Recycling metals from urban mines: what ILs can do and what they cannot do.

Isabelle Billard,

CNRS, Grenoble, France

Isabelle.billard@grenoble-inp.fr

Outline

- Science in Grenoble and at Lepmi/recycling group
- Urban mines and metal wastes: new challenges
- ILs : what did they acheive ? A short review
- ILs: what can’t they perform ?
- Conclusion and perspective

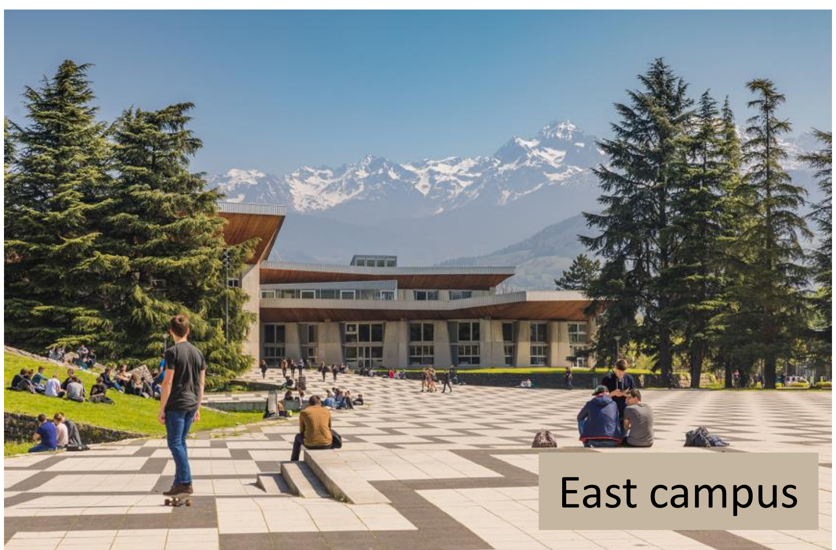
Outline

- **Science in Grenoble and at Lepmi/recycling group**
- Urban mines and metal wastes: new challenges
- ILs : what did they acheive ? A short review
- ILs: what can't they perform ?
- Conclusion and perspective

Grenoble, France : science and technology at the mountains


European photon & neutron science N-W campus


Institute for geosciences and environment


East campus


STMicro electronics

Research at Lepmi, recycling group

- Fundamental aspects:
  - Second lifes and aging of batteries
  - New liquid/liquid extraction systems (ILs, ABS, DES …)

(extraction mechanisms, mass transfer at the interface…)

- Current applied topics:
  - Recovery of metals (Co, Li etc.) from drone batteries
  - Recovery of Ag and carboard from printed carboard circuits
  - Valorisation of fine incineration ashes
  - H_2 bioproduction






Outline

- Science in Grenoble and at Lepmi/recycling group
- **Urban mines and metal wastes: new challenges**
- ILs : what did they acheive ? A short review
- ILs: what can’t they perform ?
- Conclusion and perspective

