KU LEUVEN

RECOVERY OF RARE EARTHS FROM INDUSTRIAL WASTE RESIDUES

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THIRD INTERNATIONAL
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THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

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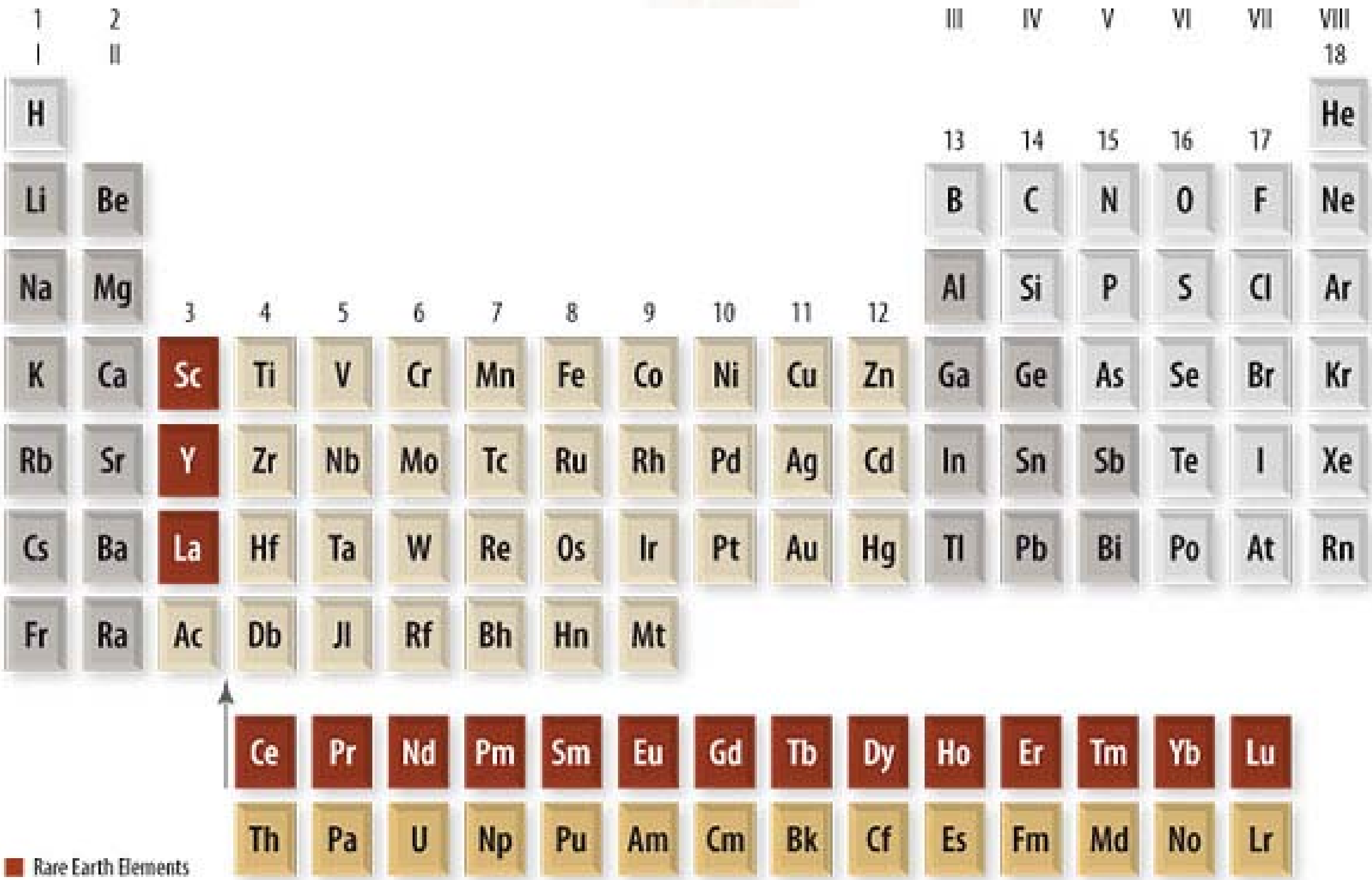
SMaRT-PRO²

