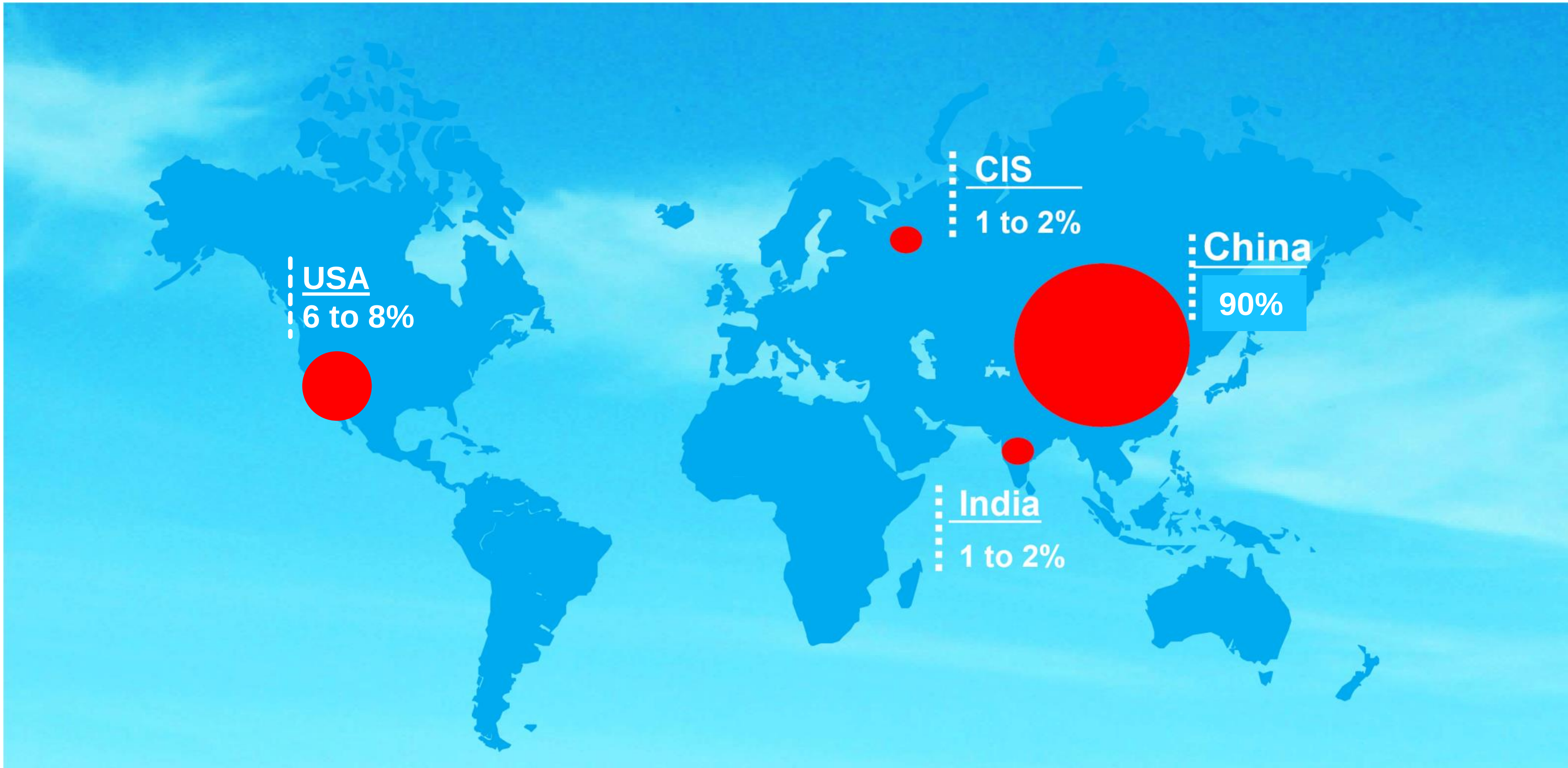
KU LEUVEN

Rare Earth Recycling and the Balance Problem

Koen Binnemans

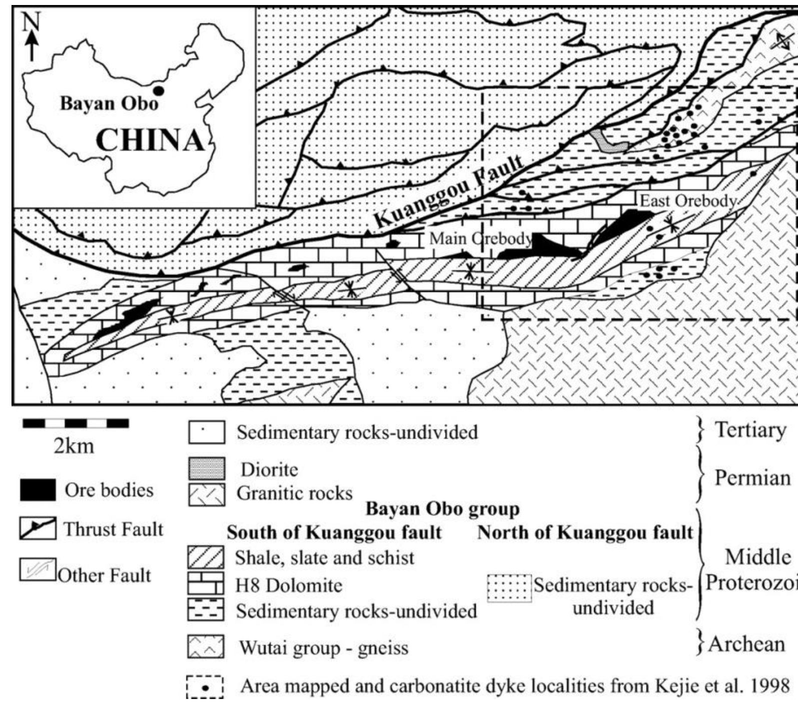
KU Leuven - University of Leuven (Belgium)

REE production is dominated by China (monopoly position)

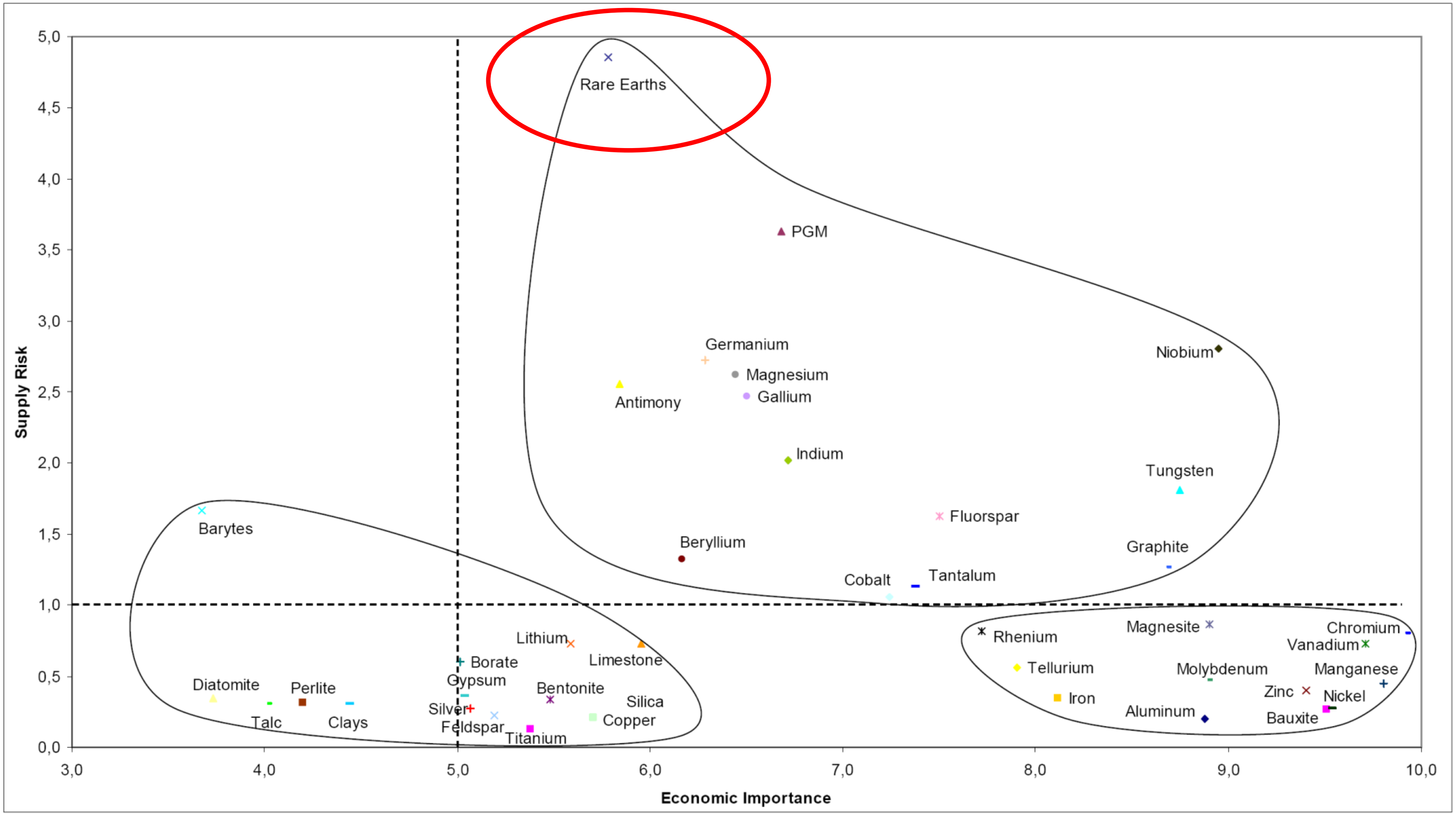


No problem of resources, but a real supply problem

Bayan Obo (Inner Mongolia, China)