Every day life with (stupid?) objects



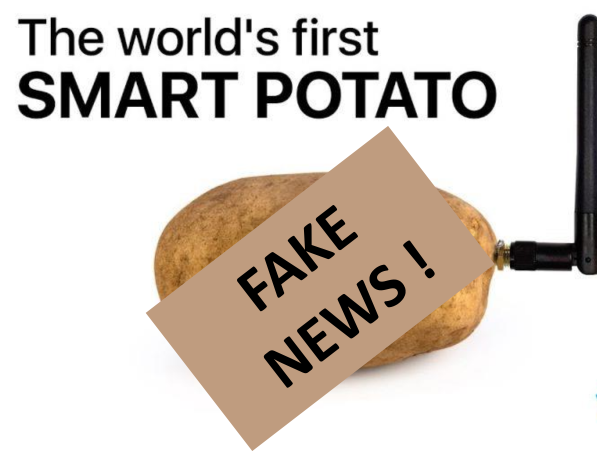




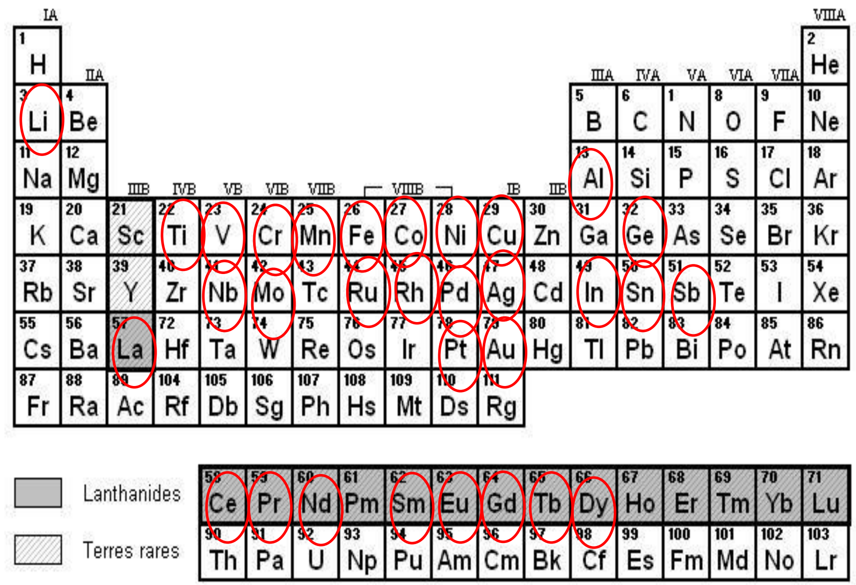


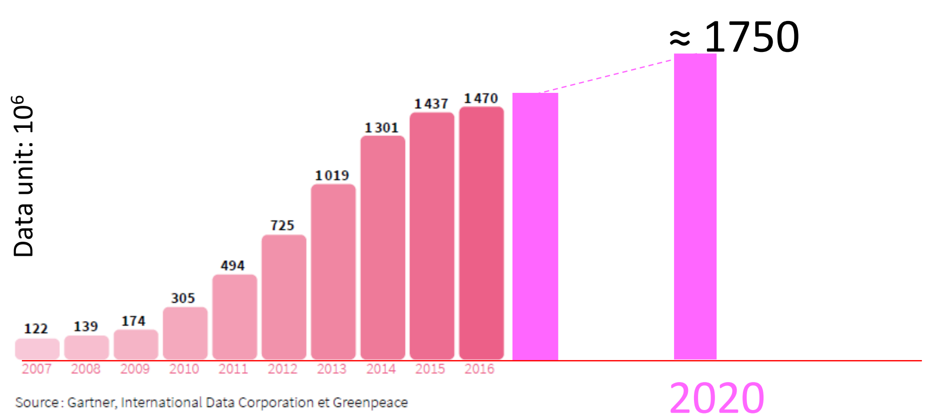


Yes, *in my opinion*, some are very stupid !



Consequence: Metal consumption





≈ 13.4 BILLIONS smartphones sold worlwide up to 2020.

≈ *Two* per each of the 7.8 billions humans of 2020 ?

What is the fate of these discarded objects ?

Discarded objects become WEEE: Waste Electronic and Electrical Equipment

- In France
  - 835 M EEE items sold in France in 2017, corresponding to 1.88 Mt of EEE
  - 0.69 Mt of household waste, + 0.06 Mt of professional WEE collected in 2017
  - Concerned recycling is difficult, most often unprofitable, and dangerous
- World wide
  - In 2009, 50 Mt of computer wastes discarded (EU: 6 Mt; USA: 21 Mt)
  - Uncontrolled landfill
  - Off shoring of low-end recycling
  - According to WHO, over 7 M humans died in 2012 owing to air pollution
- European/International regulations
  - Basel convention (1997)
  - Restriction of Hazardous Substances #1 and #2 (2003/2006; 2011/2013)

ADEME
Agence de l'Environnement et de la Maîtrise de l'Energie

OIPC ICPO INTERPOL

World Health Organization

Specific challenges brought by these new objects

Many reasons to make recycling difficult and unprofitable

Many components (ceramics, polymers, cardboard, cotton, metals, oxides…)
Metal mixtures unknown in traditional ores
Composition is varying at a very high rate due to innovation
Flows of discarded objects are not constant in time and space

Current state of metal recycling

We know how to do it !
And we do recycle (many) things !
Low ratio of recycling (at best :30% for PGM)
Polluting ways are implemented
Low rate of recycled materials in new objects

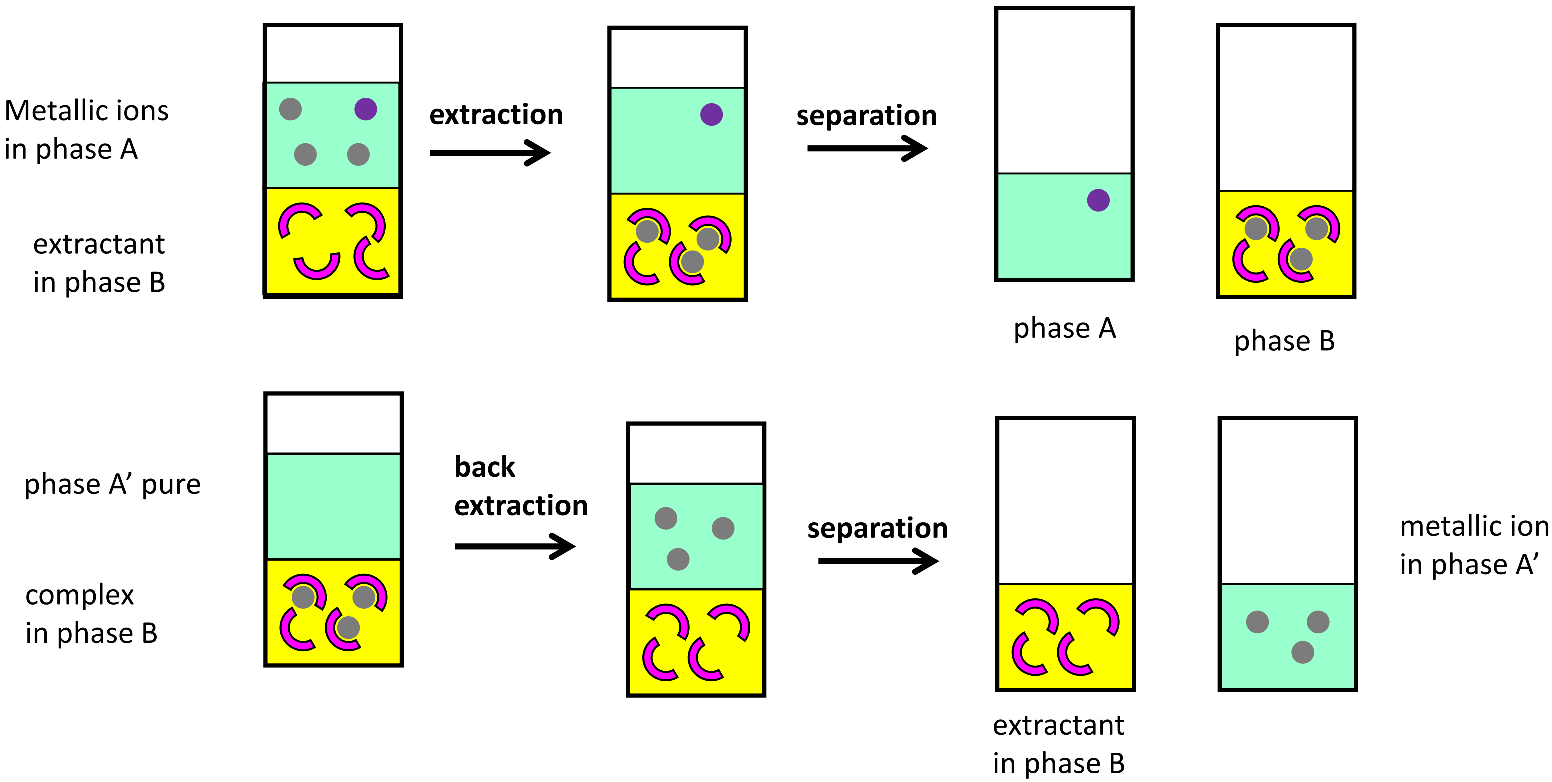
Today's processes should become greener,
avoiding Volatile Organic Compounds
and limiting pollution

