/H_2O_2.
$[Pt] = 1,2x10^{-2}$ M
$[Co] = 4,8x10^{-3}$ M

Co et Pt extraits ensemble dans la phase du haut.

Pt précipite, Co reste en solution

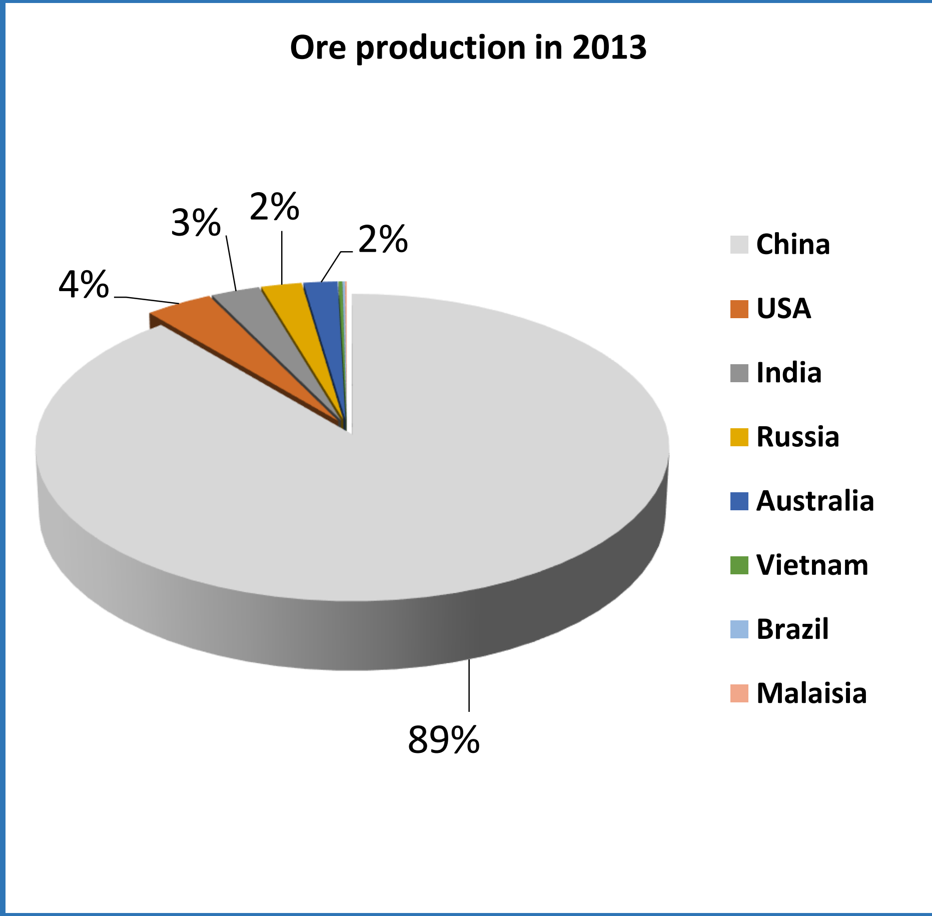
Industrial context #1: nuclear wastes

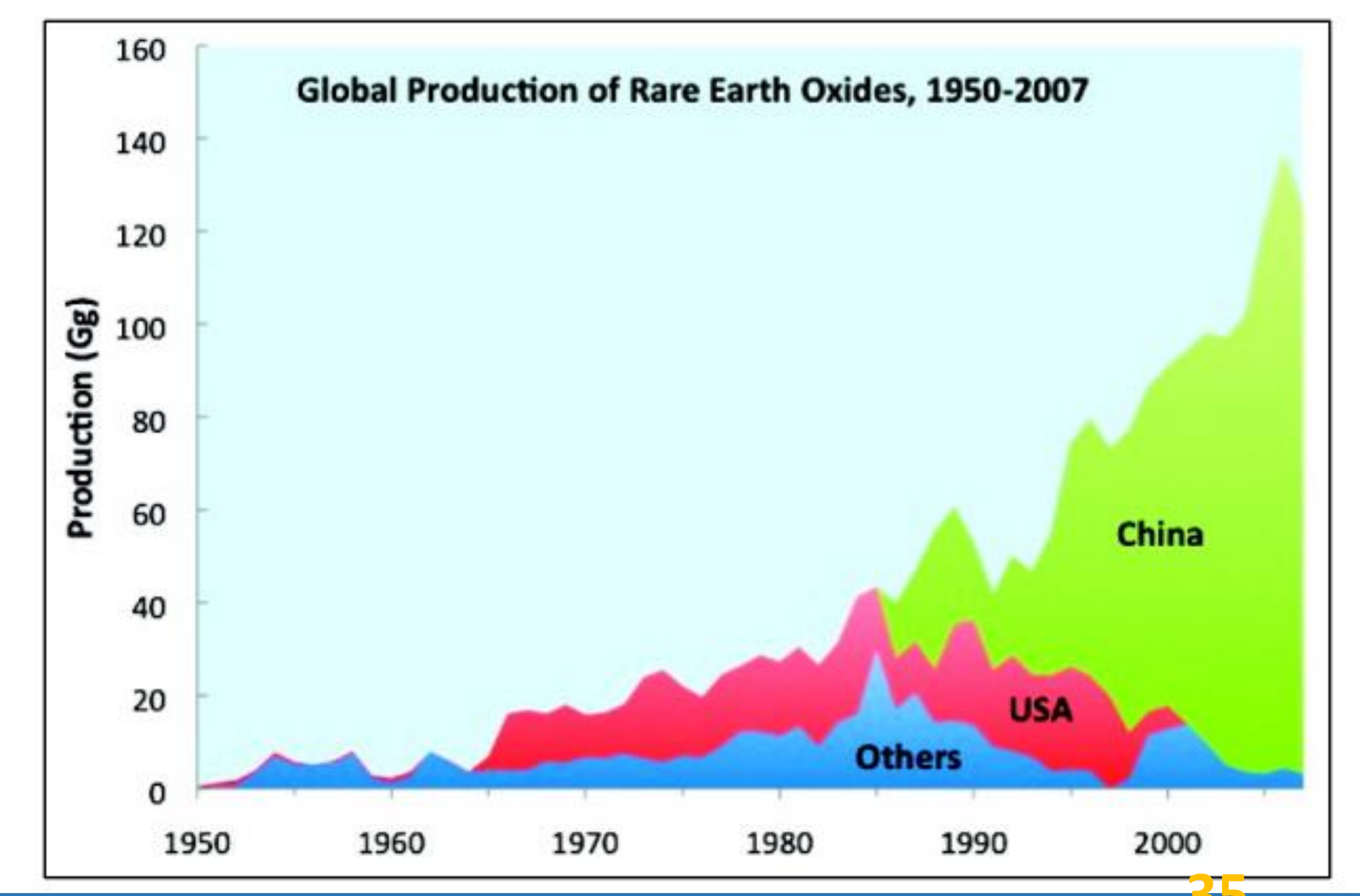


PWR 33 GWj/tU, 3,25% at t = 0.1 s

Industrial context #2: Lanthanides in a non-nuclear surrounding

Mining Ln is highly polluting, western countries have off-shored ore production. China now produces not only Ln oxides but also the technological objects without which we cannot 'survive'