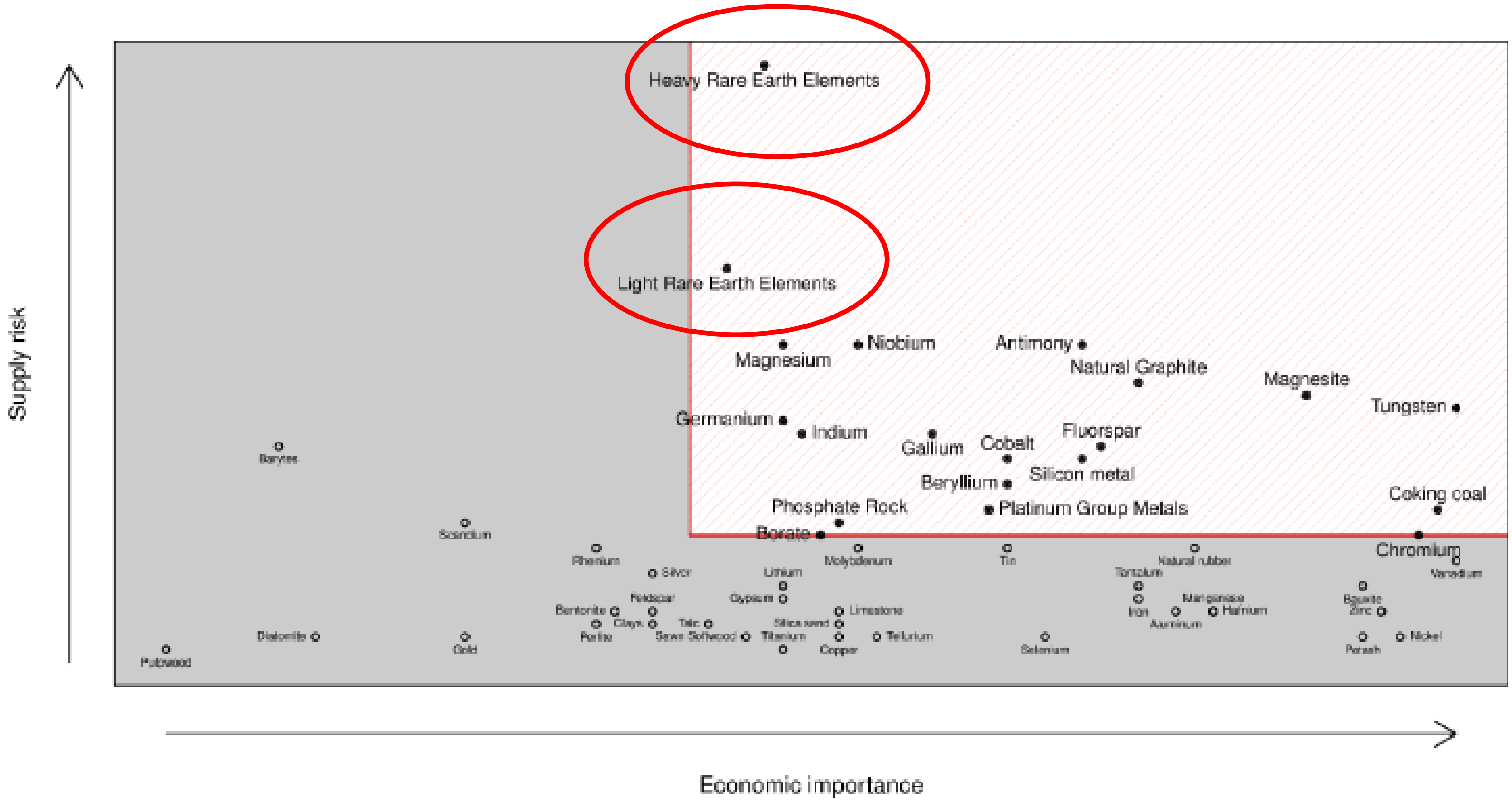


Rare earths as critical raw materials (2010)



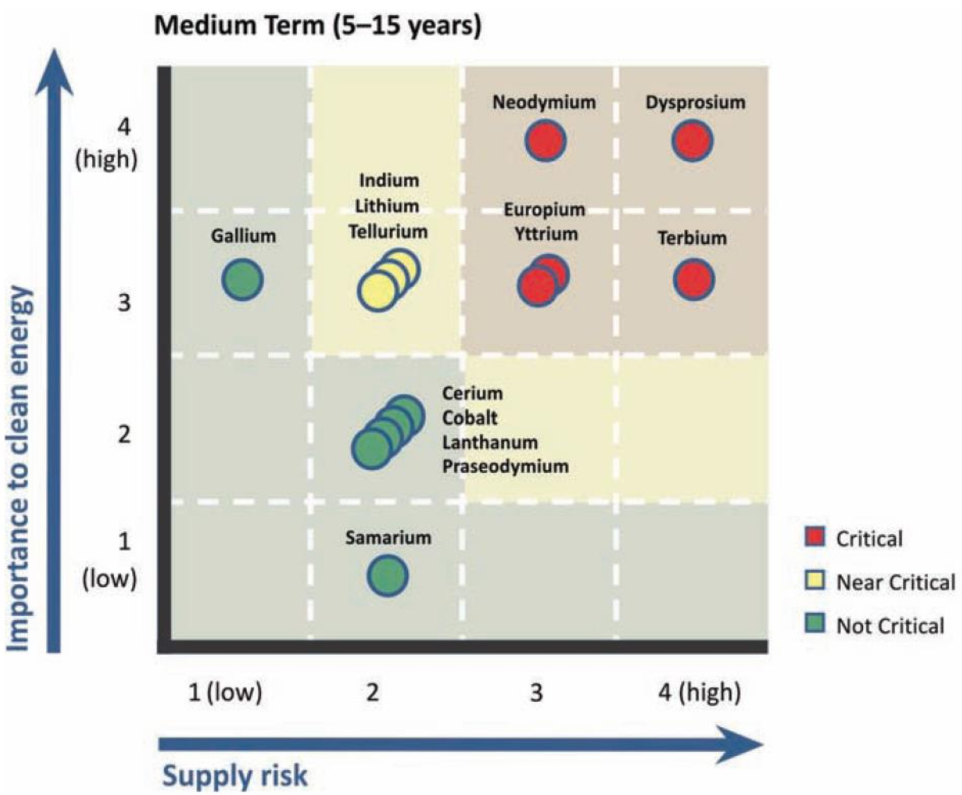
Source: report EU commission “Critical raw materials for the EU” (2010)

Rare earths are critical raw materials (2014)



Source: report EU commission “Critical raw materials for the EU” (2014)

Rare earths as critical raw materials (DOE)



Five rare earths are identified as very critical:

- neodymium
- europium
- terbium
- dysprosium
- yttrium

Essential for permanent magnets and lamp phosphors

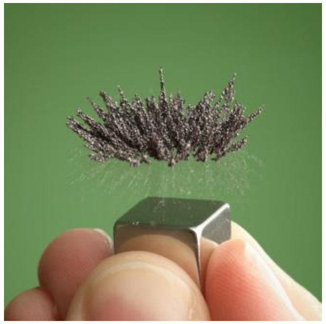
Source: report US Department of Energy(2010)

Early applications: mixed rare earths

- Mainly lanthanum and cerium
- **Catalyst industry**
  - Stabilization of zeolites for fluid cracking catalysts (FCC) during steam regeneration
- **Metallurgy (mischmetall)**
  - Graphite nodularization in cast iron
  - Ultimate desulfurization of steels
  - Lighter flints made of iron-mischmetall alloy
  - Grain growth inhibition in light metals
  - Battery alloys (NiMH)
- **Glass industry**
  - Polishing powder (CeO_2)

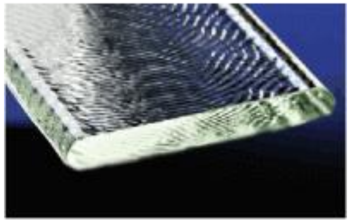
Modern applications: pure rare earths

- **Permanent magnets**
  - NdFeB (Nd,Pr,Dy)
  - SmCo (Sm)   (< 2% of market)



- **Phosphors**
  - Phosphors for trichromatic fluorescent lamps (Y, Eu, Tb, La, Ce)
  - Phosphors for CRTs (color television, computer monitors (Eu,Y)
  - X-ray intensifying screens (Gd,La,Tb)

- **Glass industry**
  - Optical glass (La)

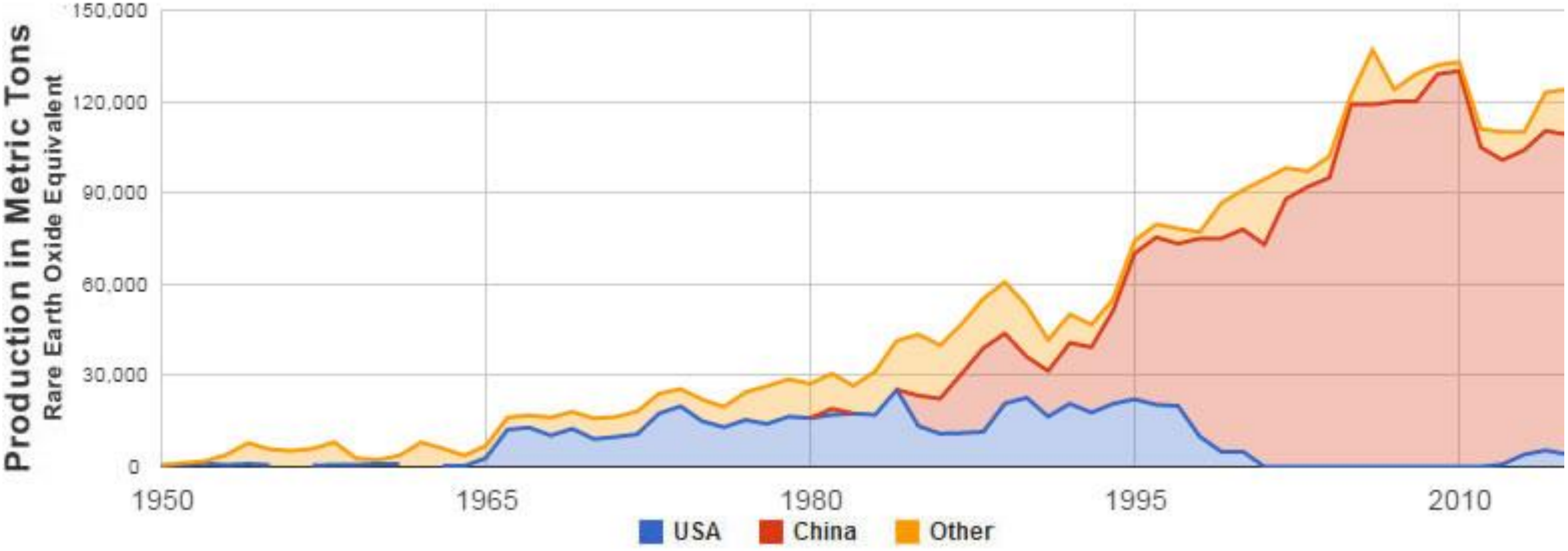


REE usage by application

Application	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Other
Magnets			23.4	69.4			2	0.2	5		
Battery alloys	50	33.4	3.3	10	3.3						
Metallurgy	26	52	5.5	16.5							
Auto catalysts	5	90	2	3							
FCC	90	10									
Polishing powder	31.5	65	3.5								
Glass additives	24	66	1	3						2	4
Phosphors	8.5	11				4.9	1.8	4.6		69.2	
Ceramics	17	12	6	12						53	
Others	19	39	4	15	2		1			19	

(source: Lynas Corporation)[8]