Outline

- Science in Grenoble and at Lepmi/recycling group
- Urban mines and metal wastes: new challenges
- **ILs : what did they acheive ? A short review**
- ILs: what can't they perform ?
- Conclusion and perspective

In this presentation, ILs are salts with a melting temperature below or equal to 100°C.

Principle of traditional liquid/liquid extraction



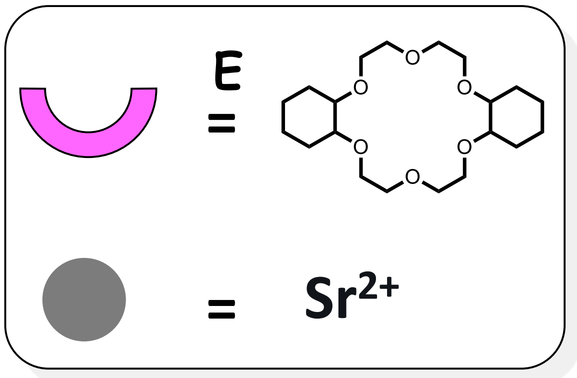
distribution ratio D: $D_M = [M]_{org}/[M]_{aq}$

- $D < 0.1$ no significant extraction
- $0.1 < D < 1$ weak extraction
- $D > 1$ significant extraction

Phase 1 // Phase 2
Phase 1 can be :
M(o.n)/acid/solvent
Phase 2 can be :
Extractant/solvent

1999: a decisive fundamental work

Sr(II)/pH=4.1/H_2O//DCH18C6/solvent



solvent	D, no E	D, with E
$C_6H_5CH_3$	0	0.76
$CHCl_3$	0	0.77

ILs appear as miraculous solvents.
This is the main basis of recycling studies

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

Magnets: what is inside ?

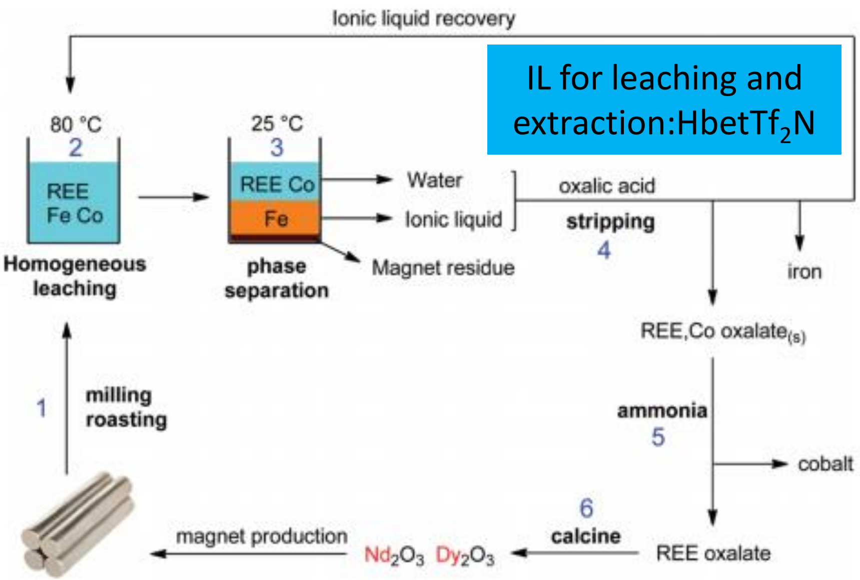
NdFeB and SmCo magnets are sharing most of the production.

Table 1 Composition of the NdFeB magnet in wt%.

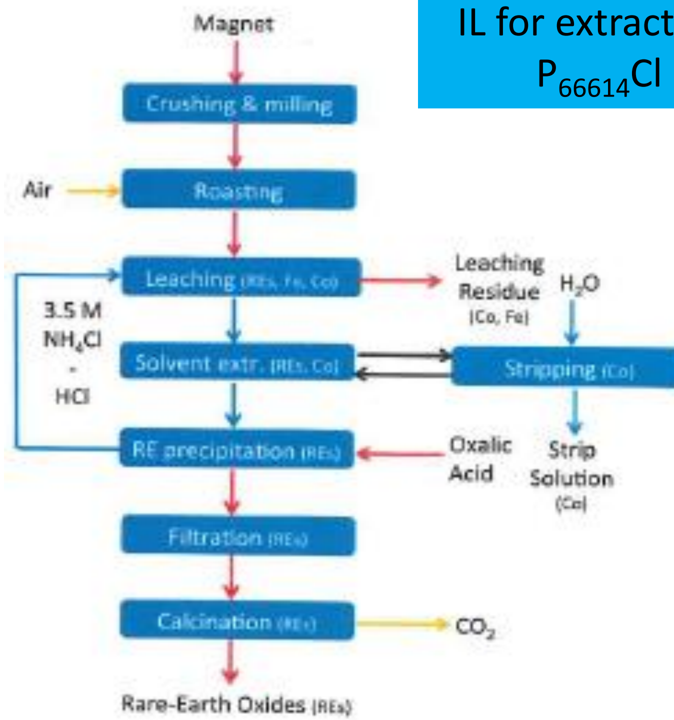
Fe	58.16	Pr	0.34
Nd	25.95	C	0.07
Co	4.22	Si	0.06
Dy	4.21	Mn	0.05
B	1.00	Cu	0.04
Nb	0.83	Ni	0.02
O	0.41	N	0.02
Al	0.34	Total	95.72