Rare earths in the periodic table



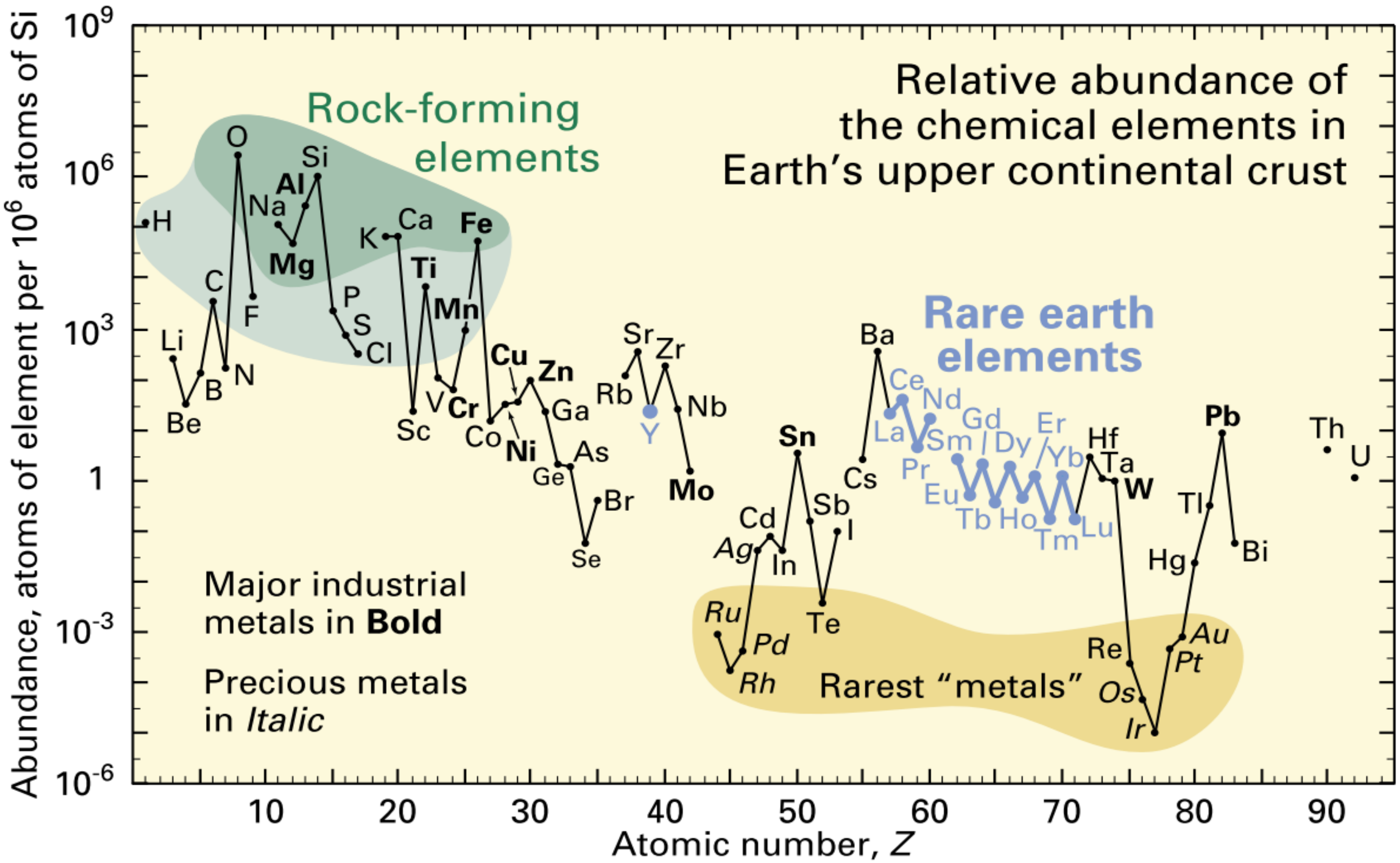
Lanthanides = series of elements La-Lu
Rare earths = lanthanides + Y + Sc
REEs = rare-earth elements

Rare earths: names and symbols

Name	Chemical Symbol	Atomic Number (Z)
Scandium	Sc	21
Yttrium	Y	39
Lanthanum	La	57
Cerium	Ce	58
Praseodymium	Pr	59
Neodymium	Nd	60
Promethium	Pm	61
Samarium	Sm	62
Europium	Eu	63
Gadolinium	Gd	64
Terbium	Tb	65
Dysprosium	Dy	66
Holmium	Ho	67
Erbium	Er	68
Thulium	Tm	69
Ytterbium	Yb	70
Lutetium	Lu	71

