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Hydrochemical Routes to Recycle NiMH Batteries and Fluorescent Lamps

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Nuclear Chemistry and Industrial Materials Recycling

Conclusions

- **A centre for multidicplinary research and development have been established in Sweden. THe competence Centre Recycling, CCR.**
- **New members are welcome from both academia, research organisations and industry. Please contact: che@chalmers.se or bms@chalmers.se**
- **A recycling route for Toyota Prius NiMH batteries has been developed and tested on semi pilot scale**
- **A recycling route for Hg contaminated fluorecent lamp waste has been developed and testing in pilot scale has begun**

CCR

Competence Centre
RECYCLING

Since 2007

VINNARE

Swedish Recycling
Återvinningsgalan 2013
AWARD
Årets Elektronikåtervinnare

Vision – CCR

To be the leading Research and Technology Development (RTD) constellation for initiating, coordinating and performing R&TD in the field of circular use of materials in Sweden

To meet this vision we will build and develop a creative, extremely multi disciplinary research and innovation environment attractive to academy and industry in Sweden and also internationally.

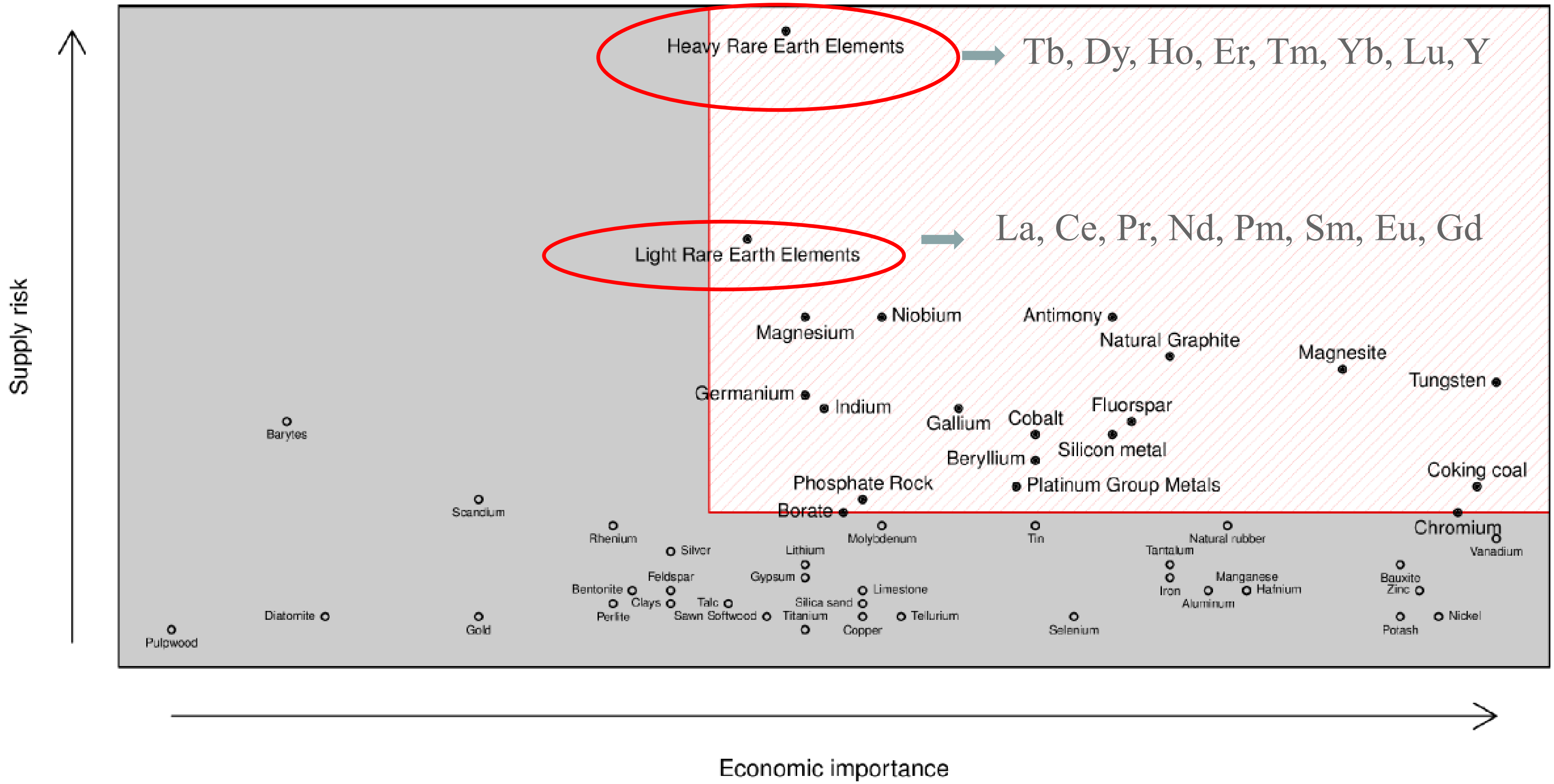
Mission

- To act as a creative R&I arena (meeting place) for the stakeholders and the value circles
- To initiate, coordinate and execute world-class research and innovation projects
- To bring research results to industrial exploitation and use in the society by creating an interdisciplinary research and innovation environment where industrial need and research excellence are combined
- To promote innovations and scientific advances that lead to a more sustainable material use in industry/society

All missions should contribute to the development of a competitive industry in Sweden and to the implementation of a sustainable, circular material use in industry/society.