Vander Hoogerstraete et al., RSC Advances, 4(2014)64099;

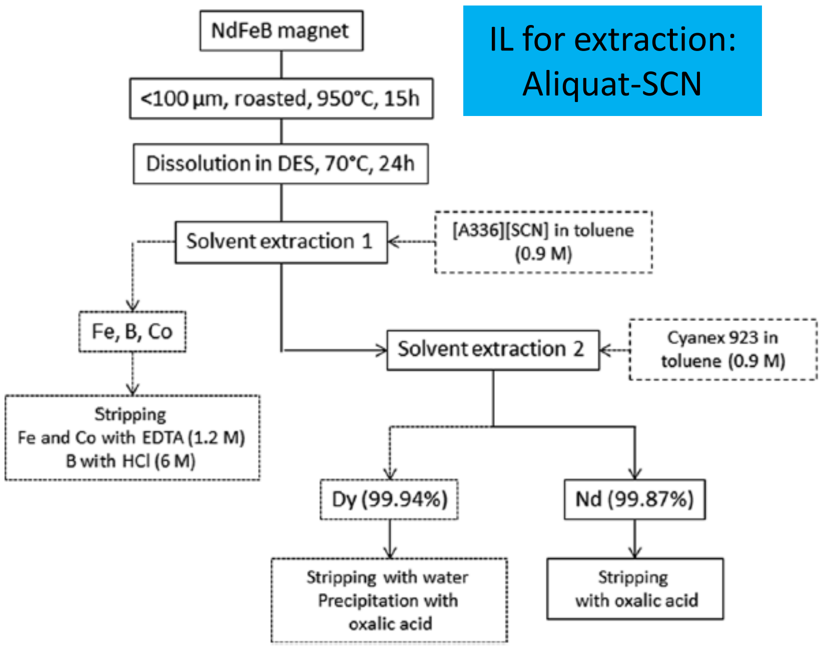
Magnets: recycling using ILs



IL for leaching and extraction:$HbetTf_2N$



IL for extraction: $P_{66614}Cl$



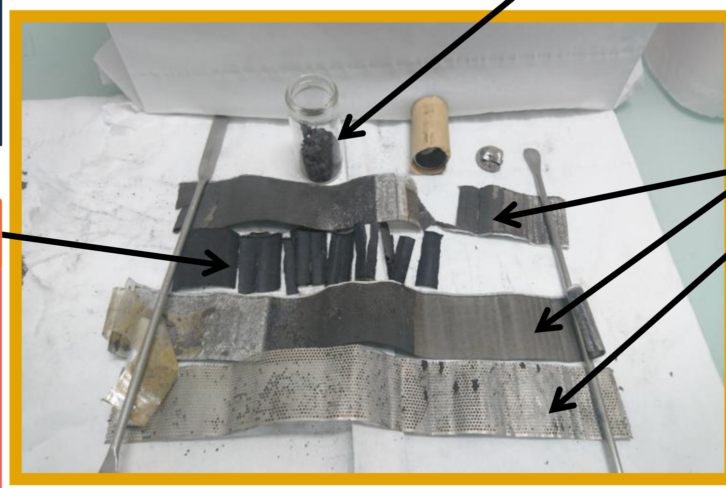
IL for extraction: Aliquat-SCN

Leaching can be performed in Cl^- or NO_3^- medium.

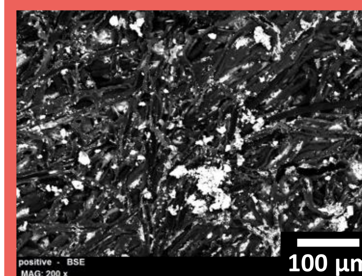
Dupont et al. Green Chem., 17(2015)2150.
Riano et al., RSC Adv., 7 (2017)32100.
Riano et al., Green Chem 17(2015)2931
And other papers from the Binnemans' group

NiMH batteries: what is inside ?