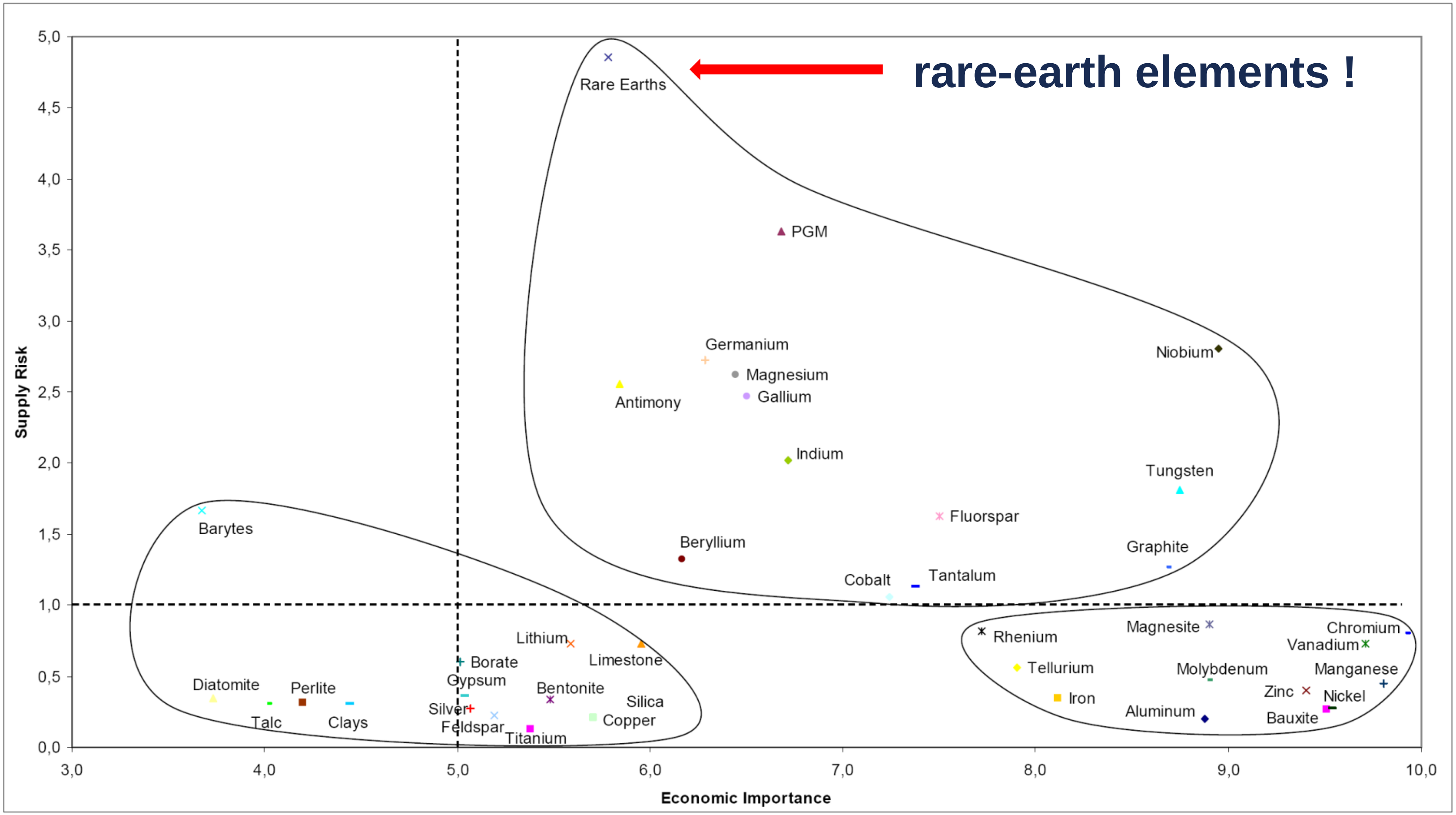
Rare earths: what do they look like?

Rare earths are not rare!