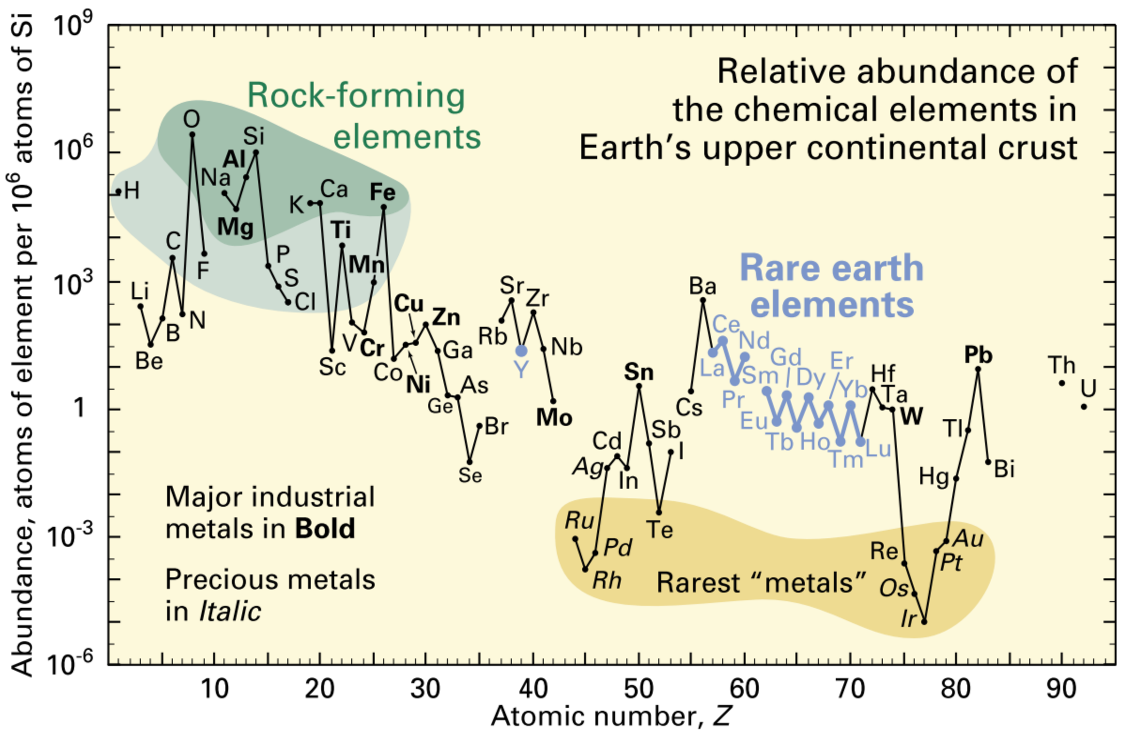
Global production of rare-earth oxides



REO production numbers do not reflect availability of individual REEs
Total REO production: 120,000 tonnes/year

Source: http://geology.com/articles/rare-earth-elements/

Relative abundance of rare earths



- Rare earths are not rare (Ce is as abundant as Cu)
- Elements become scarcer with increasing atomic number *Z* (abundance decreases over lanthanide series)
- Elements with an even *Z* are more abundant than elements with odd Z (*Oddo-Harkins rule*)

REE content of selected minerals (%)

REE	Bastnasite Mountain Pass, USA	Bastnasite Bayan Obo, China	Monazite Mt. Weld, Australia	Xenotime Lehat, Malaysia	High Y RE laterite Longnan, China	Low Y RE laterite Xunwu, China	Loparite Kola Peninsula Russia
La	33.8	23.0	25.5	1.2	1.8	43.4	25.0
Ce	49.6	50.0	46.7	3.1	0.4	2.4	50.5
Pr	4.1	6.2	5.3	0.5	0.7	9.0	5.0
Nd	11.2	18.5	18.5	1.6	3.0	31.7	15.0
Sm	0.9	0.8	2.3	1.1	2.8	3.9	0.7
Eu	0.1	0.2	0.4	Trace	0.1	0.5	0.1
Gd	0.2	0.7	<0.1	3.5	6.9	3.0	0.6
Tb	0.01	0.1	<0.1	0.9	1.3	Trace	Trace
Dy	0.03	0.1	0.1	8.3	6.7	Trace	0.6
Ho	0.01	Trace	Trace	2.0	1.6	Trace	0.7
Er	0.01	Trace	Trace	6.4	4.9	Trace	0.8
Tm	0.01	Trace	---	1.1	0.7	Trace	0.1
Yb	0.01	Trace	---	6.8	2.5	0.3	0.2
Lu	Trace	Trace	---	1.0	0.4	0.1	0.2
Y	0.1	Trace	<0.1	61.0	65.0	8.0	1.3

Consequences of REE abundances

- To get 1 ton of Eu_2O_3 from bastnäsite, one needs to produce (and sell) the following amounts of REOs (tons):

La_2O_3	300
CeO_2	450
Pr_6O_{11}	38
Nd_2O_3	118
Sm_2O_3	7.3
Gd_2O_3	1.4
Y_2O_3	0.9

Ref.: P. Falconnet, Basic and Applied Aspects of Rare Earths, 1989 (Venice –Italy) p. 27

Balance problem

- **Balance problem** = demand and supply of the individual rare-earth elements (REEs) have to be equal at any time
- Also called: *Balancing problem*
- Became an issue when applications shifted from the use of mixed rare earths to pure rare earths
- Of importance for REE manufacturers
- Concept introduced by P. Falconnet (Rhône-Poulenc)
  P. Falconnet, Less-Common Metals **111**, 9-15 (1985).

- Literature:

  K. Binnemans et al. *JOM* 65, 846-848 *(*2013).
  K. Binnemans and P.T. Jones, *J. Sust. Metall.* 1, 29–38 (2015).

Balance problem

- Ideal situation: perfect balance between demand and production of all REE elements
- Market in balance corresponds to lowest price for any REE: production costs are shared by all elements
- Market in balance is very difficult to obtain, because of changes in demand by changes in applications
- Compromise between two alternatives:
  - Adjusting overall production to optimize production costs: creates surpluses of some REEs and shortages of other REEs (increases price of elements high in demand)
  - Increasing overall production to meet demand of all REEs and stockpiling other REEs (increases overall price)

K. Binnemans and P.T. Jones, *J. Sust. Metall.* 1, 29–38 (2015).

Neodymium-driven LREE market

- Present light REE market is driven by demand for Nd for NdFeB magnets (about 25,000 tons)
- Sufficient quantities of REE ores have to be mined to produce at least 25,000 tons of Nd
- **Excess of La, Ce, Sm**

Dysprosium-driven HREE market

- Balance problem is less a problem for HREE market (much smaller volumes than LREE)
- Present heavy REE market is driven by demand for Dy for NdFeB magnets (about 1,600 tons)
- Excess of Gd, Ho, Tm, Yb, Lu (stockpiled)

Rapidly changing REE markets

- New applications can bring REE market rapidly out of balance
- Presently: market driven by Nd and Dy
- Before 1985:
  - No Nd metal produced in industrial quantities
  - No industrial applications for Dy
- 1980s: market driven by Sm
  (SmCo magnets)
- 1960s-1970s: market driven by Eu
  (color TV screens)
- **Decline in use of Eu, Y, Tb in lamp phosphors**

Balance problem: possible solutions

- **Diversification of REE resources**
- **Recycling**
- Substitution
- Reduced use
- New high-volume applications for La, Ce

K. Binnemans and P.T. Jones, *J. Sust. Metall.* 1, 29–38 (2015).

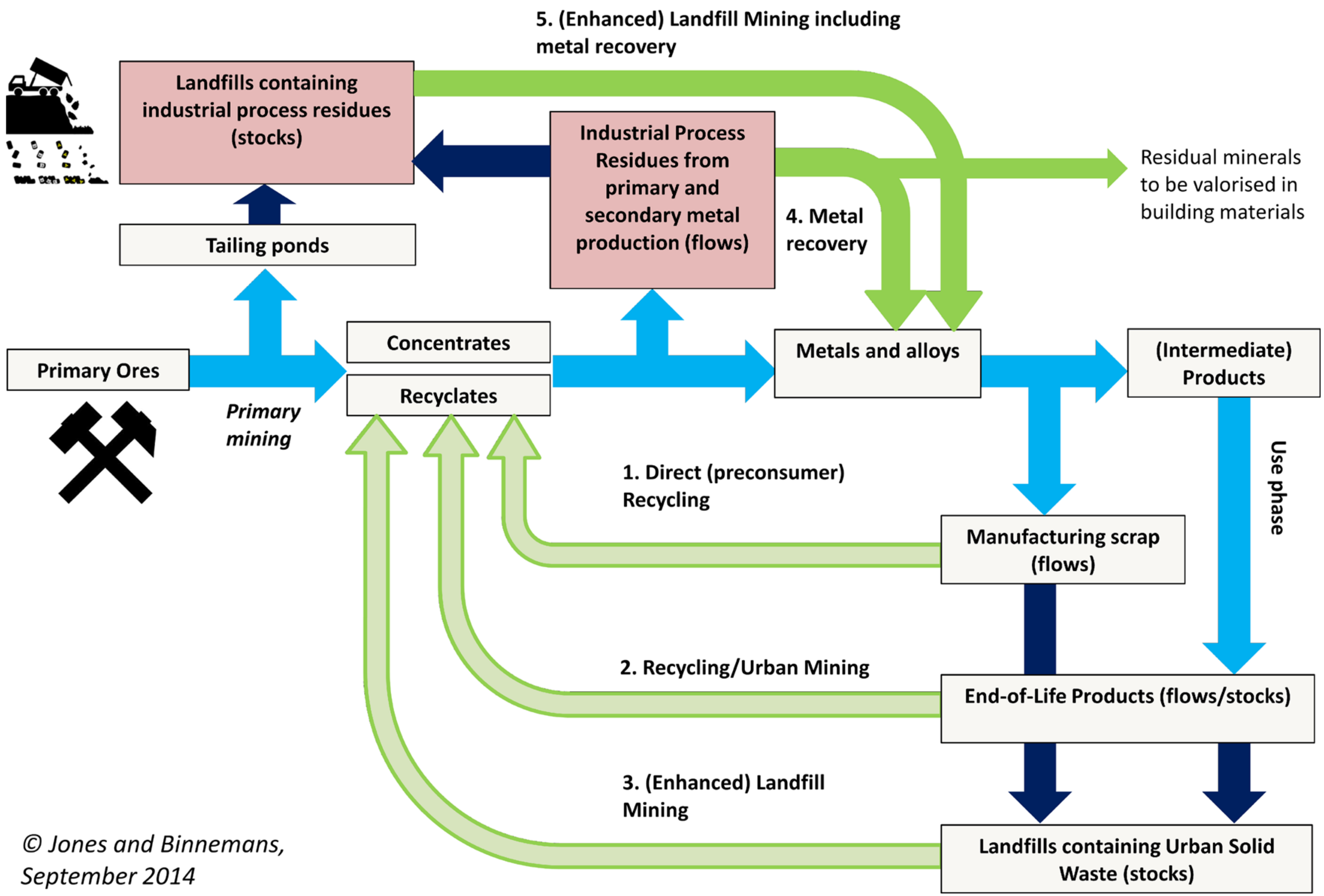
Diversification of REE resources

- Bastnäsite $(Ce,La)(CO_3)F$
- Monazite $(Ce,La,Nd,Th)PO_4$
- Xenotime YPO_4
- Ion-adsorption clays