SUPPO



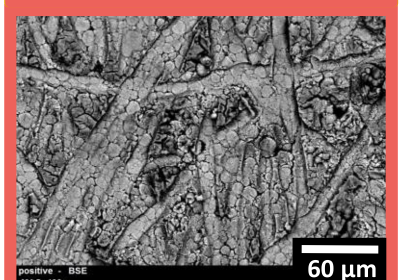
Negative electrode



(at. %)
Ni: 30.1
Co: 7.6
Mn: 3.7
K: 53.4
REE: 5.2

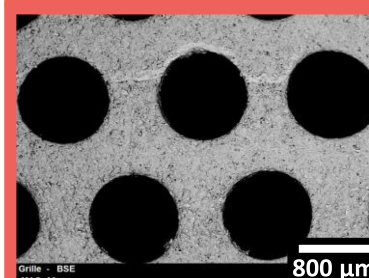
Separators

Positive electrode



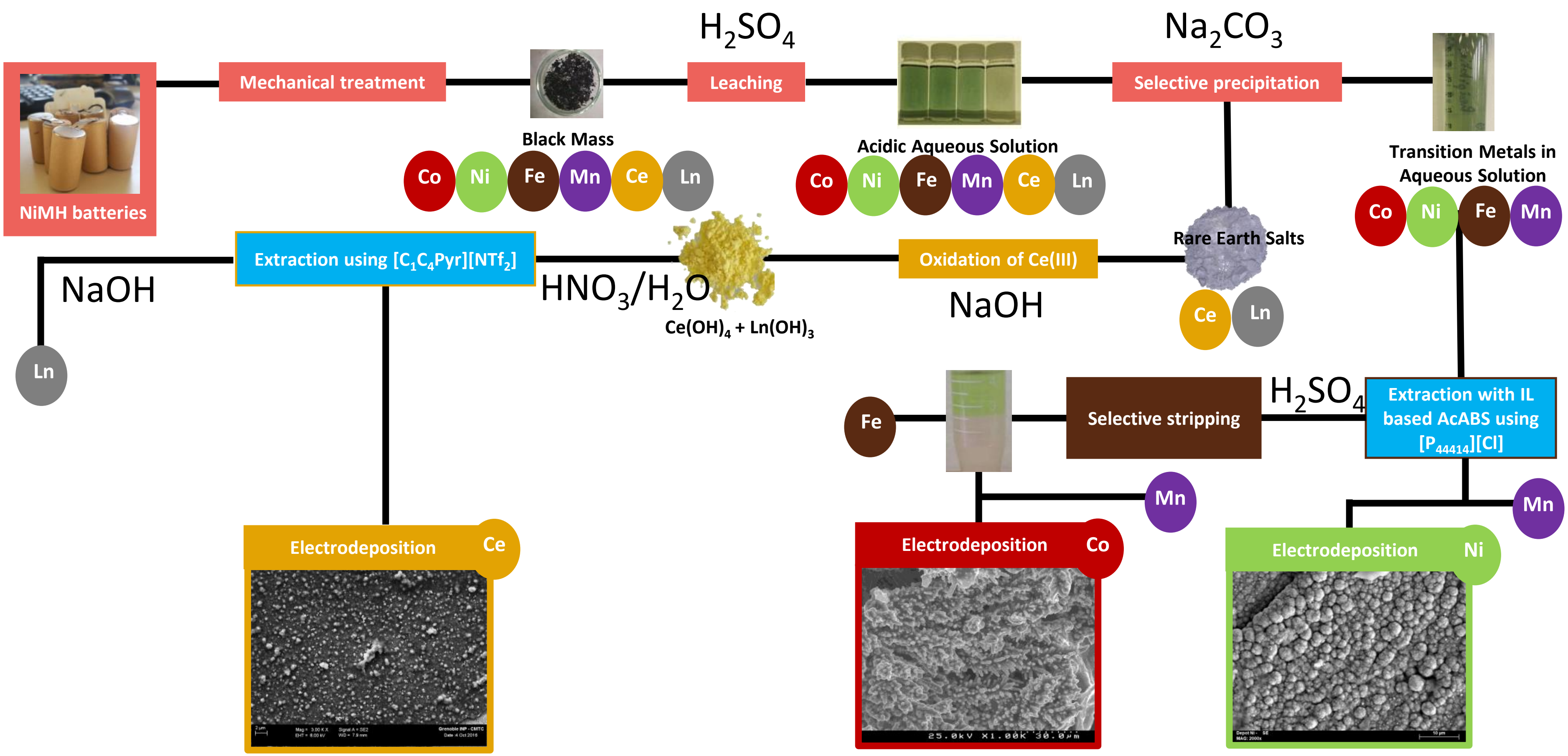
(at. %)
Ni: 50.2
Co: 3.4
Mn: 1.2
K: 40.8
REE: -

Metallic grid



(at. %)
Fe: 27.3
Ni: 72.7

NiMH batteries: recycling using ILs



Purity (at. %): 56.2 % not optimised 99.2 %

Directly from $C_1C_4pyrNTf_2$

Gras et al., Sep. Pur. Technol. 178(2017)169
Gras et al., Angew. Chem. Int. Ed., 57(2018)1563

Phosphor lamps

Table 1 Overview of the lamp phosphors considered in this work and the approximate content found in lamp phosphor waste[3]

Name	Formula	Waste fraction[a] (wt%)	Value
HALO	$(Sr,Ca)_{10}(PO_4)_6(Cl,F)_2:Sb^{3+},Mn^{2+}$	40–50	Low
YOX	$Y_2O_3:Eu^{3+}$	20	High
BAM	$BaMgAl_{10}O_{17}:Eu^{2+}$	5	Low
LAP	$LaPO_4:Ce^{3+},Tb^{3+}$	6–7	High

[a] Approximate fraction found in lamp phosphor waste; the remaining consists of SiO_2 (as fine glass particles), Al_2O_3, and small quantities of ıosphors like CAT which behaves similarly to BAM, and CBT.