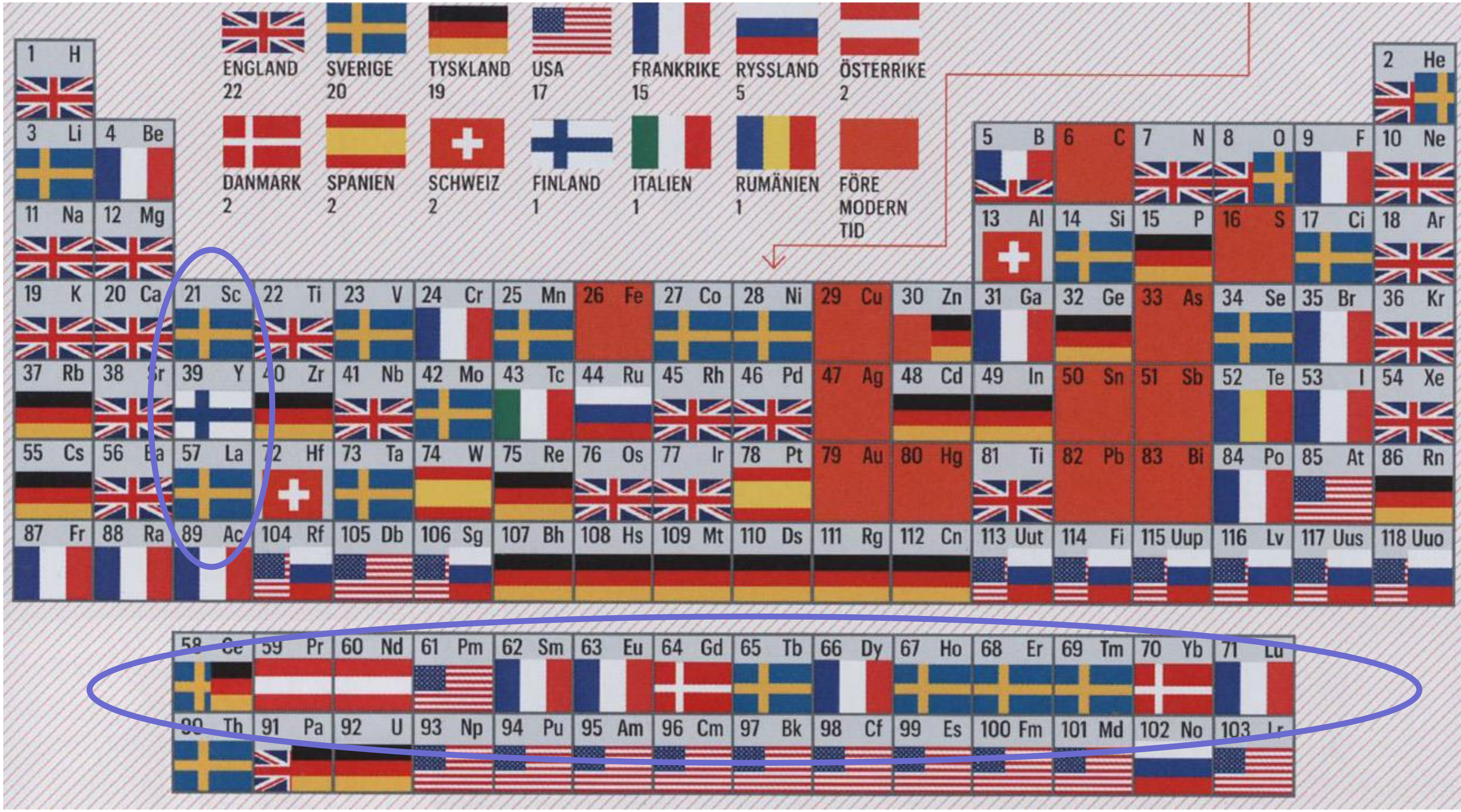
Obtaining access to non-energy raw materials is becoming a challenge to many resource-dependent countries all over the world.

REEs presently have the highest supply risk for the EU.



European Commission – Critical raw materials for EU. Report of the Ad-hoc Working Group on defining critical raw materials (2014)

REM: the Nordic elements



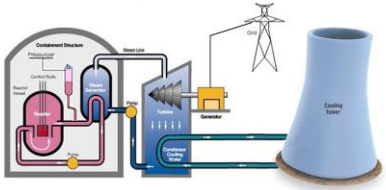
REEs applications

Essential in many technologies

Phosphors; luminescence

Magnets

Glass and ceramics
Polishing
Catalysts
H_2 storage
Nuclear sector



Metal alloys
Batteries

... and many others!

Öko-Institut e.V., Study on Rare Earths and Their Recycling. 2011

Distribution of materials by criticality category

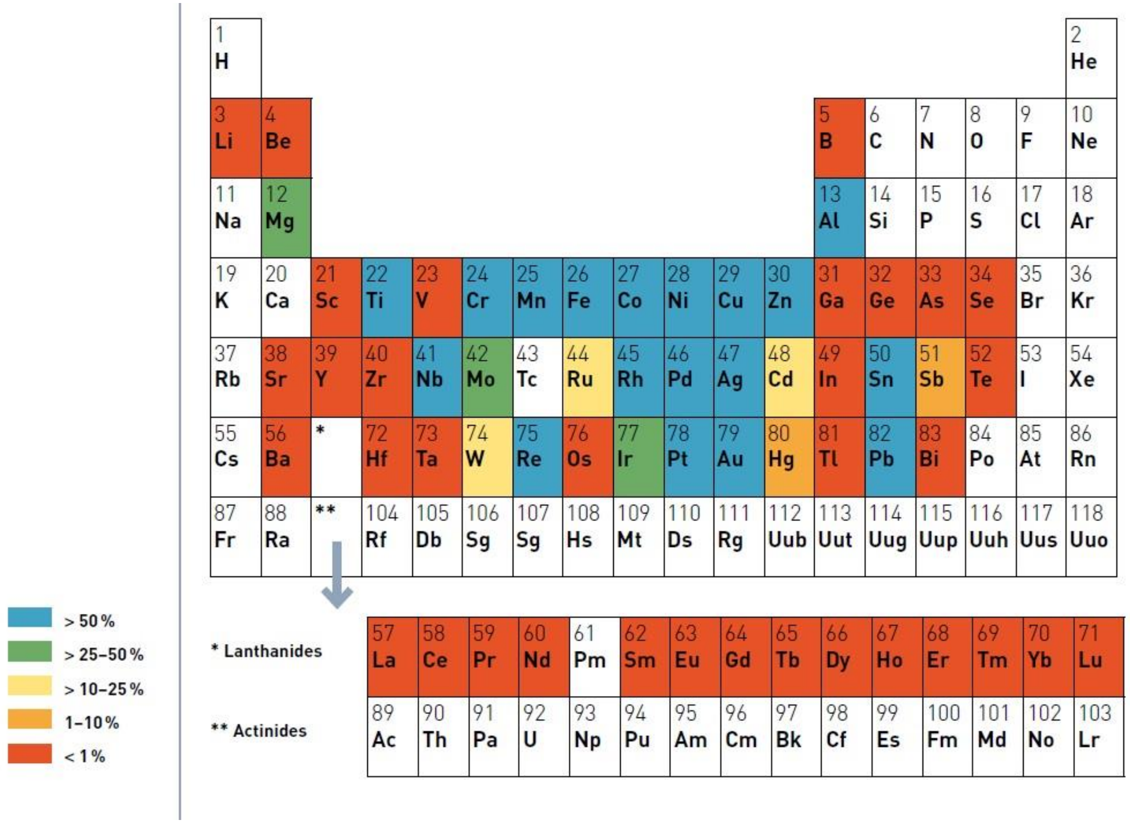
Short term: 0-5 y
Medium term: 15-20 y

Short Term	Medium term
Critical	**Critical**
• Dysprosium • Europium • Neodymium • Terbium • Yttrium	• Dysprosium • Europium • Neodymium • Terbium • Yttrium
Near-Critical	**Near-Critical**
• Cerium • Indium • Lanthanum • Tellurium	• Lithium • Tellurium
Not Critical	**Not Critical**
• Cobalt • Gallium • Lithium • Manganese • Nickel • Praseodymium • Samarium	• Cerium • Cobalt • Gallium • Indium • Lanthanum • Manganese • Nickel • Praseodymium • Samarium

US Department of Energy. Critical Materials Strategy. 2011.

This has focused attention towards the possibility of recovering REEs from various end-of-life products.

But how much of the REEs are recovered from end-of-life products?



Developing an industrial process for the recovery of REEs is of great importance!