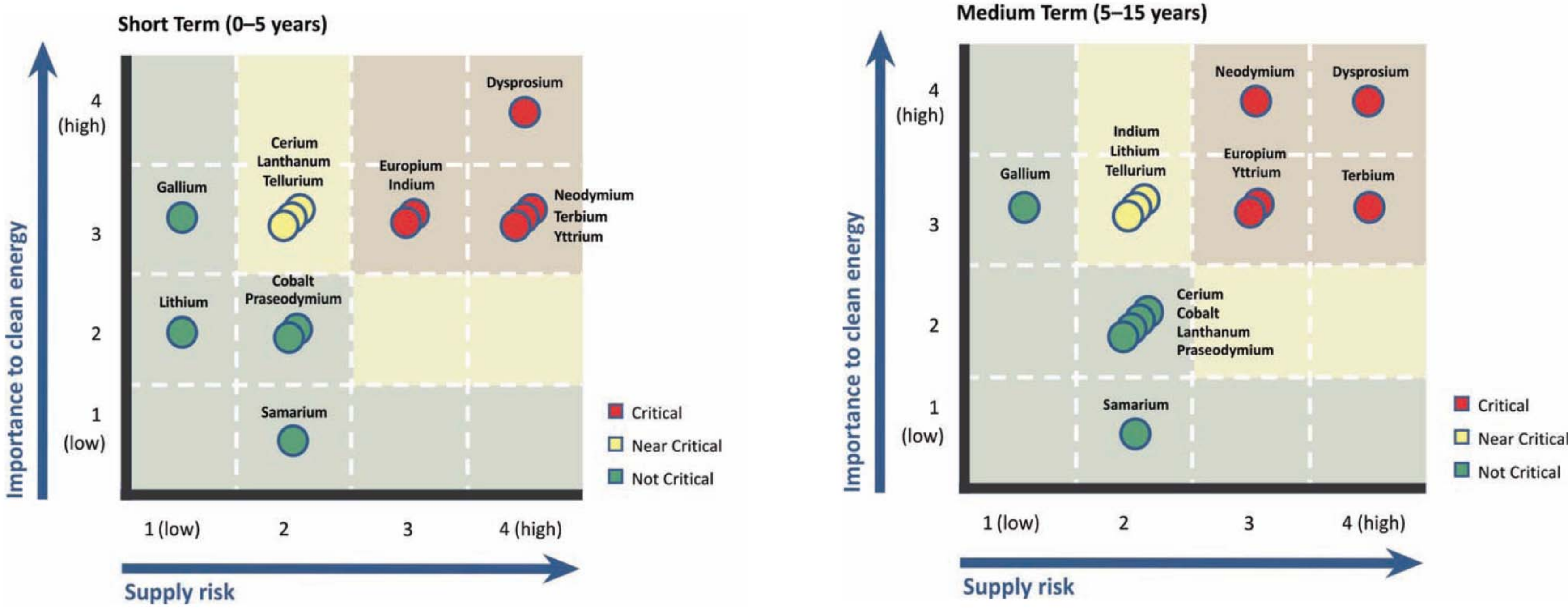
Source: US Geological Survey

Rare earths as critical raw materials



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

Supply risk of rare earths

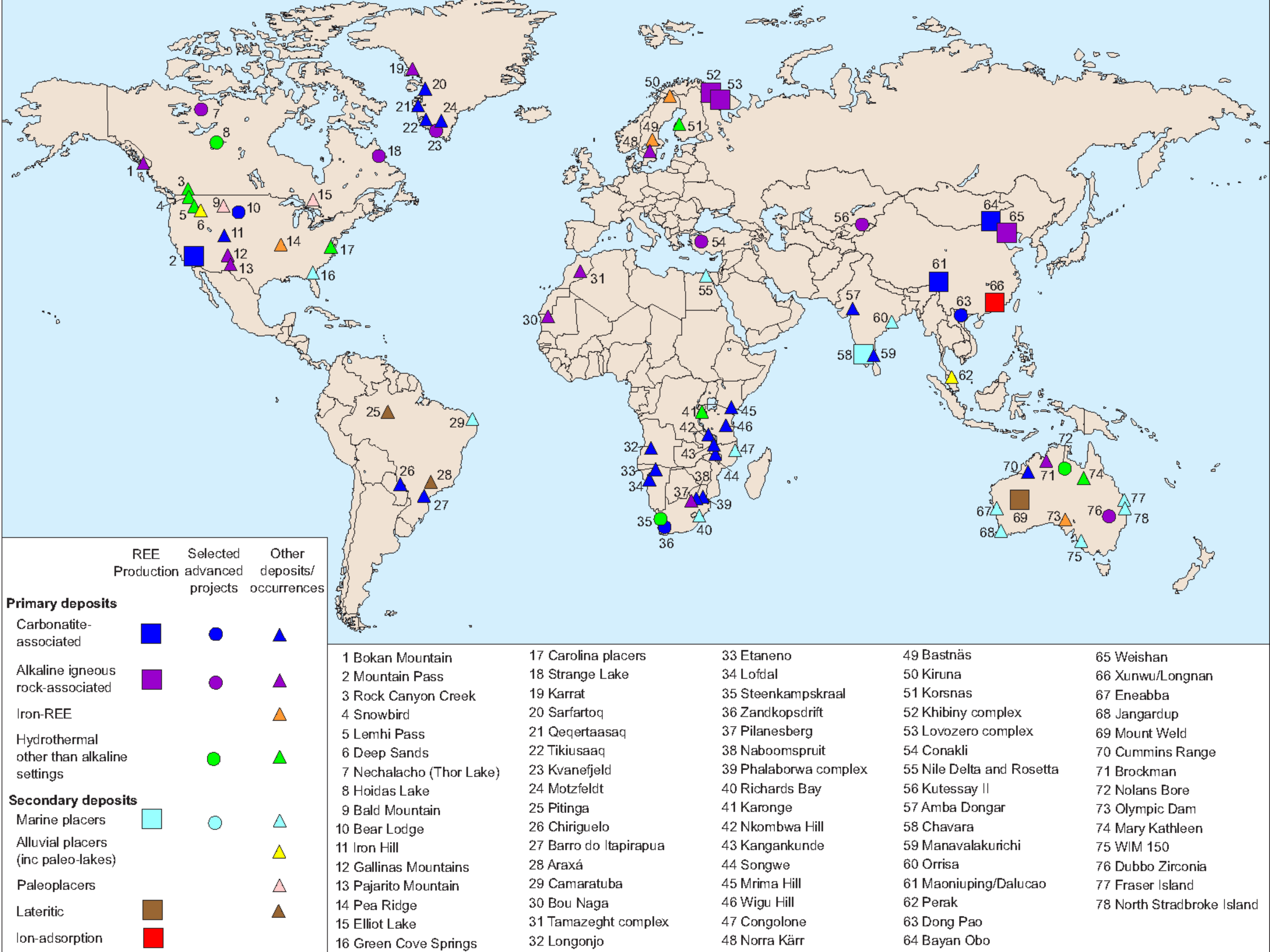


Source: report US Department of Energy(2010)