- Eudialyte $Na_4(Ca,Ce)_2(Fe^{2+},Mn,Y)ZrSi_8O_{22}(OH,Cl)_2$
- Allanite $(Ce,Ca,Y)_2(Al,Fe^{3+})_3(SiO_4)_3OH$
- Loparite $(Ce,La,Na,Ca,Sr)(Ti,Nb)O_3$

- Combining REE ores of different deposits allows making REE concentrate that reflects better market needs of individual REEs

Recycling = closing the materials loop



Recycling and the balance problem

- Recycling of NdFeB magnets to recover Nd and Dy means that less primary ores have to be mined to ensure supply of Nd and Dy
- Less mining means less over production of cerium, samarium, ...
- Recycling of Eu, Tb, Y from lamp phosphors helps to maintain the balance of HREE

Ref: K. Binnemans et al. JOM 65, 846–848 (2013)

Recycling of rare earths

- *Less than 1%* of the REEs were being recycled in 2011
  inefficient collection, technological issues, lack of incentives
- Main sources:
  - lamp phosphors (**Eu**, **Tb**, **Y**, Gd, La, Ce)
  - permanent magnets (**Nd**, Pr, Tb, **Dy**)
  - nickel metal hydride batteries (**La**, Ce) + Ni

Key reference

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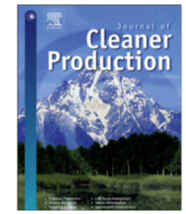

Review

Recycling of rare earths: a critical review

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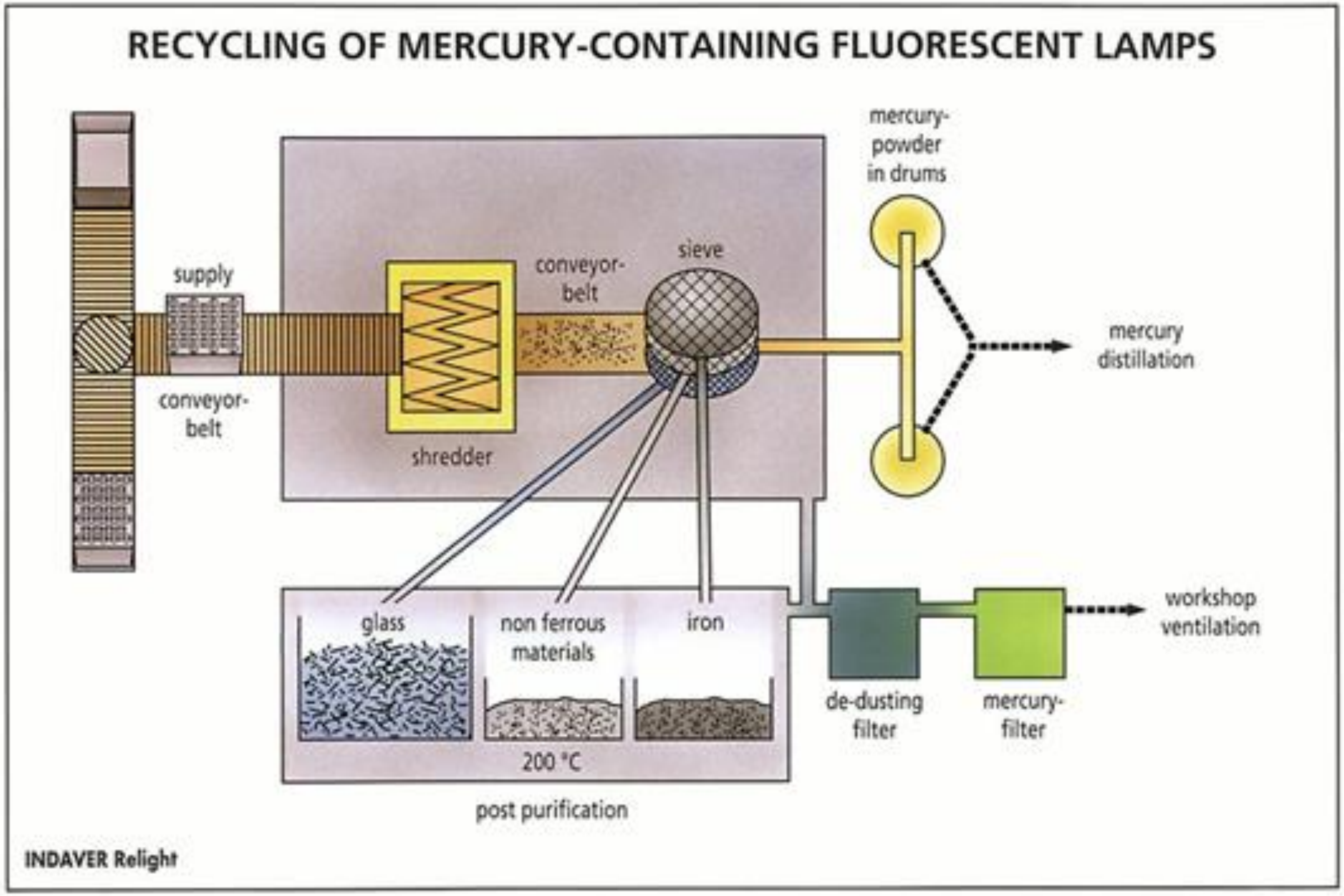
Lamp phosphors

Year	Phosphors		
1960	$Ca_5(PO_4)_3Cl:Sb^{3+},Mn^{2+}$ (white)		
1974	$BaMg_2Al_{16}O_{27}:Eu^{2+}$	$CeMgAl_{10}O_{19}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$
1990	$BaMgAl_{10}O_{17}:Eu^{2+}$ $(Sr,Ca)_5(PO_4)_3Cl:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$ $CeMgAl_{10}O_{19}:Tb^{3+}$ $(Gd,Ce)MgB_5O_{10}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$
2005	$BaMgAl_{10}O_{17}:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$	$Y_2O_3:Eu^{3+}$

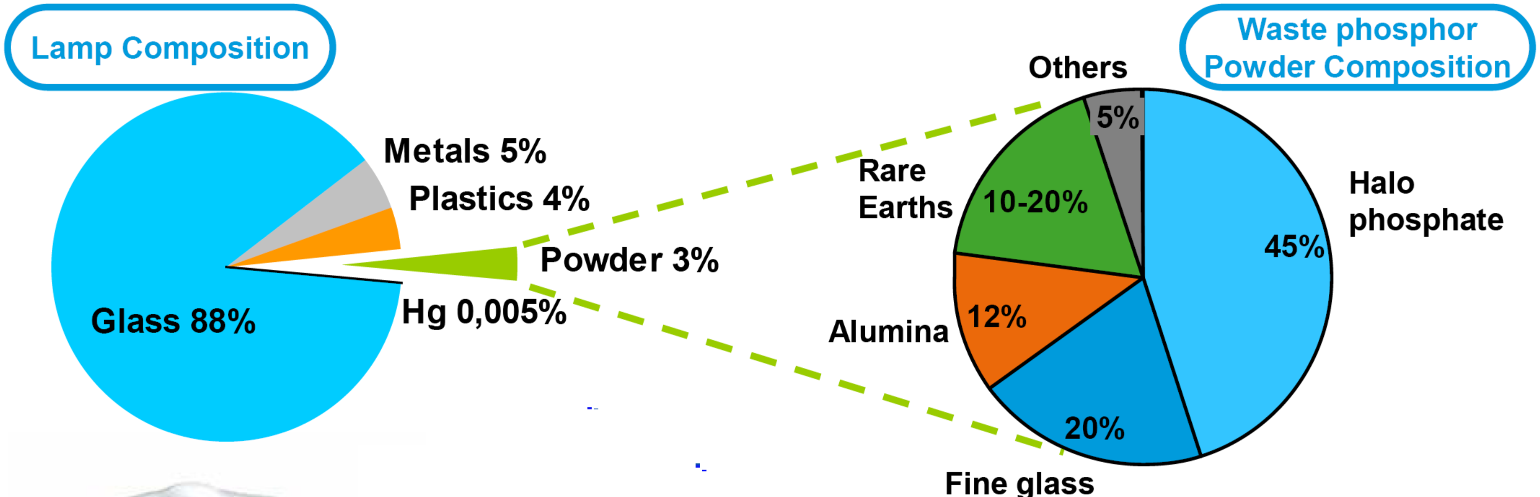
Different options for recycling of lamp phosphors

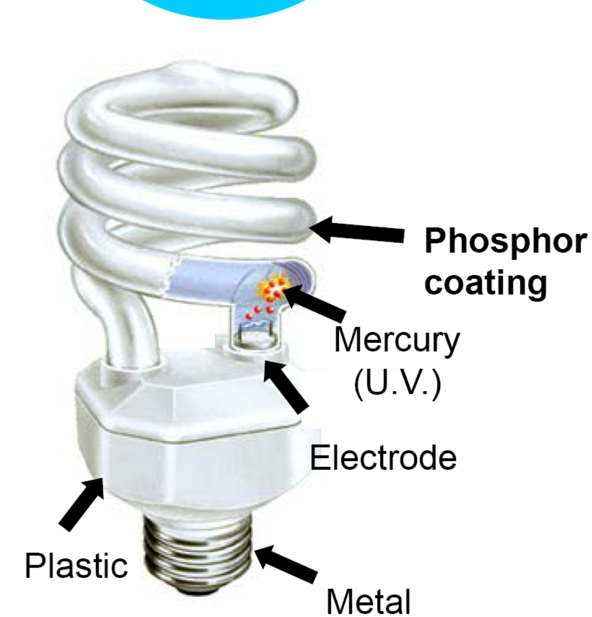
- Direct re-use
- Separation of phosphors in individual components
- **Recovery of REE content**