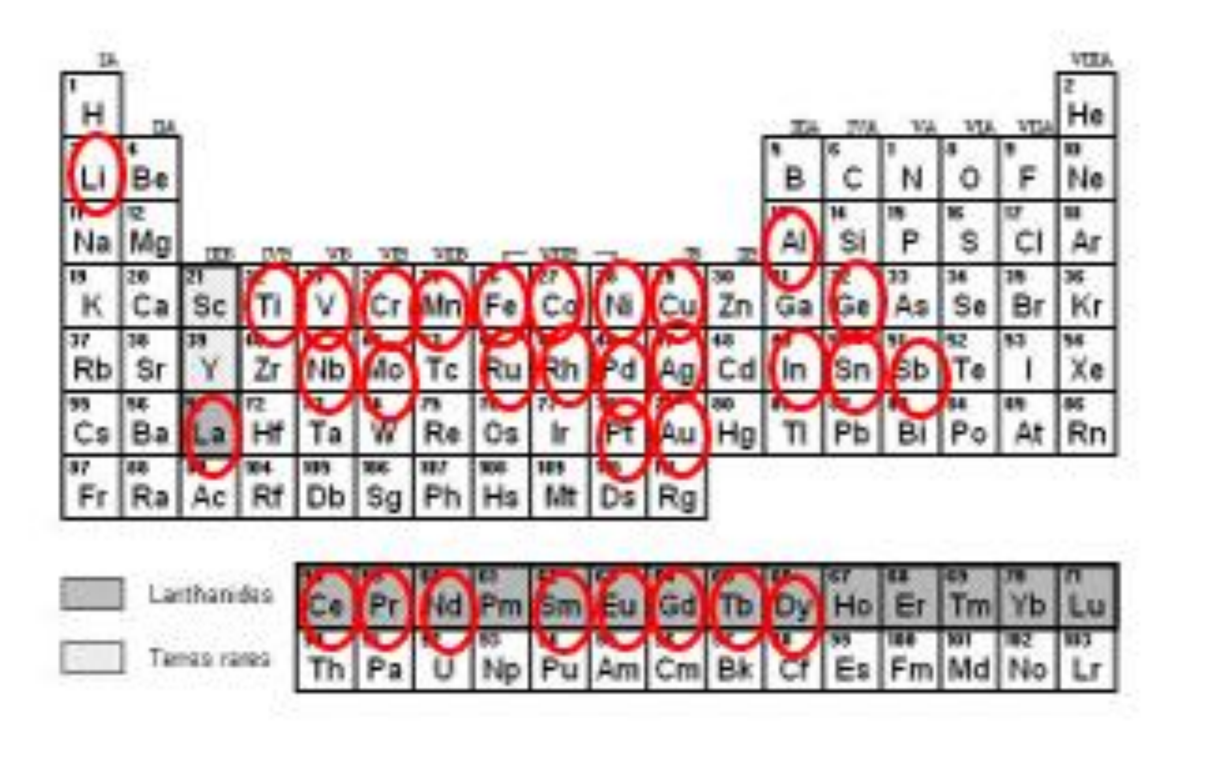




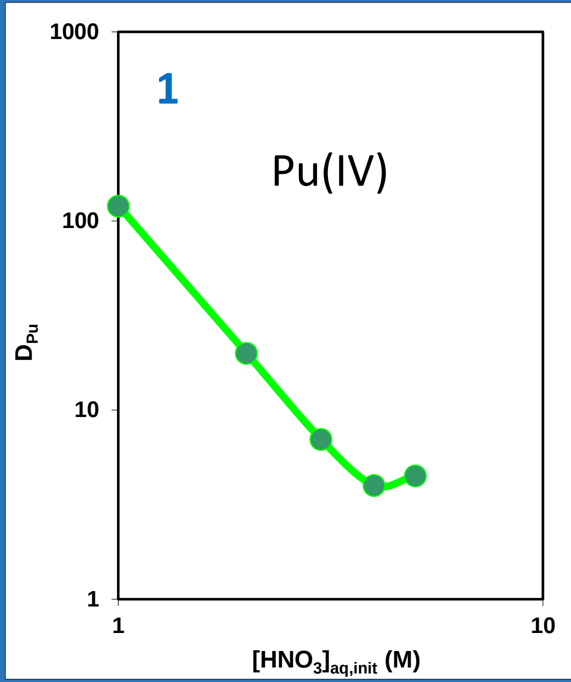
Industrial context #3: PGM and *d*-metals

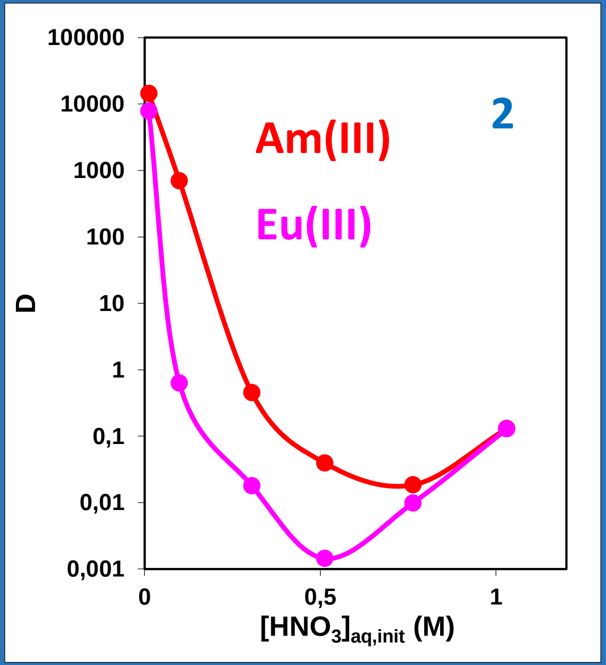
- **PGM for :**
  - Automotive catalytic converters
  - Membrane Assembly Electrodes of PEMFC

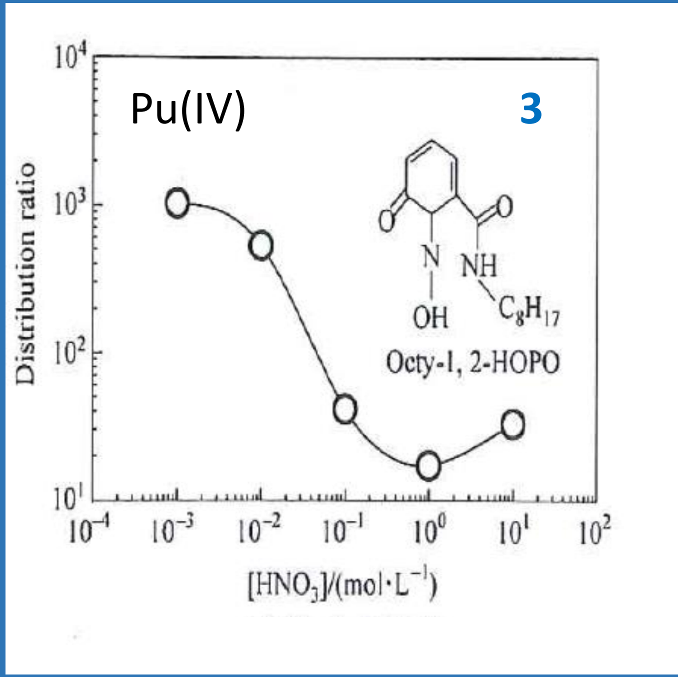
- ***d*-metals for:**
  - Batteries
  - Magnets
  - A lot more



A common, undesired, phenomenon







Many boomerangs behaviours in the litterature:

Sr(II), Eu(III), Am(III) …

1) Pu(IV)/HNO_3//phosphonate/$C_1C_4imTf_2N$ Rout et al., Radiochimica Acta, 98(2010)459

2) Billard et al., unpublished

3) Pu(IV)/HNO_3//HOPO/$C_8C_1imTf_2N$ Cocalia et al., Tsinghua Sci. Technol. 11(2006)188