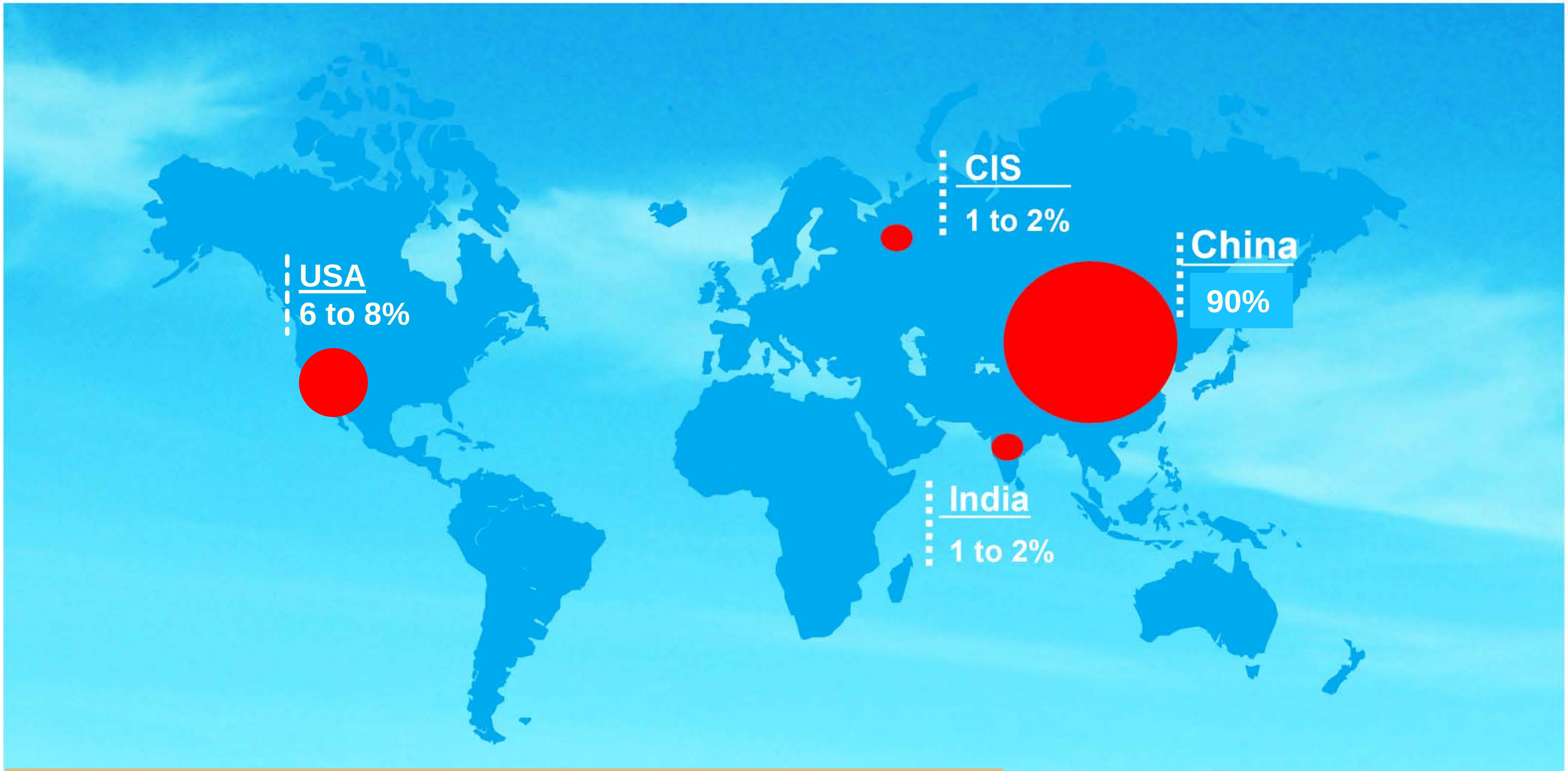
Rare-earth ore minerals

- **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 $(Ce,La,Na,Ca,Sr)(Ti,Nb)O_3$