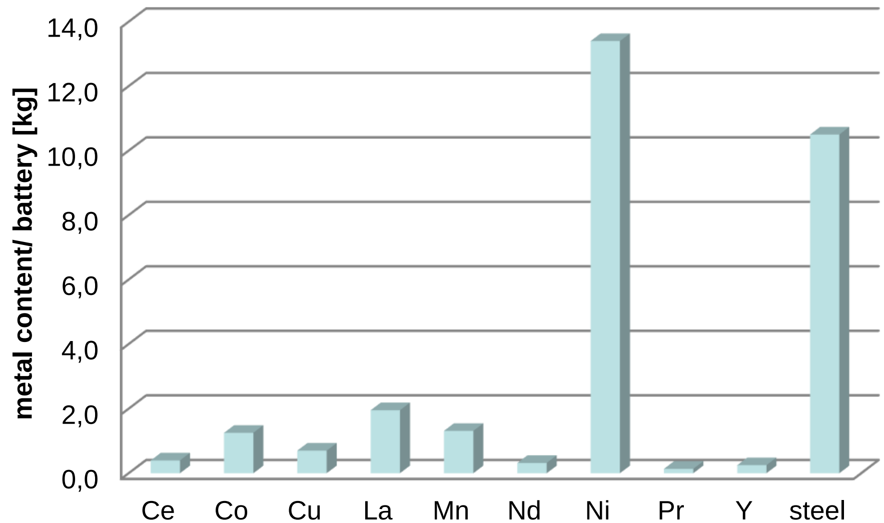
UNEP. Recycling Rates of Metals: A Status Report. 2011

The focus of today's presentation: HEV NiMH batteries and fluorescent lamps.

Recovery of metals from NiMH batteries

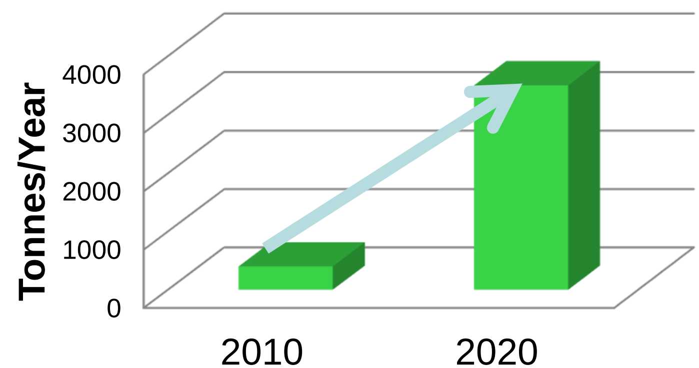
NiMH as a secondary raw material

Metal content:

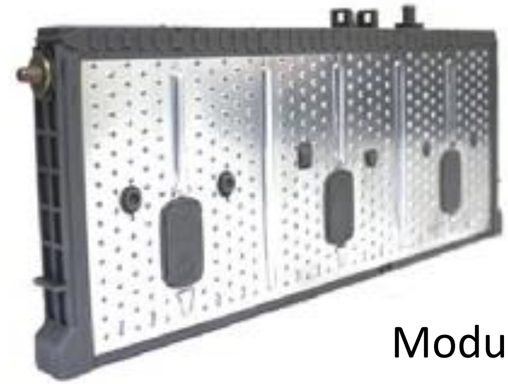


3kg of REEs/ battery

REEs consumption for HEV battery production



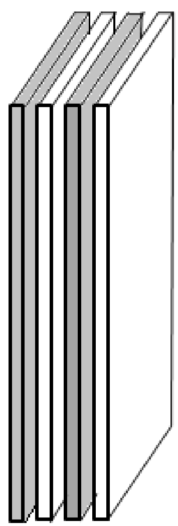
Battery construction



Modul

Cathode:

nickel grid
+
$Ni(OH)_2$



Anode:

steel grid
+
$MmNi_{5-x-y-z}Co_xMn_yAl_z$

(Mm: mixture of La, Ce, Pr, Nd) $LaNi_5$

REEs are present mostly in anode material

Hydrometallugical process developed at Chalmers

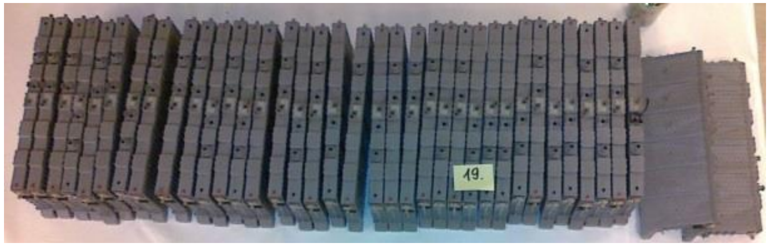
1. Dismantling of batteries

2. Leaching of electrode material with HCl

3. Solvent extraction using Cyanex 923

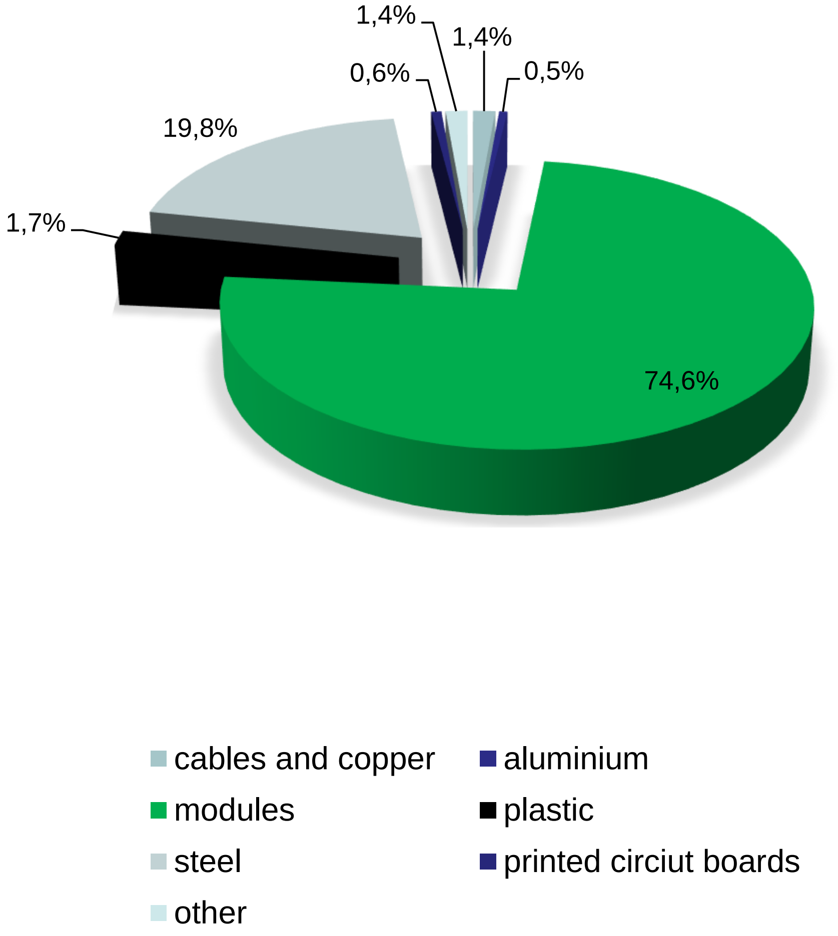
NiMH battery dismantling

Toyota Prius Battery – before dismantling



Battery modules —38

Other parts



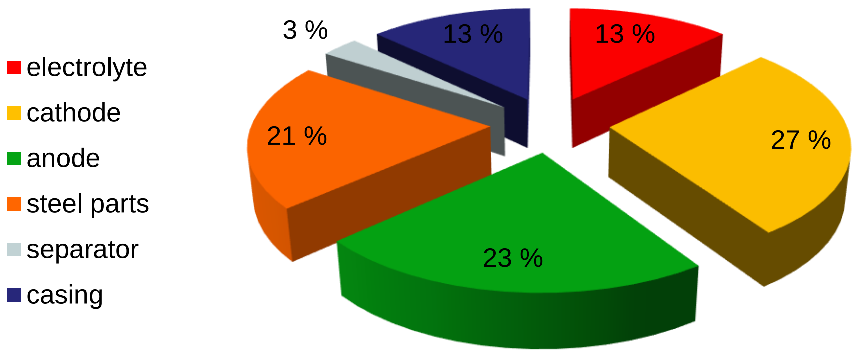
NiMH module dismantling

Module before dismantling

Module casing — 6 units

Cathodes and anodes

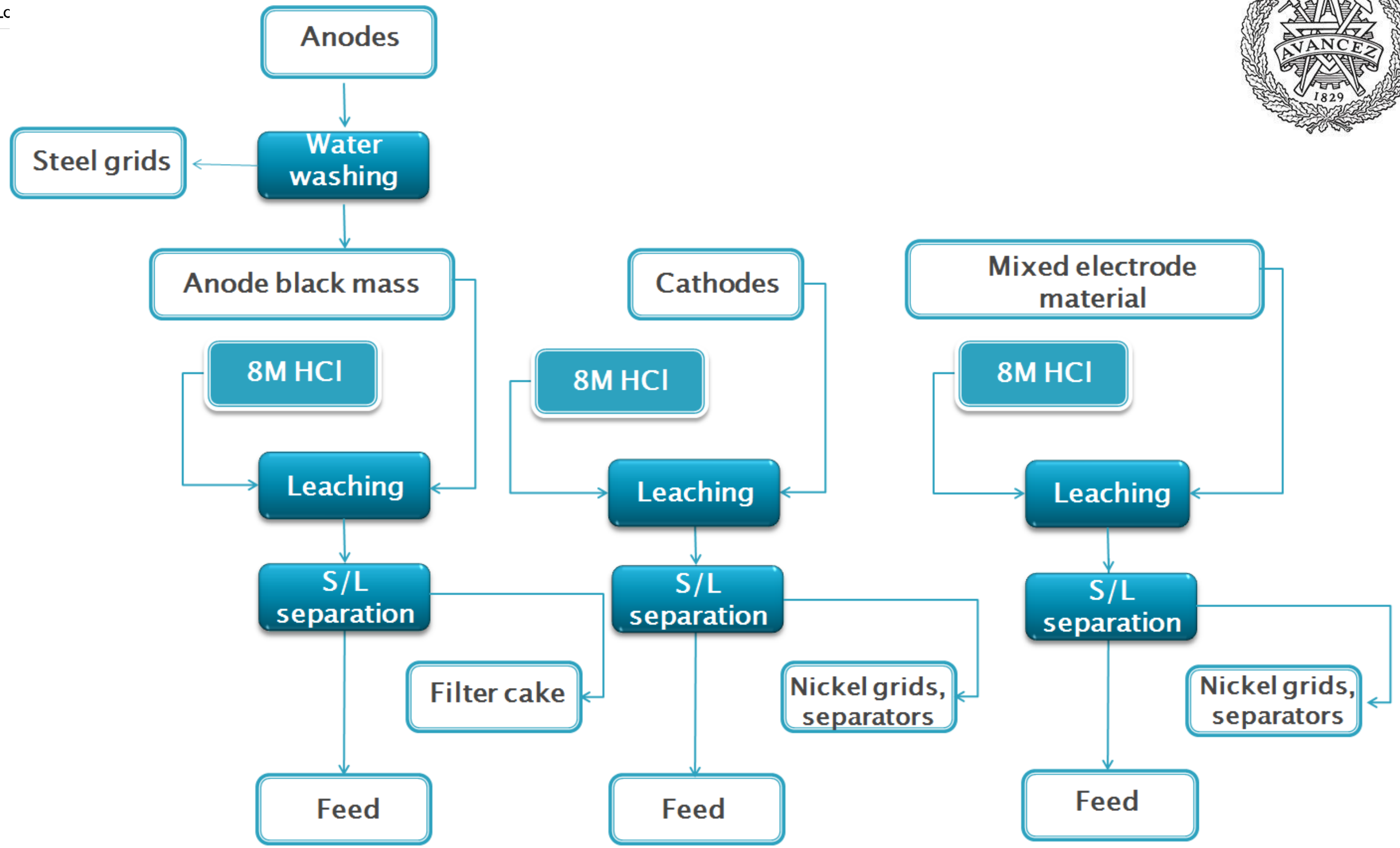
Material balance of modules



Element	Cathode material [wt.%]	Anode material [wt.%]
Al	0.5	2.7
Ce	nd	4.8
Co	8.4	4.1
Fe	2.6	0.4
K	16.7	0.4
La	nd	23.8
Mg	0.7	0.1
Mn	4.4	10.1
Nd	nd	3.9
Ni	63.4	47.4
Pr	nd	1.7
Y	1.2	1.4
Zn	0.8	0.1

Leaching

- glass reactor with double wall (with heating/cooling system)
- volume: 2 or 5L
- titration devices



material	s/l ratio	Leaching temperature	pH
anodic	1/ 3.75	50-70°C	1
cathodic	1/ 1.96	30°C	1
mixed	1/ 2.7	30°C	1

Molar concentration of metals in the solutions after leaching:

Element	Anodic material (+50% reflux of raffinate)	Cathodic material	Mixed material (+30% reflux of raffinate)
Al	0.07	0.01	0.05
Ce	0.08	nd	0.04
Co	0.09	0.54	0.19
Fe	0.003	0.01	0.007
K	0.001	0.04	0.009
La	0.23	nd	0.14
Mg	nd	0.09	0.03
Mn	0.13	0.01	0.1
Nd	0.023	nd	0.02
Ni	3.3	3.3	3.1
Pr	0.01	nd	0.01
Y	0.01	0.05	0.02
Zn	nd	0.03	0.01

Solvent extraction

- **Extractant:** *Cyanex 923:*

  mixture of trialkyl-phosphine oxides: $R_3P(O)$, $R_2R'P(O)$, $RR'_2P(O)$, $R'_3P(0)$