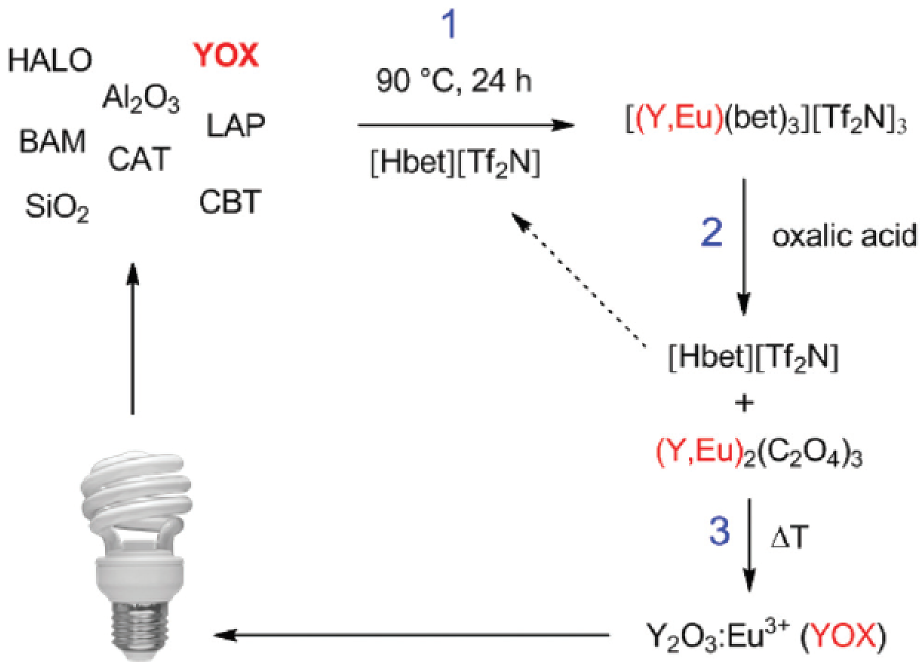


Fig. 13 Overview of the proposed recycling process for lamp phosphor waste, based on the selective dissolution and revalorization of YOX with the protonated functionalized ionic liquid [Hbet][Tf$_2$N]. Step 1: selective dissolution of YOX, step 2: stripping with pure oxalic acid (regenerates the ionic liquid), step 3: direct resynthesis of YOX.

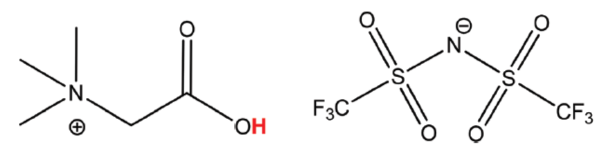


Fig. 1 Structure of the ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf$_2$N]. The acidic proton of the betaine group is highlighted in red.

Dupont et al., Green Chem., 17(2015)856

Outline

- Science in Grenoble and at Lepmi/recycling group
- Urban mines and metal wastes: new challenges
- ILs : what did they acheive ? A short review
- **ILs: what can’t they perform ?**
- Conclusion and perspective

Listing ILs disappointments

ILs are toooo costly, even if you recycle them very efficiently

The cost of the IL amount sequestered is unacceptable for companies

ILs are still too toxic and have too much environmental impacts

Life Cycle Analysis is mandatory and is mainly not in favor of ILs

ILs are *not* « designer solvents »

A provocative opinion, I know…

ILs, once diluted, behave as independent ions

Loss of compounds, synthesis of undesired other ILs etc.

New IL usages do not solve the above problems

ABS, DES etc.

ILs do not brew you coffee… they are not the panacea for any recycling problem

They are part of the solutions, together with acids, bases, heat etc.

In fact, *recycling* is a second best option.
Better usages, eco-design, second lifes…
it all depends on you/us !

Outline

- Science in Grenoble and at Lepmi/recycling group
- Urban mines and metal wastes: new challenges
- ILs : what did they acheive ? A short review
- ILs: what can't they perform ?
- Conclusion and perspective

What shall we do next ?

- Fundamental science
  - Mandatory for understanding (plus : it is fun !)
    - Extraction mechanisms (is unification possible?)
    - Thermodyamics and kinetics of mass transfer
- Applied studies
  - Very useful for the planet (i.e. : feel good activity)
    - Butts and paper wastes (Jeong et al. ACS Sust. Chem. Eng. 6(2018)4510)
    - All other liquid wastes (industries, wastewaters etc.)
    - Food packaging (Kaiser et al., Recycling, 3(2018)1)

taking a step back
from these issues
is vital

Pickling baths: Sinoimeri et al., PCCP, 22(2020)23226 + patent.

Matching green chemistry, costs and science ?
1. general thoughts

- What does green chemistry means ? (make our planet great again, yes we can etc…)
  - ‘Better’, ‘greener’ are words, not scales or limits

- « Money money makes the world happy »
  - Still true in 2021 but should it stay that way ? (climate change)
  - Regulations at rescue ? (REACH and others ?)
  - Public opinion ? (we/you/I have a role *and* a responsability)

Doing science may guide political choices

Matching green chemistry, costs and science ?
2. one applied limited suggestion

- ILs studied in lab are not cheap, not green, in general
  - Functionalisation often (always ?) worsens the problem
  - Looking for green non toxic ILs is a real difficult job
- Some industries already did the job !
  - Plenty of fully non toxic chemicals in catalogs
  - Compounds are already approved, tested, secured etc.
  - Compounds are cheap and available in ton scales
  - Who cares a compound is an IL or is not, if it makes the job ?

Convincing industries to share knowledge and extend competences is a difficult frustrating experience but it is worth it !