Crushing and sieving of fluorescent lamps



Composition of waste lamp phosphor fraction

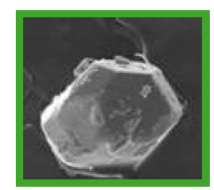




RE based phosphors

BAM
$BaMgAl_{10}O_{17}:Eu^{2+}$

YOX
$Y_2O_3:Eu^{3+}$



LAP
$(La,Ce)PO_4:Tb^{3+}$
CAT
$CeMgAl_{10}O_{19}:Tb^{3+}$

Rhodia
Member of the Solvay group

Composition of waste lamp phosphor fraction

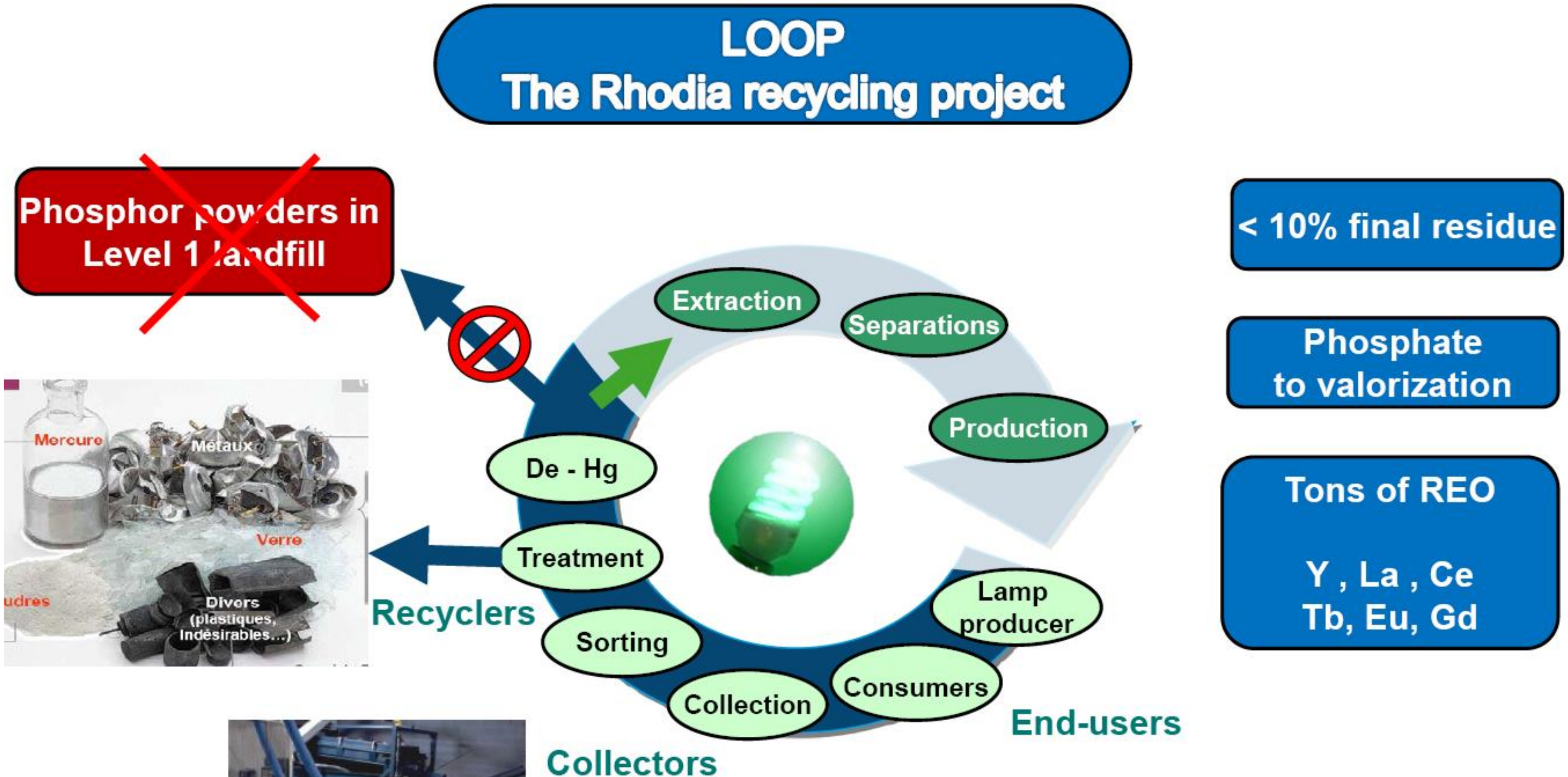
Per 100 g (without SiO_2)*

Eu_2O_3	**1 g**
Gd_2O_3	2 g
CeO_2	2 g
Y_2O_3	**22 g**
La_2O_3	1 g
Tb_4O_7	**<1 g**
Al_2O_3	7 g
CaO	35 g
BaO	1 g
MnO	1 g
Sb_2O_3	1 g
P_2O_5	27 g

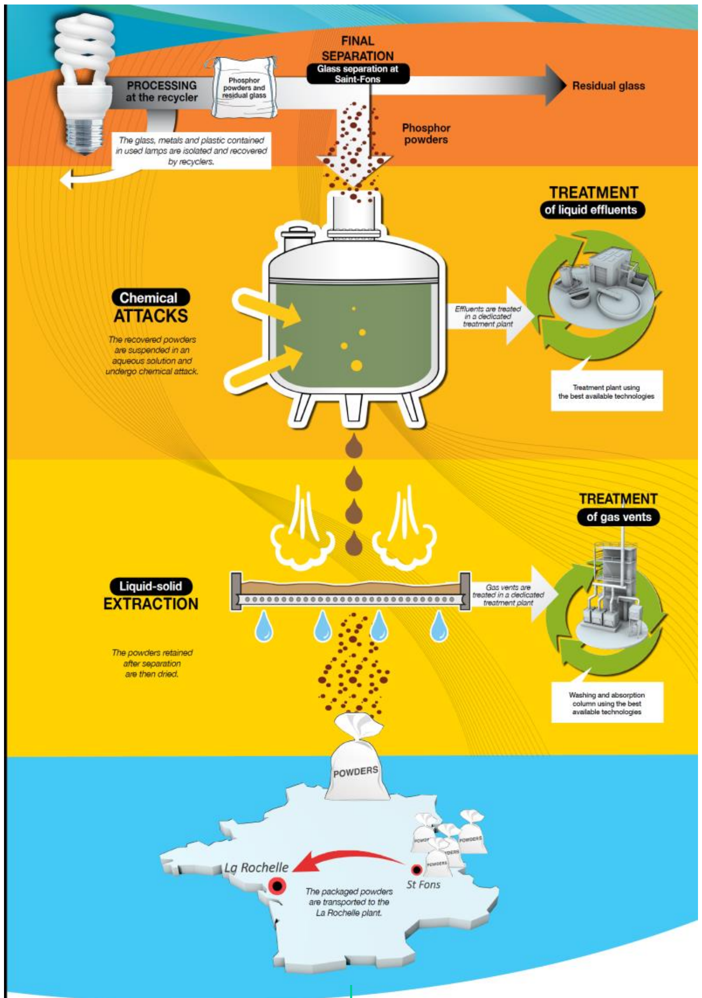
Name	Compound	Waste fraction (wt%)	Value
BAM	$BaMgAl_{10}O_{17}:Eu^{2+}$	5	Low
LAP	$LaPO_4:Ce^{3+},Tb^{3+}$	5	**High**
CAT	$(Ce,Tb)MgAl_{11}O_{19}$	5	**High**
YOX	$Y_2O_3:Eu^{3+}$	**20**	**High**
HALO	$(Sr,Ca)_{10}(PO_4)_6(Cl,F)_2:Sb^{3+}, Mn^{2+}$	**40-50**	Low
Others	SiO_2 / Al_2O_3 / Hg (trace)	15-25	Low

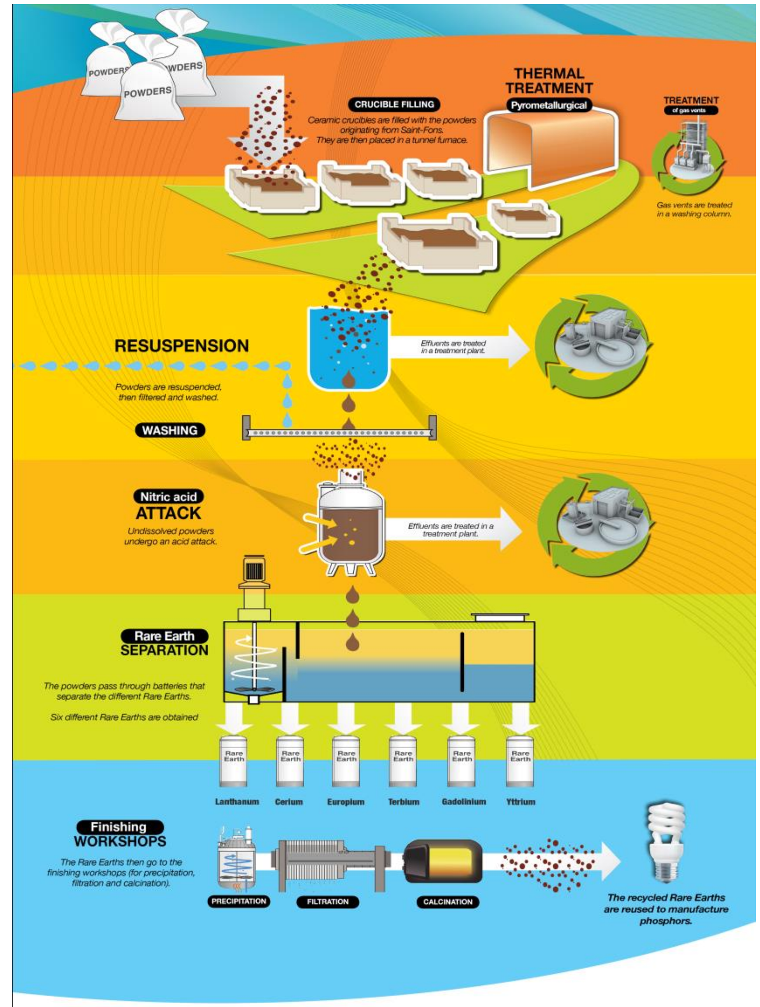
*Source: Solvay patent: *J. J. Braconnier and A. Rollat, Solvay, European Patent,* EP 2419377 A1, 2012.