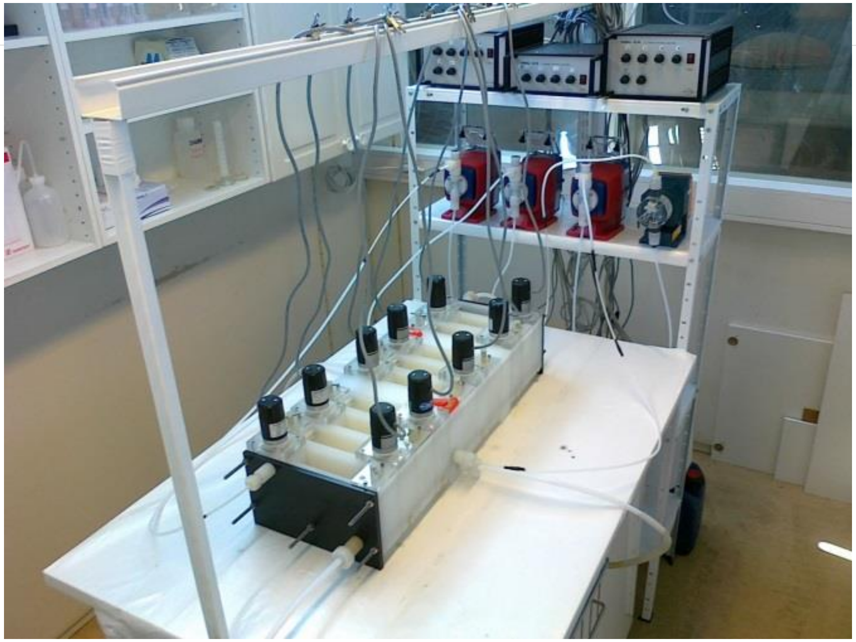
  R = $[CH_3(CH_2)_7]$ - normal octyl,

  R'= $[CH_3(CH_2)_7]$ - normal hexyl

- **Solvent:** kerosene

- **Equipment:**

- PVDF mixer-settlers (volume: 120, 500 ml)
- electromagnetic pumps



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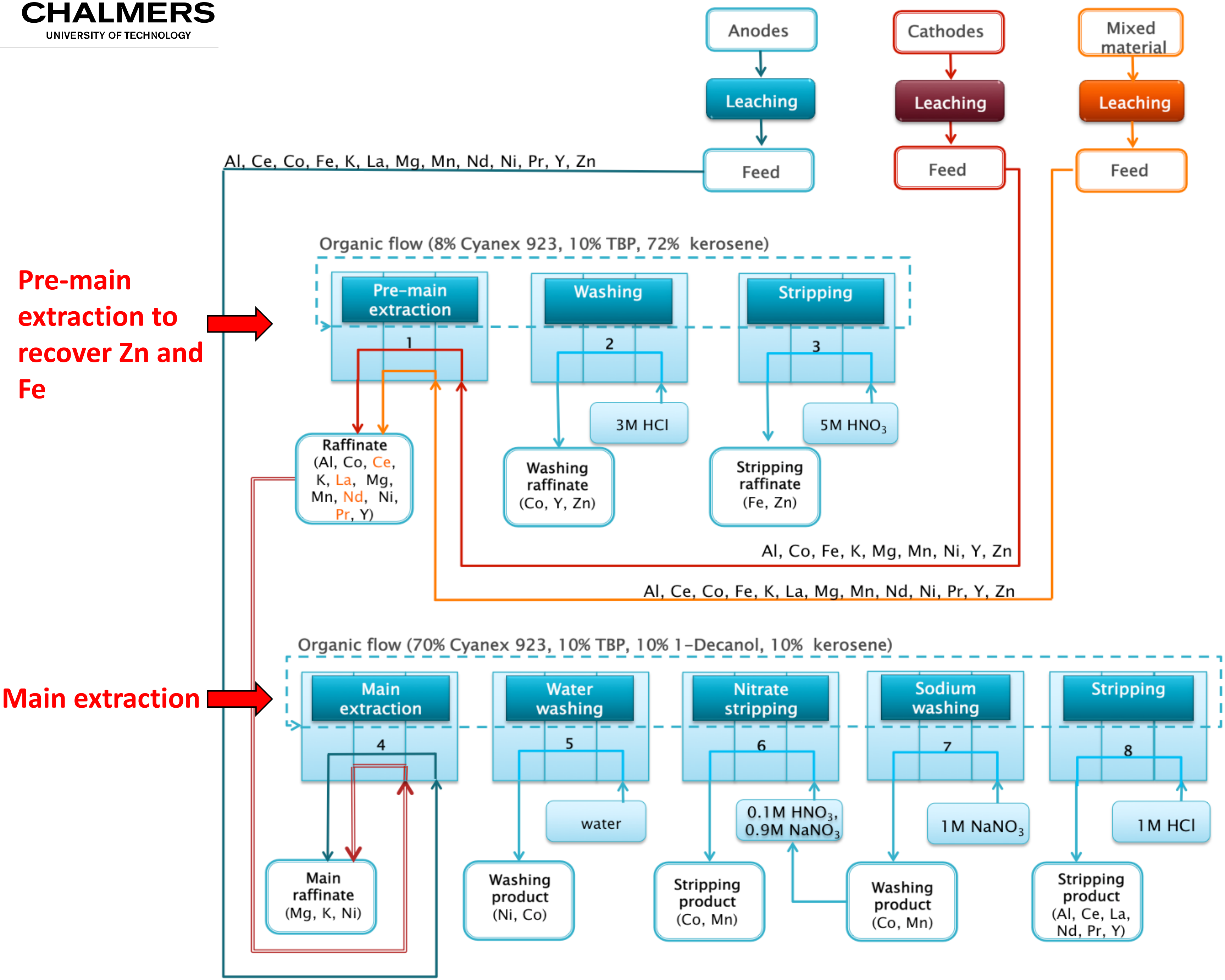
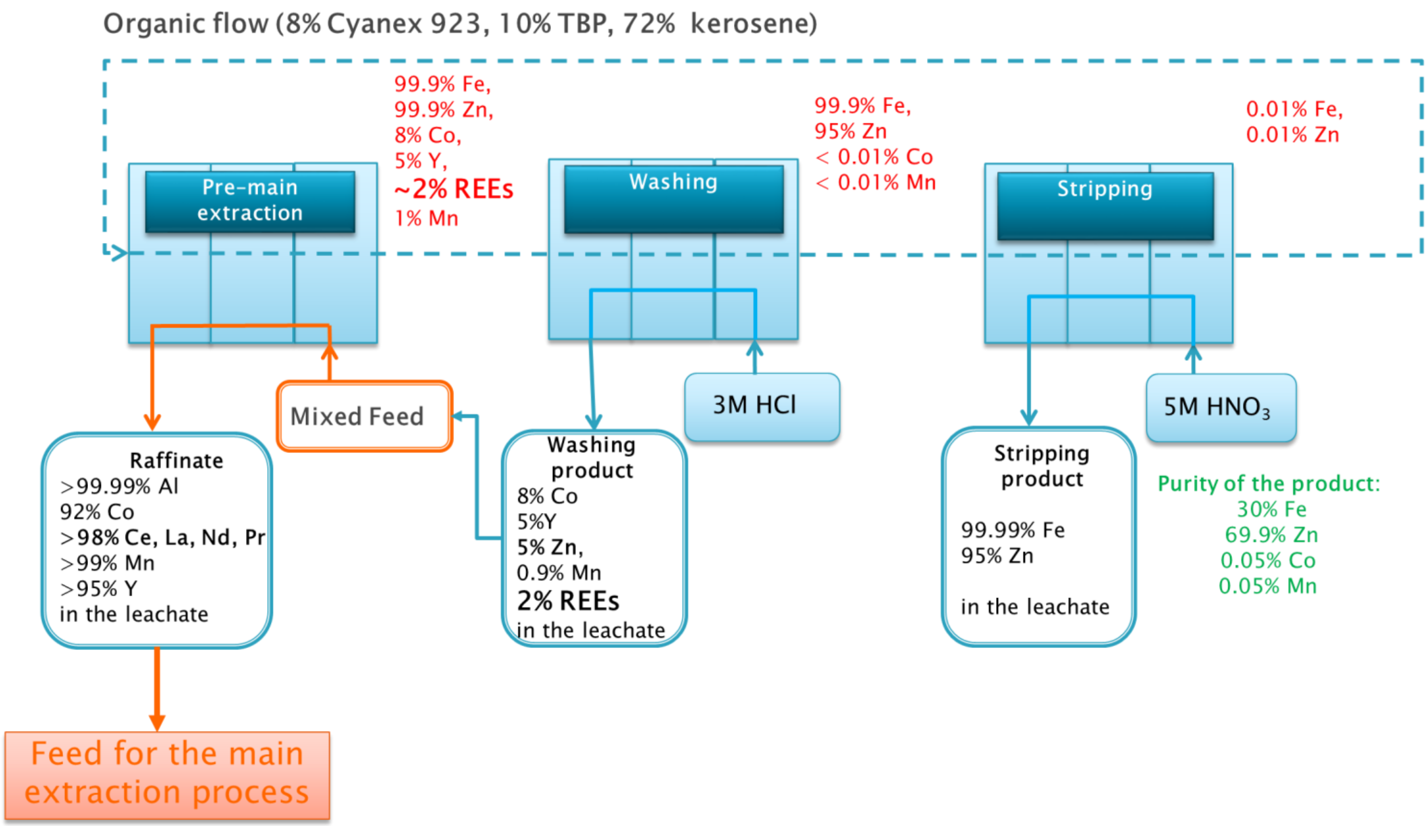