Institutions, fundings and supports

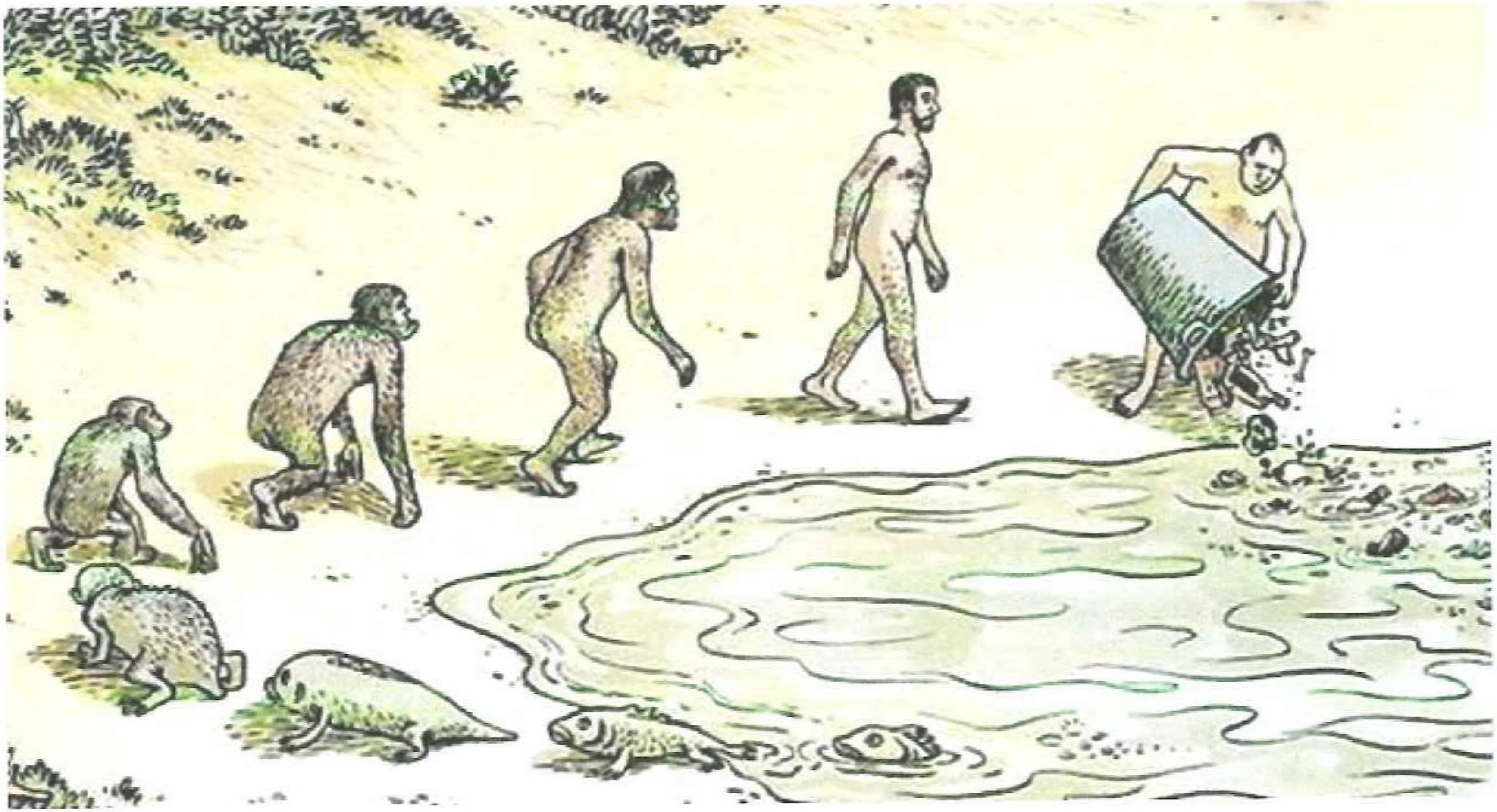
Co-leading of an Interdisciplinary Research program #1 :
eco-design, second lifes, recycling

European project : Novel methods for enhanced recovery of metals and minerals from fine incineration ash

Steel company. Recycling of valuables from pickling used baths

Multidisciplinary initiatives: ENiDES (Extraction of Ni with DES, using plants for polluted soils)

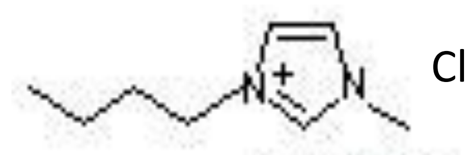
Thanks for your attention !

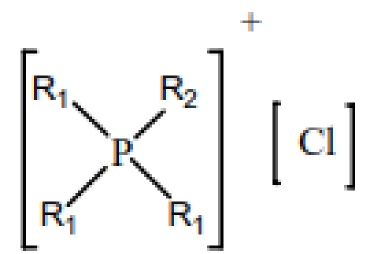


Aqueous biphasic systems (ABS): a chemical (r)evolution

ABS are liquid mixtures being either mono or biphasic depending on chemical composition and temperature

- 1958: Uppsala, Sweden: H_2O/polymer/inorganic salt
  - Used for separation of proteins
  - Poor efficiency
- 2003: Tuscaloosa, USA: H_2O/ionic liquid/inorganic salt
  - Used for separation of short chain alcohols
  - Moderate efficiency
- 2018: Grenoble, France: H_2O/ionic liquid/mineral acid
  - Used for the separation of metallic ions
  - High effciency





R_1: butyl C_4
R_2 : tetradecyl C_{14}

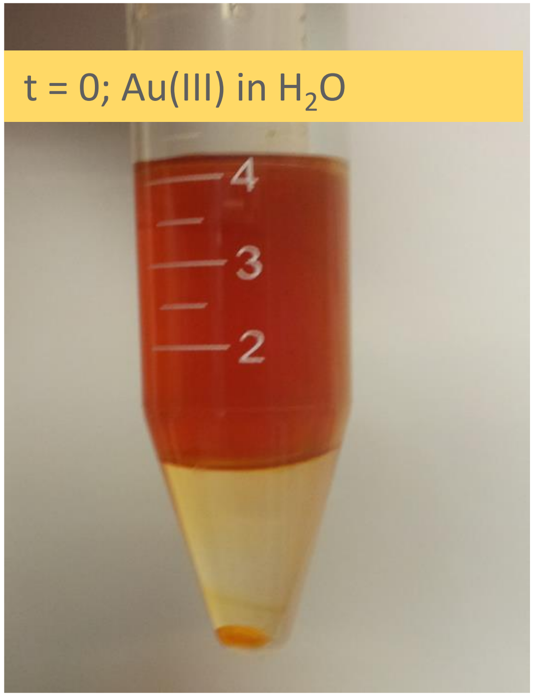
C_1C_4imCl and P_{44414}Cl are hydrophilic ionic liquids