REE Production
Selected advanced projects
Other deposits/ occurrences
Primary deposits
Carbonatite-associated
Alkaline igneous rock-associated
Iron-REE
Hydrothermal other than alkaline settings
Secondary deposits
Marine placers
Alluvial placers (inc paleo-lakes)
Paleoplacers
Lateritic
Ion-adsorption
1 Bokan Mountain
2 Mountain Pass
3 Rock Canyon Creek
4 Snowbird
5 Lemhi Pass
6 Deep Sands
7 Nechalacho (Thor Lake)
8 Hoidas Lake
9 Bald Mountain
10 Bear Lodge
11 Iron Hill
12 Gallinas Mountains
13 Pajarito Mountain
14 Pea Ridge
15 Elliot Lake
16 Green Cove Springs
17 Carolina placers
18 Strange Lake
19 Karrat
20 Sarfartoq
21 Qeqertaasaq
22 Tikiusaaq
23 Kvanefjeld
24 Motzfeldt
25 Pitinga
26 Chiriguelo
27 Barro do Itapirapua
28 Araxá
29 Camaratuba
30 Bou Naga
31 Tamazeght complex
32 Longonjo
33 Etaneno
34 Lofdal
35 Steenkampskraal
36 Zandkopsdrift
37 Pilanesberg
38 Naboomspruit
39 Phalaborwa complex
40 Richards Bay
41 Karonge
42 Nkombwa Hill
43 Kangankunde
44 Songwe
45 Mrima Hill
46 Wigu Hill
47 Congolone
48 Norra Kärr
49 Bastnäs
50 Kiruna
51 Korsnas
52 Khibiny complex
53 Lovozero complex
54 Conakli
55 Nile Delta and Rosetta
56 Kutessay II
57 Amba Dongar
58 Chavara
59 Manavalakurichi
60 Orrisa
61 Maoniuping/Dalucao
62 Perak
63 Dong Pao
64 Bayan Obo
65 Weishan
66 Xunwu/Longnan
67 Eneabba
68 Jangardup
69 Mount Weld
70 Cummins Range
71 Brockman
72 Nolans Bore
73 Olympic Dam
74 Mary Kathleen
75 WIM 150
76 Dubbo Zirconia
77 Fraser Island
78 North Stradbroke Island

REE production is dominated by China



No problem of resources, but a real supply problem

REEE export quota

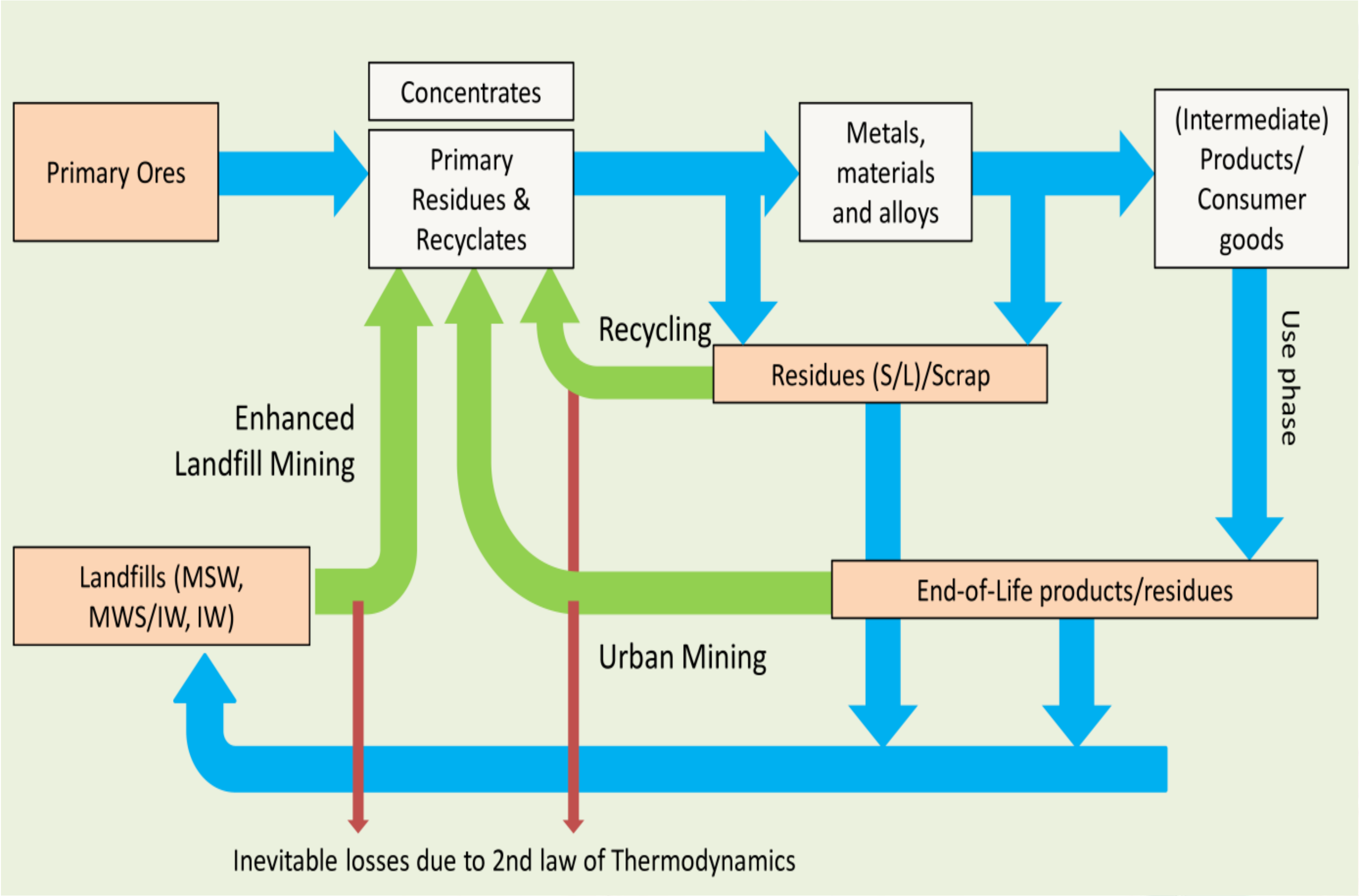
- China introduced REE expert quota due to sharp increase in domestic demand
- Export quota:
  - 2009: 50145 tonnes
  - 2012: 31130 tonnes
- Quota do not reflect availability of individual REEs