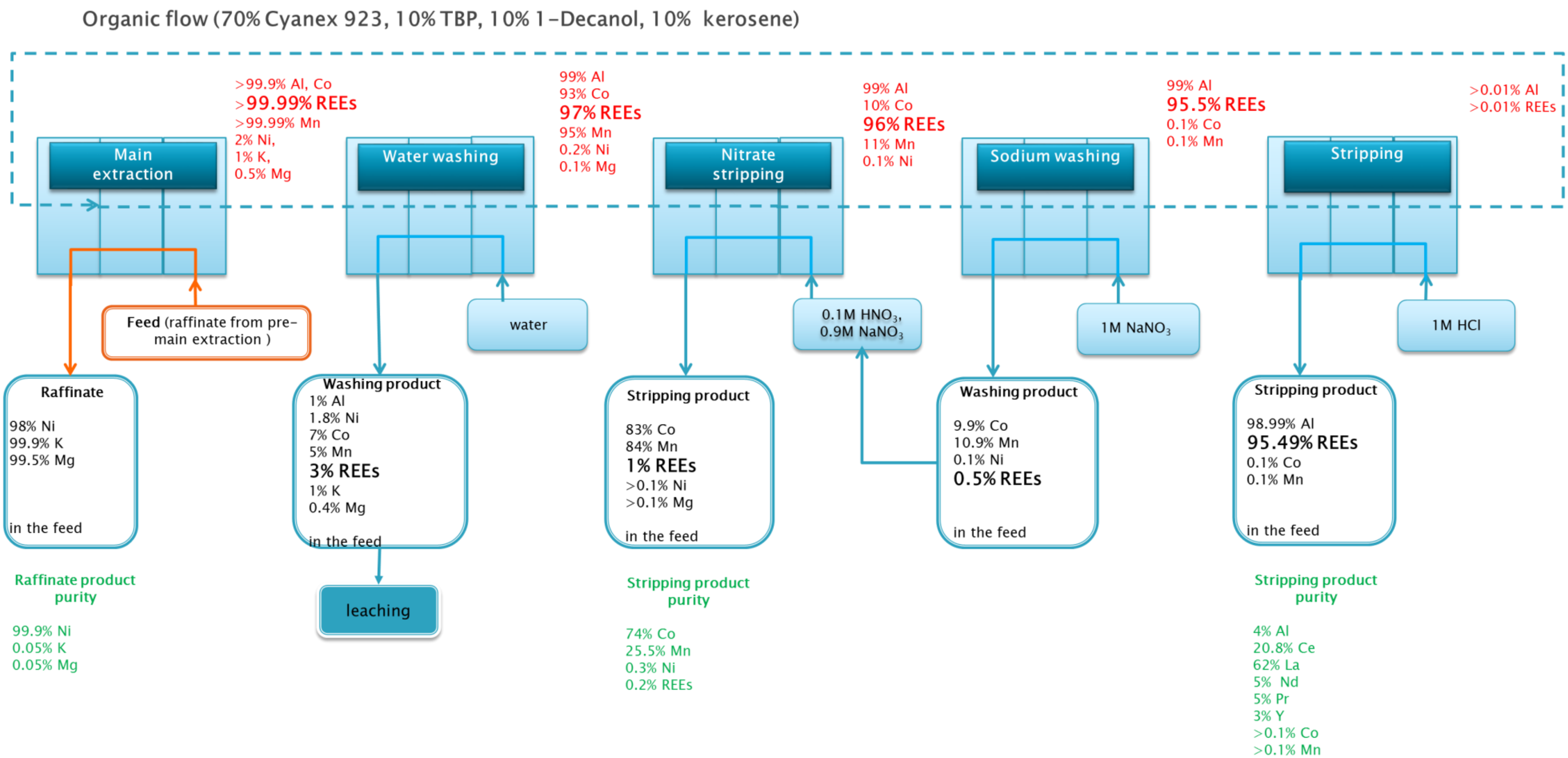
"Pre-main extraction" for recovery of Zn and Fe from "mixed" leachate



Values in red relate to metal in the organic feed. Values in black relate to metal in the aqueous feed.

All the values are reported in regard to the metal concentration in the mixed leachate.