Solvay's lamp recycling process

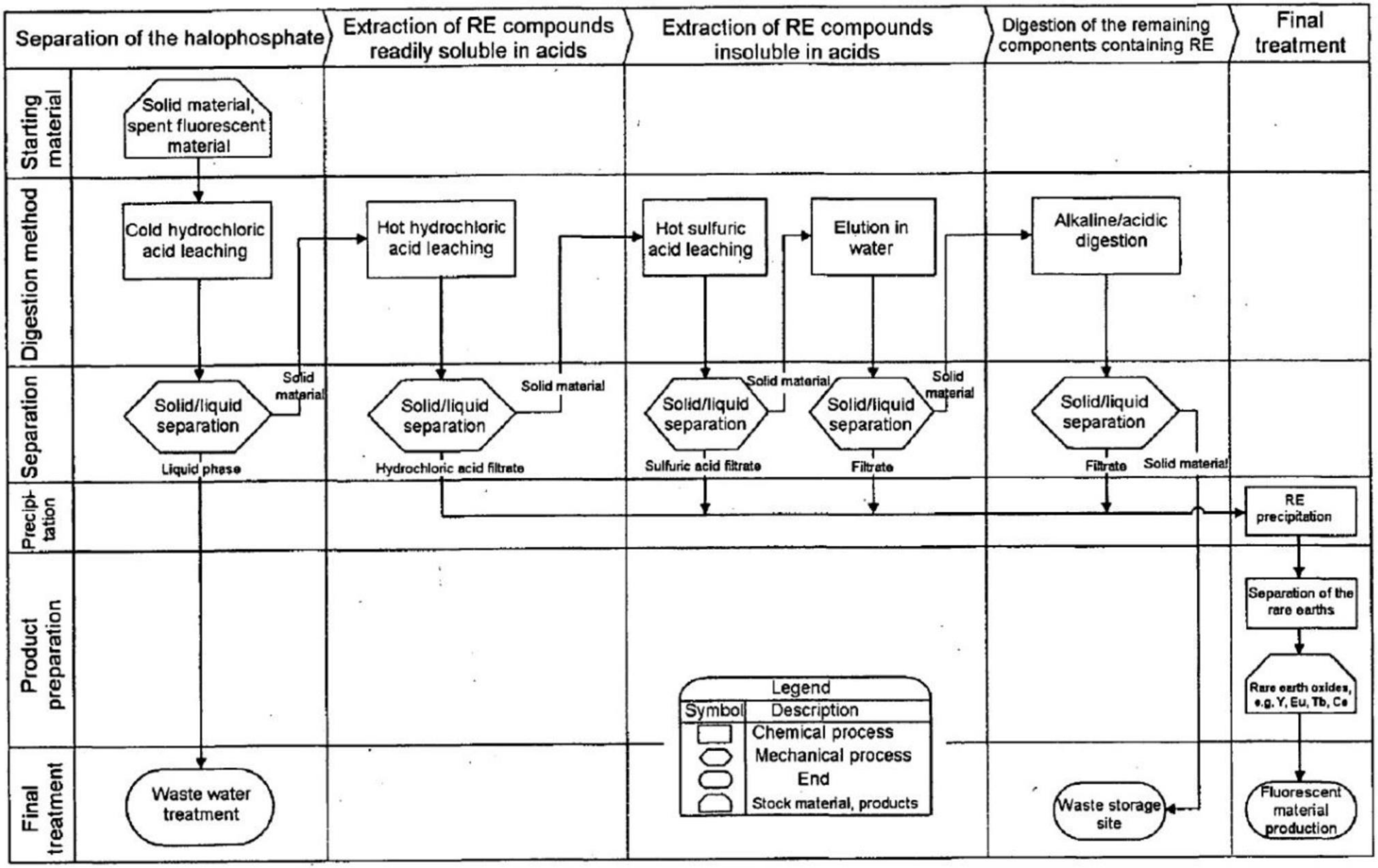


Solvay's lamp recycling process





http://www.solvay.com/en/binaries/Process-Saint-Fons-151777.pdf
http://www.solvay.com/en/binaries/Process-La-Rochelle-EN-151498.pdf

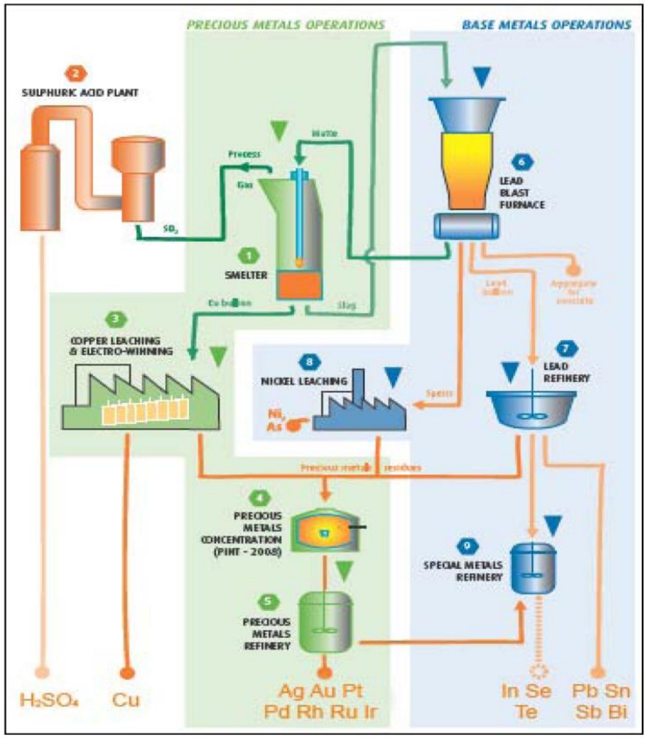


Ref.: Otto, R., Wojtalewicz-Kasprzac, A., 2012. Method for Recovery of Rare Earths From Fluorescent Lamps. US Patent 2012/0027651 A1

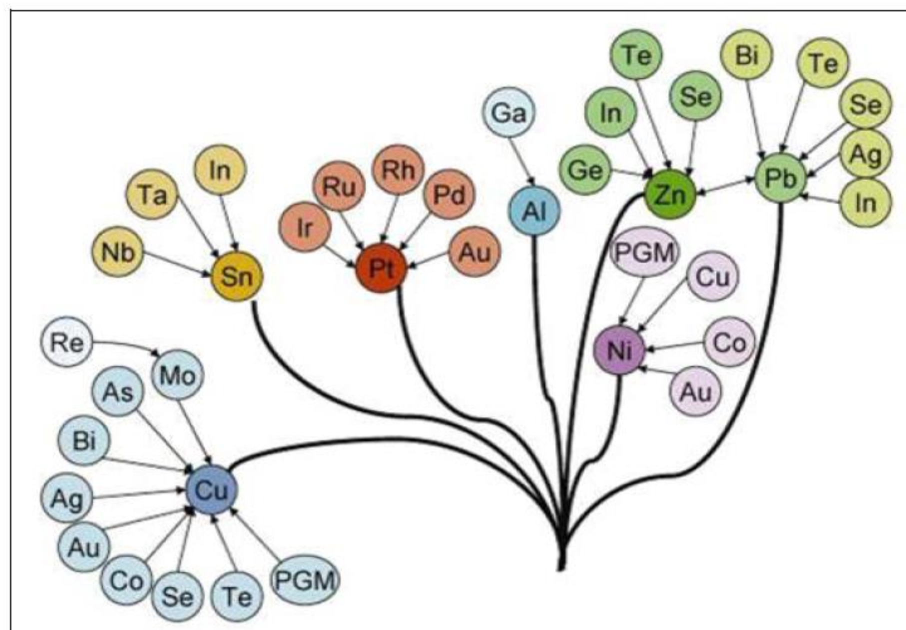
Recycling of REE from NdFeB magnets

- Main focus on NdFeB magnets (98-99% of the market)
  During pyrometallurgical recycling of metals from electronic scrap and used catalysts, they end up as oxides in slags. Concentration in oxide slags is too low for recycling
- In many applications, the amount of REE per item is low (a few grams), so that deep-level dismantling is recommended to recover REE-containing objects.
- Dismantling can be automated (e.g. Hitachi)

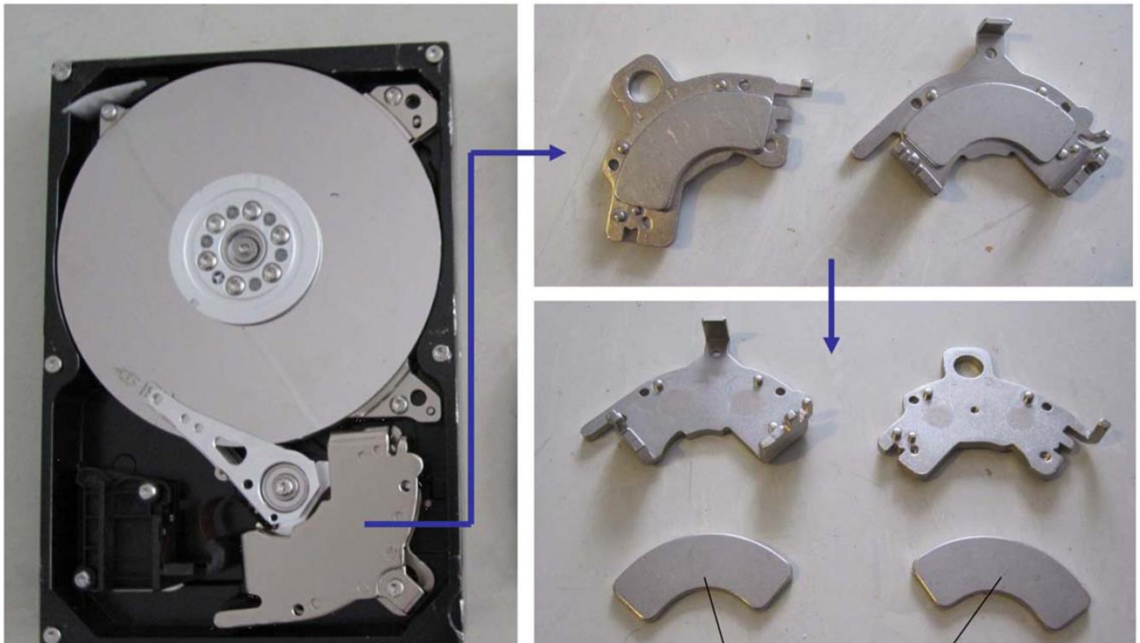
Umicore's metal recycling plant (Hoboken, Belgium)