  Balance problem
- Quota cause serious problems for REE users outside of China

How to tackle the REE supply challenge?

- To *substitute* critical rare earths by less critical metals
- To invest in *sustainable primary mining* from old or new REE deposits
- *Technospheric mining*
  - *direct recycling* of pre-consumer manufacturing REE scrap/residues
  - *urban mining* of post-consumer (often complex multi-material) End-of-Life products
  - *landfill mining* of historic (and future) urban and industrial waste residues containing REEs

Technospheric mining



Source: P.T. Jones et al. *JOM*, **63** (12), 14-15, 2011.

Rare-earth recycling

- *Less than 1%* of the REEs were being recycled in 2011

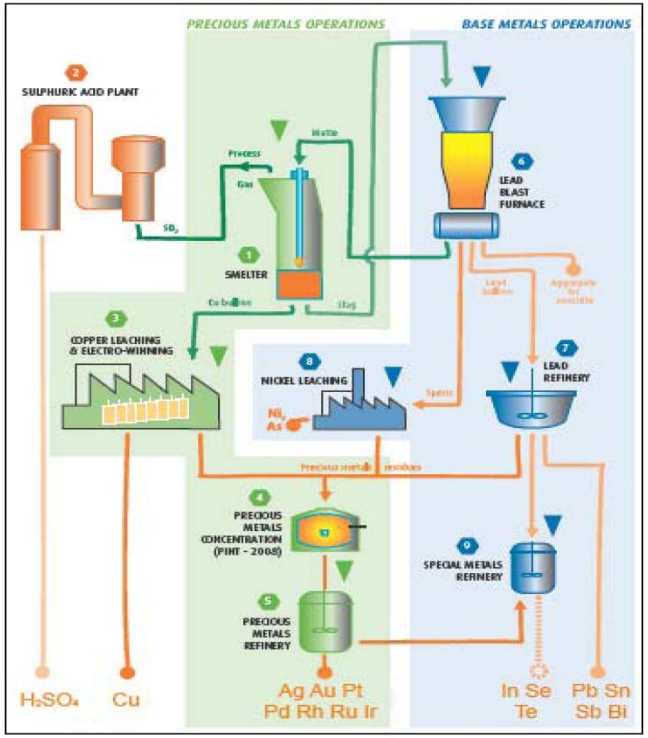
  inefficient collection, technological issues, lack of incentives
- Main sources:
  - permanent magnets (**Nd**, Pr, Tb, **Dy**)
  - nickel metal hydride batteries (**La**, Ce)
  - lamp phosphors (**Eu**, **Tb**, **Y**, Gd, La, Ce)
- Advantages:
  - no issues with radioactive thorium
  - composition of the obtained REE concentrate is less complex
  - high concentrations, small volumes

Review: K. Binnemans et al. *Journal of Cleaner Production* (2013), in press.