"Main extraction" for metal recovery from "mixed" leachate



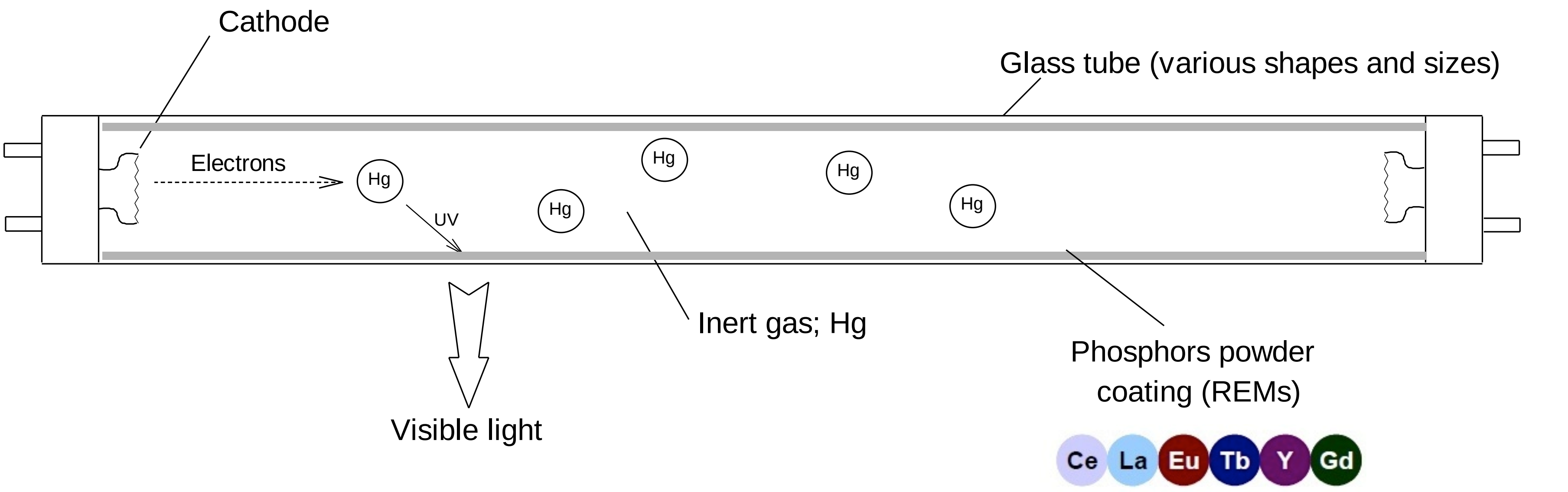
Values in red relate to metal in the organic feed. Values in black relate to metal in the aqueous feed.

All the values are reported in regard to the metal concentration in the initial aqueous feed.

- Hydrometallurgical method for recovery and separation metals from car NiMH batteries have been developed and tested in a pilot plant scale.
- Three different starting materials can be obtained for processing - depending on the way of dismantling – cathodic, anodic and mixed material.
- Metals ions present in the leaching liquors can be separated using solvating extractant trialkylphosphine oxide mixture Cyanex 923.
- Zn and iron can be removed from solution after leaching cathodic and mixed material using pre-main extraction process.
- Ni, Mg and K can be separated from feed after main extraction process, because they are not extracted at given conditions.
- Co, Mn is recovered by stripping using nitrate and sodium strip.
- Al, Ce, La, Nd, Pr and Y are stripped from organic phase using 1MHCl.

Recovery of REEs from fluorescent lamp waste

Fluorescent lamps



Phosphor type	*Possible compounds*
Red phosphor	$Y_2O_3:Eu^{3+}$
Blue phosphor	$BaMgAl_{10}O_{17}:Eu^{2+}$ $(Sr,Ca,Ba)_5(PO_4)_3Cl:Eu^{2+}$
Green phosphor	$CeMgAl_{10}O_{17}:Tb^{3+}$ $LaPO_4:Ce^{3+},Tb^{3+}$ $(Ce,Tb)MgAl_{11}O_{19}$ $(Ce,Gd,Tb)MgB_5O_{10}$

Phosphors-containing fraction obtained after crushing of end of life fluorescent lamps:

Large amounts of impurities: glass (mainly), small plastic and metallic parts, packaging remains.

REEs content in a waste phosphors fraction after some removal of glass impurities

Metal	g metal/kg waste	Metal	g metal/kg waste	Metal	g metal/kg waste
Al	13.12 ± 0.19	K	0.43 ± 0.02	W	0.21 ± 0.01
B	2.91 ± 0.04	Mg	2.55 ± 0.04	Zn	0.42 ± 0.0004
Ba	15.67 ± 0.36	Mn	2.57 ± 0.03	Y	187.15 ± 4.42
Ca	97.00 ± 2.49	Na	2.58 ± 0.09	Eu	11.39 ± 0.24
Cd	0.26 ± 0.004	Ni	0.10 ± 0.002	Gd	5.51 ± 0.08
Cr	0.03 ± 0.0003	Pb	0.21 ± 0.004	Ce	3.06 ± 0.098
Cu	0.13 ± 0.002	Sb	1.25 ± 0.02	La	2.14 ± 0.13
Fe	1.74 ± 0.02	Si	0.26 ± 0.002	Tb	1.76 ± 0.04
Hg	0.30 ± 0.002	Sn	0.07 ± 0.001	*Total REEs*	*211 ± 5.01*

Bastnäsite ore mined at Mountain Pass for the production of REEs contains approx. 90 g/kg RE oxides ***(Molycorp Inc.)***

Selective leaching of metals (4 stages)

1. Leaching of Hg with I2/KI solution in 2 h. at ambient temperature (>90% efficiency);

2. Leaching of other impurity metals (notably Ca) with nitric acid. Short contact time (15 min.) leaches >90% of the Ca, with minor REEs losses (2-3%);