- REEs lost to oxide slags (low concentration)
- slags used as building material



Amounts of rare earths in electronic devices



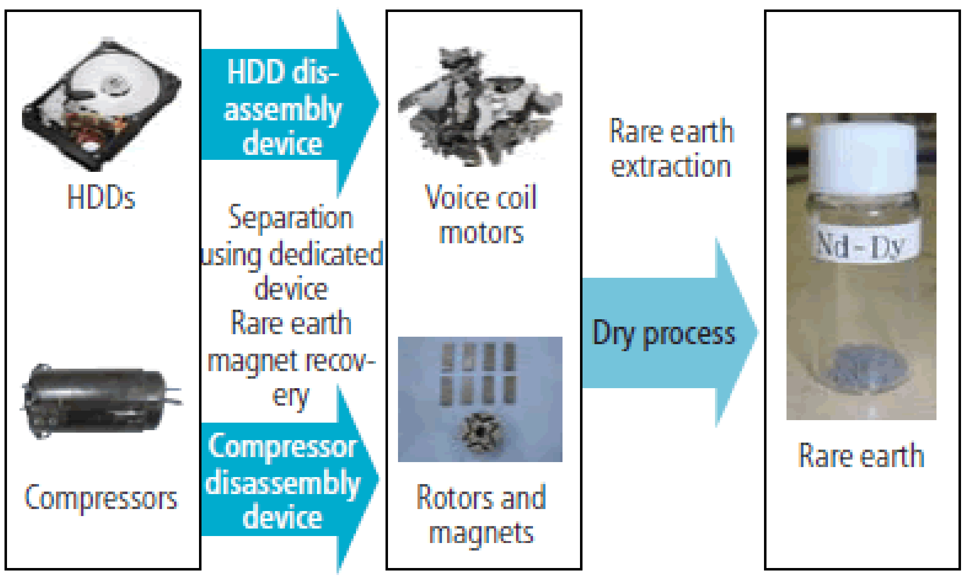
Neodymium iron boron magnets

Magnets: 2 wt.% of HDD
REE: 0.6 wt.% of HDD

Source: Öko-Institut

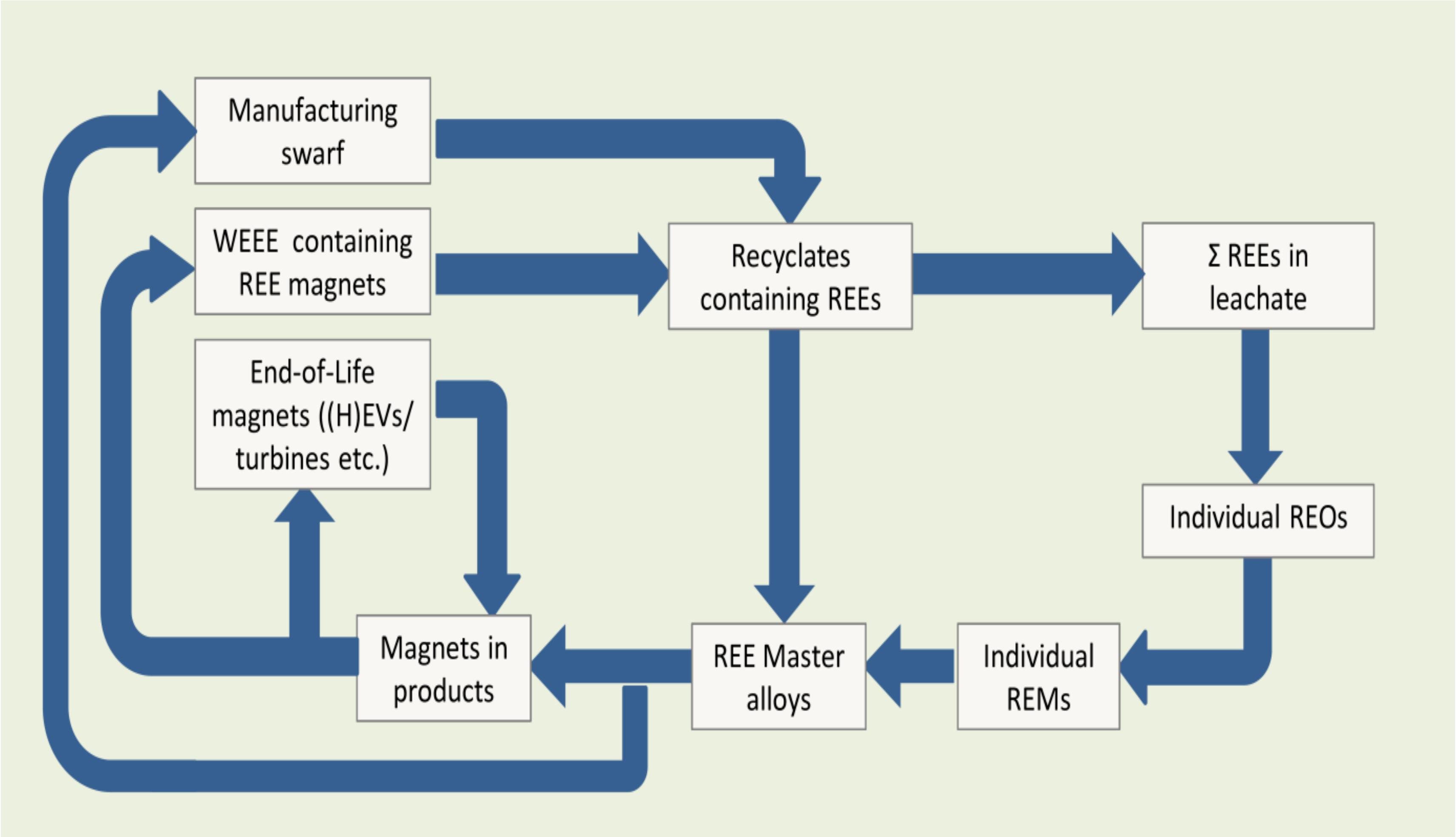
Mobile phones: only 0.1 to 0.25 g of REEs

Dismantling by Hitachi



Source: Hitachi

Flow sheet for recycling of magnets



Different options for recycling of magnets

- Direct re-use in current form/shape
- Reprocessing of alloys to magnets after hydrogen decrepitation
- Hydrometallurgical methods (dissolution in acids)
- Pyrometallurgical methods (high temperatures)

Direct re-use in current form/shape

- Advantages:
  - Most economical way of recycling (low energy input, no consumption of chemicals)
  - No waste generated
- Disadvantages:
  - Only for large easily accessible magnets (wind turbines, large electric motors and generators in hybrid and electric vehicles
  - Not available in large quantities in scrap today

Reprocessing of alloys to magnets after hydrogen decrepitation

- Advantages
  - Less energy input required than for hydrometallurgical and pyrometallurgical routes
  - No waste generated
- Disadvantages
  - Not applicable to mixed scrap feed, which contains magnets with large compositional variations
  - Not applicable to oxidized magnets

For more information: see lecture of Allan Walton

Hydrometallurgical methods

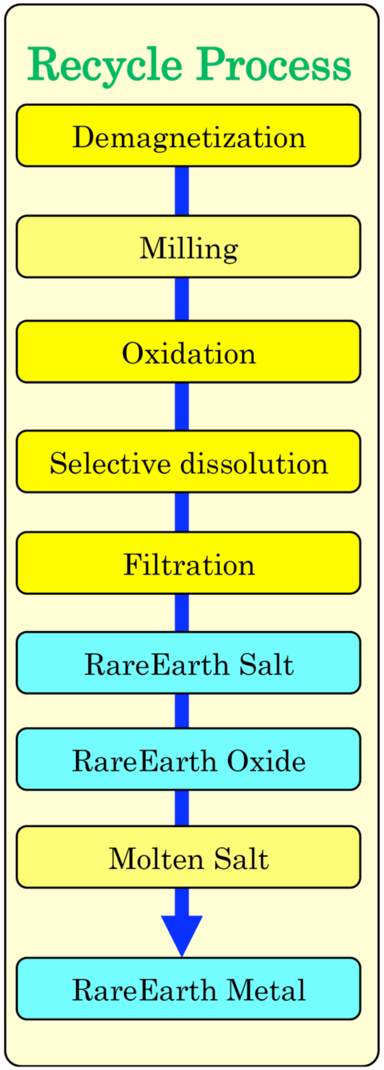
- Advantages
  - Generally applicable to all types of magnet compositions
  - Applicable to non-oxidized and oxidized alloys
  - Same processing steps as those for extraction of rare earths from primary ores
- Disadvantages
  - Many process steps required before obtaining new magnets
  - Consumption of large amounts of chemicals
  - Generation of large amounts of waste water

Pyrometallurgical methods (liquid metal extraction)

- Advantages
  - Generally applicable to all types of magnet compositions
  - No generation of waste water
  - Fewer processing steps than hydrometallurgical methods
  - Direct melting allows obtaining master alloys
  - Liquid metal extraction allows obtaining REEs in metallic state
- Disadvantages
  - Larger energy input required
  - Direct smelting and liquid metal extraction cannot be applied to oxidized magnets
  - Electroslag refining and the glass slag method generate large amounts of solid waste

Magnet recycling by SANTOKU

- SANTOKU Corporation has opened in 2012 a plant in Tsuruga (Japan) for recycling Nd and Dy from magnets
  - Motor magnets (air conditioners)
  - Magnet production scrap
- Demagnetization by heating (6 hours at 573 K)
- Milling under 75 micron by jaw crusher and pulverizer
- Oxidation by stirring for 12 hours in an alkaline solution
- Selective dissolution in HCl
- Magnet alloys prepared by molten salt electrolysis