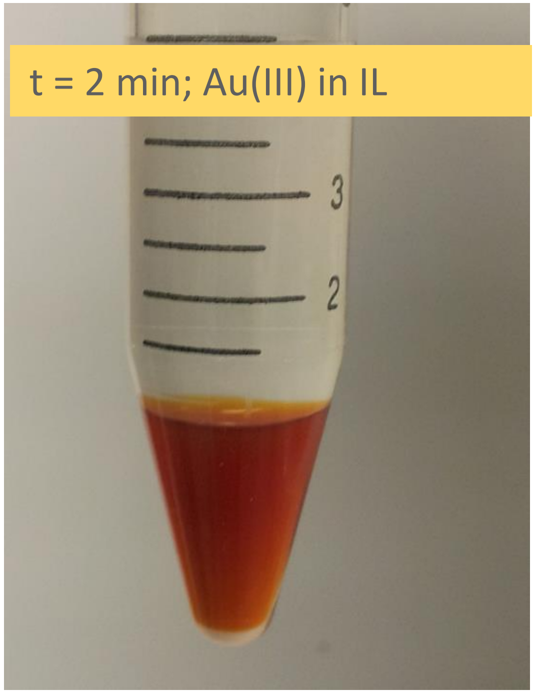
Albertsson, Nature, 182(1958)709; Gutowski, Broker, Willauwer, Huddleston, Swatloski, Holbrey, Rogers, JACS, 125(2003)6632;
Gras, Papaiconomou, Schaeffer, Chainet,Tedjar, Coutinho, Billard, Angew. Chem. Int. Ed., 57(2018)1563
Gras, Papaiconomou, Coutinho, Billard, Patent WO2018087364A1

ILs do not need extractants

Dai et al. first demonstrated that « simple » ILs can extract metal ions without the help of extractant.

$AuCl_4^-/[H^+][Cl^-]$ // $[C_8C_1im^+][Tf_2N^-]$





N. Papaiconomou et al., Green Chem. 14(2012)2050
Papaiconomou et al., RSC Advances, 4(2014)48260-48266

Extraction mechanisms can be very different from those in molecular solvents

In molecular solvents, extracted species are neutral
In ILs, they can be positive, negative or neutral.

Ion exchange means loss of IL ions and aqueous phase pollution together with water transfer to the other phase

U(VI)/HNO_3/H_2O//TBP/solvent

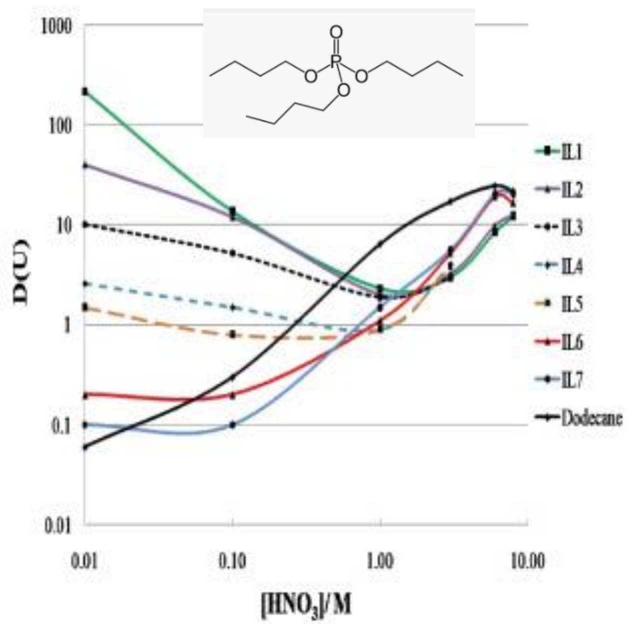
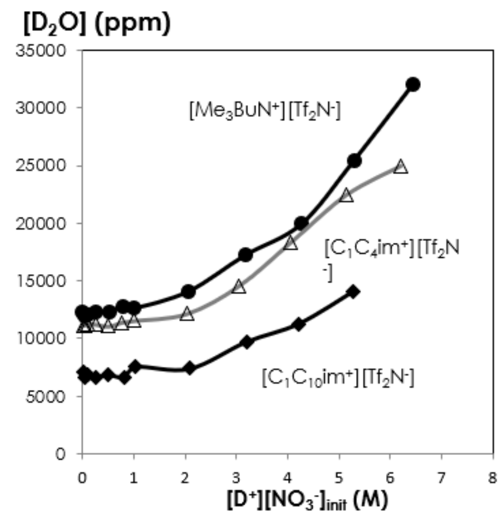
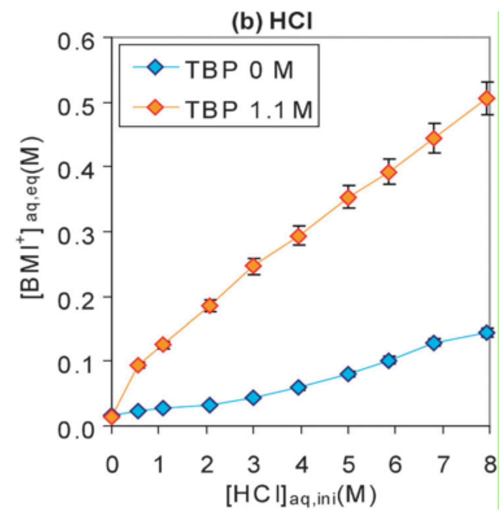


Fig. 2 Dependency of D(U), on [HNO_3] at constant TBP (1.2 M) concentration in ionic liquids and dodecane.

Bell et al. Dalton Trans. 40(2011)10125.





Mazan et al., RSC Advances, 4(2014)13371;

Extraction mechanisms, review papers by : Dietz Sep Sci. Technol., 41(2006)2047; Billard et al., Anal. Bioanal. Chem., 400(2011)1555; Stojanovic et al., Sep. Sci. Technol., 47(2012)189; Kolarik, Solv. Ext. Ion Exch. 31(2013)24;
Mutual solubilities: Rickert et al., Talanta, 72(2007)315; Gaillard et al., PCCP, 14(2012)5187-5199; Fagnant et al., Inorg. Chem. 52(2013)549.