3. Leaching of Eu and Y left in the residue (>95% efficiency) with nitric acid, at ambient temperature (<24 h.);

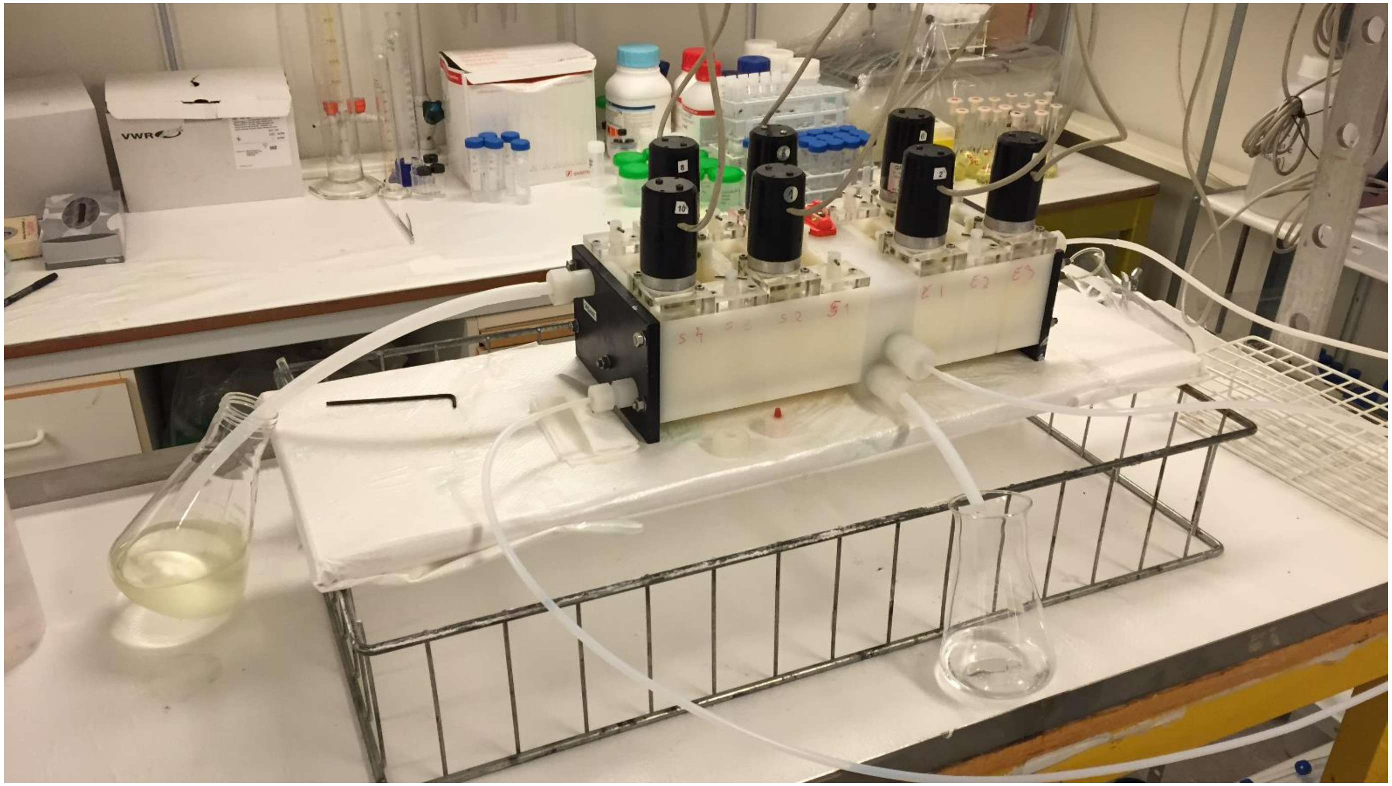
4. The other four REEs (Ce, La, Tb and Gd) are harder to leach and require concentrated acids/temperature/ultrasound. Selective leaching (sort-of) possible. Aleternate method: alkali fusion.

Metal concentration in the REEs-rich leachate of a fluorescent lamp waste fraction (3rd leaching stage)

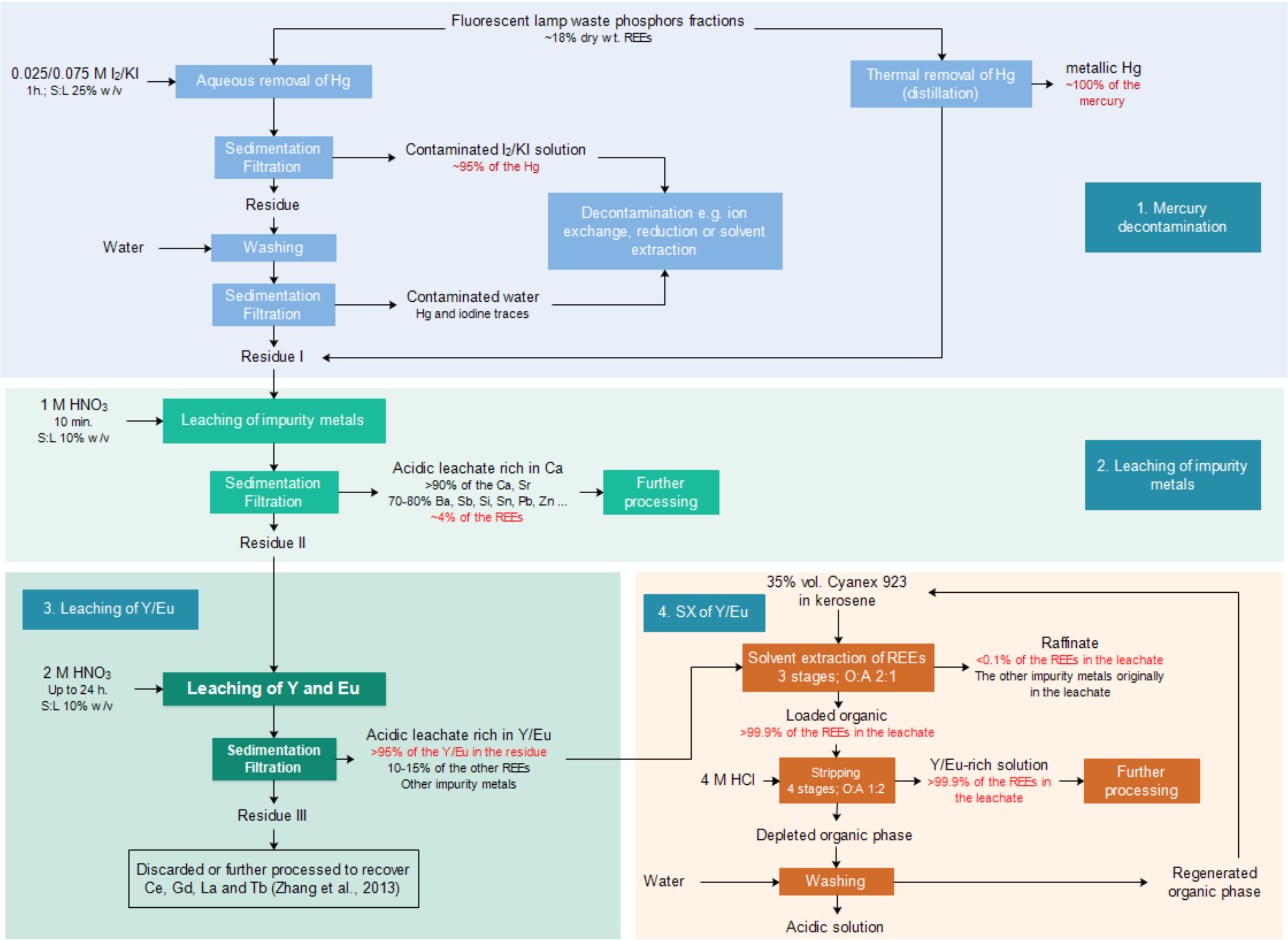
Metal	Concentration (g/L)	Metal	Concentration (g/L)
Al	0.12	La	0.003
B	0.11	Mg	0.058
Ba	0.11	Mn	0.042
Ca	1.18	Ni	0.002
Cd	0.005	Pb	0.004
Ce	0.055	Sb	0.050
Cr	0.0003	Si	0.044
Eu	1.51	Tb	0.038
Fe	0.03	Y	25.45
Gd	0.14	Zn	0.004

Solvent extraction in mixer-settlers

- **3 extraction stages; 50% v/v Cyanex 923 in kerosene; O:A = 2:1;**
- **Stripping with HCl.**



Current flowsheet



Conclusions

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