Source: SANTOKU

Different options for recycling of NiMH batteries

- Hydrometallurgical routes
- Pyrometallurgical routes

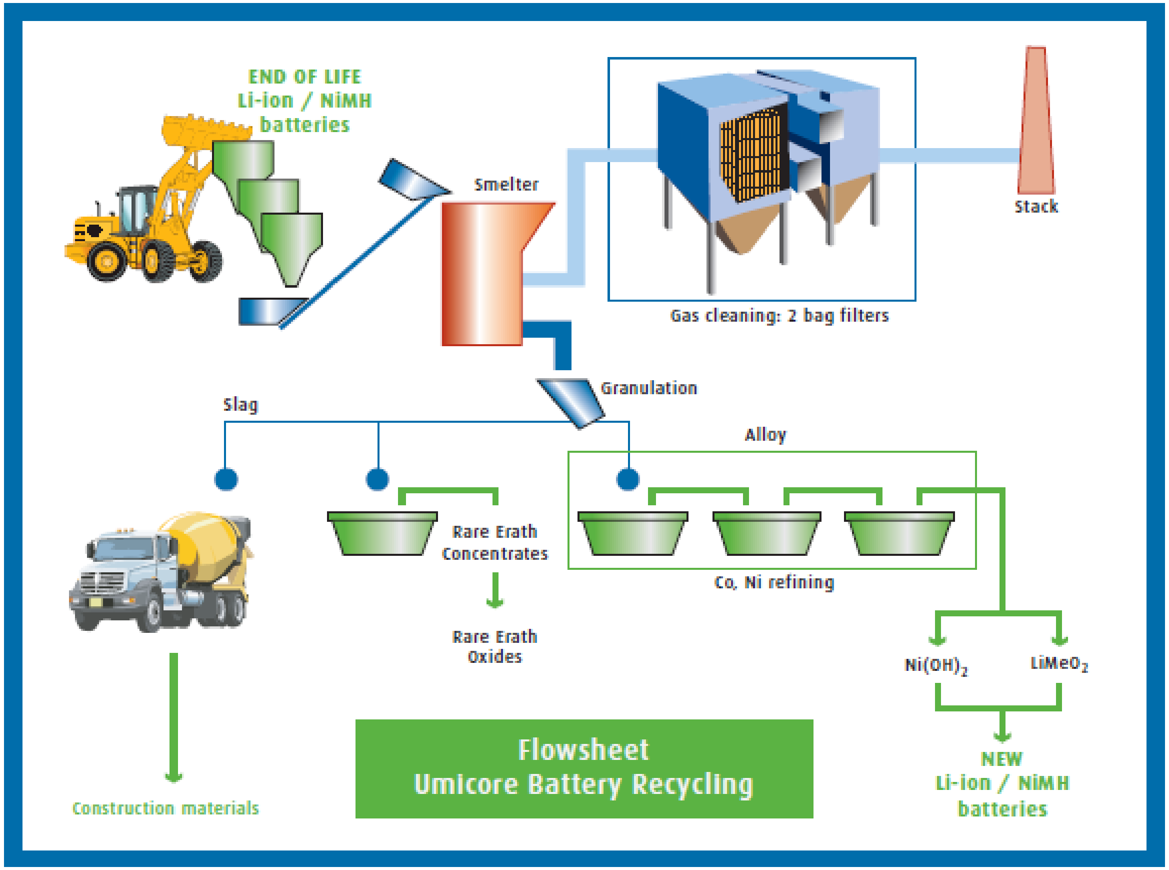
Hydrometallurgical routes

- Advantages
  - Low investment costs
  - Recycling possible of different waste fractions (cathode and anode materials, metals from casing) that can be marketed separately
- Disadvantages
  - Many manual operations are required for dismantling of batteries and separating the different components
  - Large consumption of chemicals

Pyrometallurgical routes

- Advantages
  - Well-developed technology
  - Energy recovery from plastic casings and other organic components
  - Same processing steps used for extracting REEs from slags as from primary ores
- Disadvantages
  - High investment cost for furnace
  - REEs need to be extracted from slags
  - REEs are obtained as mixtures and further separation is required

Recycling process for NiMH/ Li-ion batteries @Umicore



Source: Maurits van Camp (Umicore)

Recycling process for NiMH/ Li-ion batteries @Umicore

- Process developed for NiMH batteries
  - First industrial scale process
- Co-operation with Solvay
  - Umicore produces REE-concentrate
  - Umicore separates REO from harmful elements
  - Solvay refines REE concentrate
  - For EOL Portable NiMH batteries only
- Process of recovery of REE is not compatible with process of recovery PGM from exhaust catalysts

Balance problem: possible solutions

- *Diversification of REE resources*
- *Recycling*
- **Substitution**
- **Reduced use**
- **New high-volume applications for La, Ce**

K. Binnemans and P.T. Jones, *J. Sust. Metall.* 1, 29–38 (2015).

Substitution

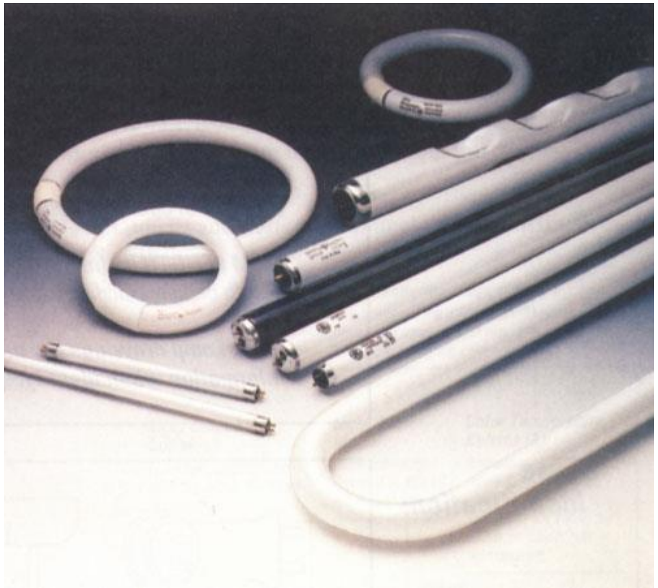
- Replace critical metals by less critical ones
- NdFeB magnets

  Nd → Pr

  Dy → Tb
- SmCo magnets
- Non-REE magnets

- Fluorescent lamps → LEDs
- CRT → LCD → OLED

Fluorescent lamps



Lamp phosphors

Year	Phosphors		
1960	$Ca_5(PO_4)_3Cl:Sb^{3+},Mn^{2+}$ (white)		
1974	$BaMg_2Al_{16}O_{27}:Eu^{2+}$	$CeMgAl_{10}O_{19}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$
1990	$BaMgAl_{10}O_{17}:Eu^{2+}$ $(Sr,Ca)_5(PO_4)_3Cl:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$ $CeMgAl_{10}O_{19}:Tb^{3+}$ $(Gd,Ce)MgB_5O_{10}:Tb^{3+}$	$Y_2O_3:Eu^{3+}$
2005	$BaMgAl_{10}O_{17}:Eu^{2+}$	$(La,Ce)PO_4:Tb^{3+}$	$Y_2O_3:Eu^{3+}$

LEDs

- Blue LED + yellow phosphor = white light

  blue LED: GaN or GaInN
  yellow phosphor: Ce-doped $Y_3Al_5O_{12}$ (Ce:YAG)

Reduced use

- Less Dy in NdFeB magnets:
  by grain boundary diffusion, Dy is concentrated near grain boundaries
- Dy-free NdFeB magnets
- Removal of Nd from concentrate for making mischmetal

New high-volume applications for La, Ce

- Compared to the other REEs, La and Ce are very abundant and cheap
- For western REE mining companies, La and Ce content of their ores often have negative effect on REE basket value
- Oversupply of La and Ce can be partially overcome by developing new high-volume applications
- Research towards new applications must be facilitated

Water purification

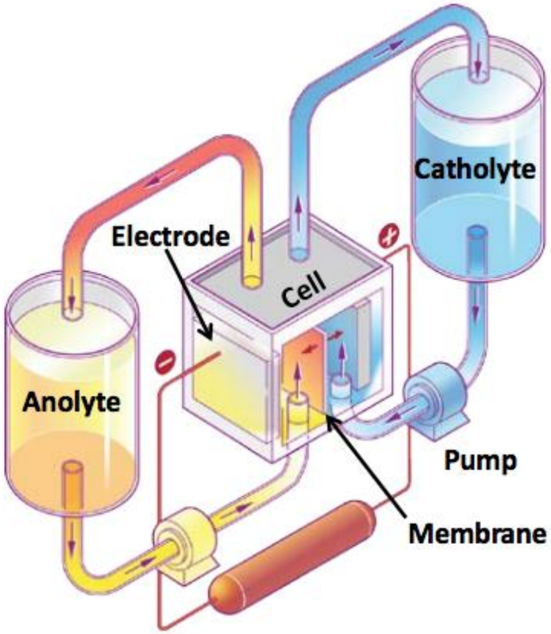
- Phosphate removal from swimming pools
- Rapid and stable precipitation of P in municipal and industrial wastewater facilities
- Concentrated $LaCl_3$ (or mixed $REECl_3$ solution)
- $LaPO_4$ has a very low solubility in water

sorbx® 100

Molycorp

Cerium redox flow batteries

- Batteries with large storage capacities: store electricity produced by wind turbines and solar cells
- Chemical energy is stored in dissolved redox couples in external tanks
- Easy upscaling (larger tank volumes)
- Charge/discharge in electrolysis cell
  with ion-exchange membranes
- Cerium redox flow batteries
  (*balance problem*)



Source: newenergyandfuel.com

Cerium redox flow batteries

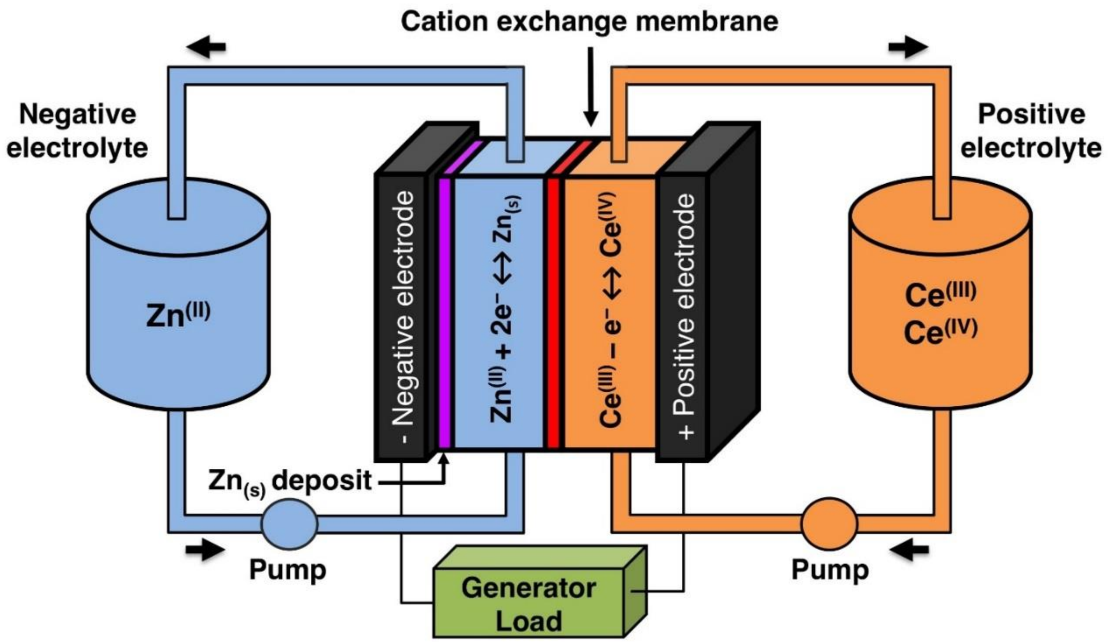


Diagram of the Divided Zinc-Cerium Flow Battery

Source: wikipedia

Thermal stabiliser of PVC (La, Ce)

- Stabilisers added to PVC to protect against thermal decomposition during processing > 200 °C, and to protect against heat and UV irradiation during use.
- (Pb), (Cd), Zn, Sn, Ba, Ca salts (mainly stearates)
- La and Ce salts have stronger stabilising effect than Ca and Zn salts at the same dose.
- About 3 kg of REE stabilisers for 1 tonne of PVC
- (global PVC production: >40 million of tonnes)

Conclusions

- Availability of REEs is determined not only by production volumes of REE ores, but also by natural abundances of individual REEs
- Matching supply and demand of all REEs is a challenge (**balance problem**)
- Present market is driven by Nd and Dy demand
- New applications could change market situation rapidly
- Solutions to balance problem

  New REE ores

  Recycling

  Substitution and reduced use

  New high-volume applications (La, Ce)