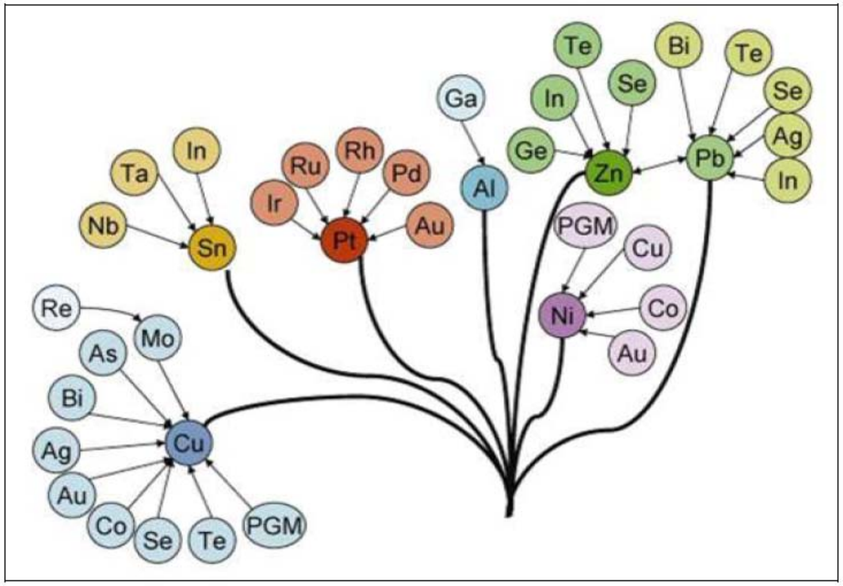
Industrial waste residues

- Much lower concentrations of REEs than the End-of-Life consumer goods considered for recycling (often well below 1% of REOs)
- Volumes of these residues are enormous; total amounts of REEs are large
- Main waste streams:
  - metallurgical slags
  - bauxite residue (red mud)
  - phosphogypsum
  - mine tailings
  - waste water streams

Metallurgical slags (e.g. Umicore)

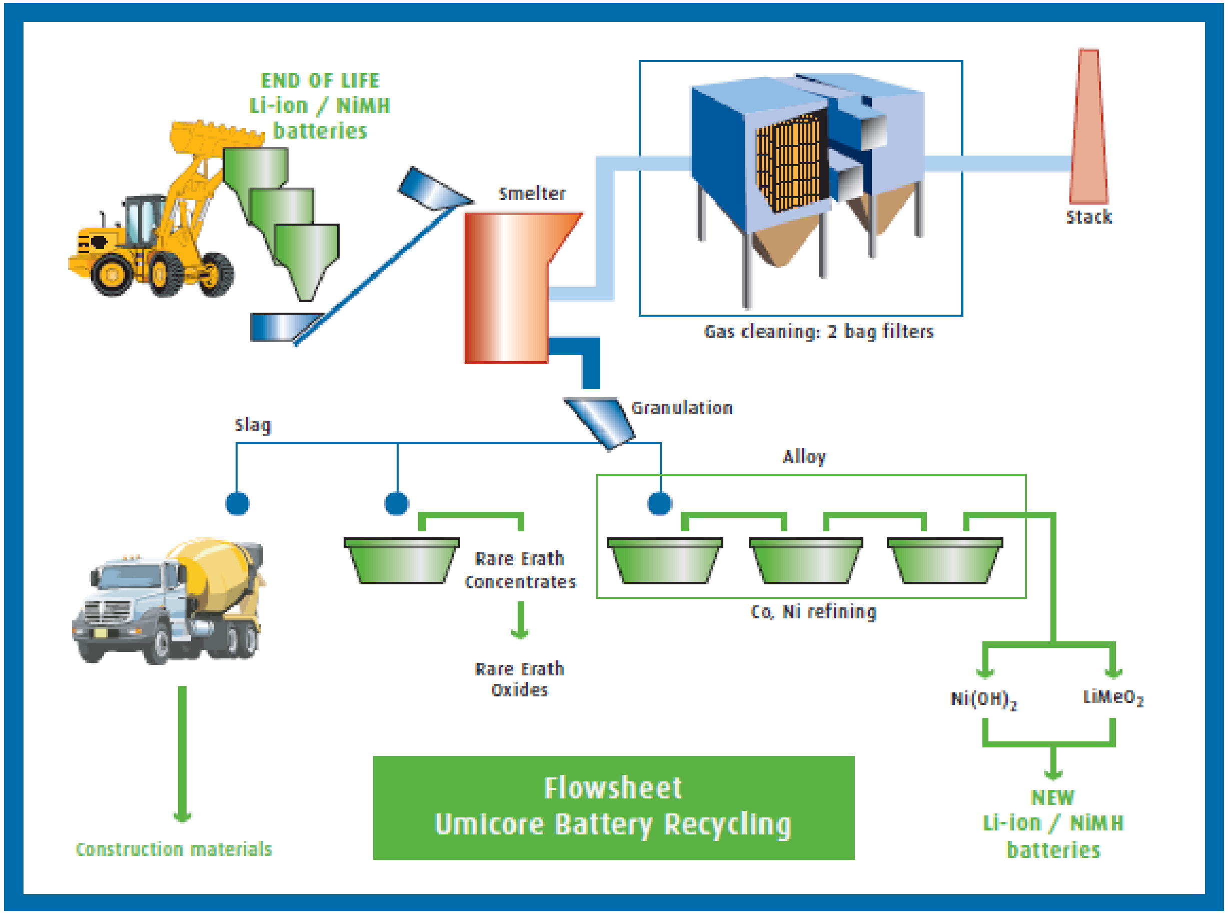


umicore
materials for a better life



- REEs lost to oxide slags (low concentration)
- mainly Ce (automobile catalysts)
- Slags used as building material

Slags of battery smelter (Umicore)

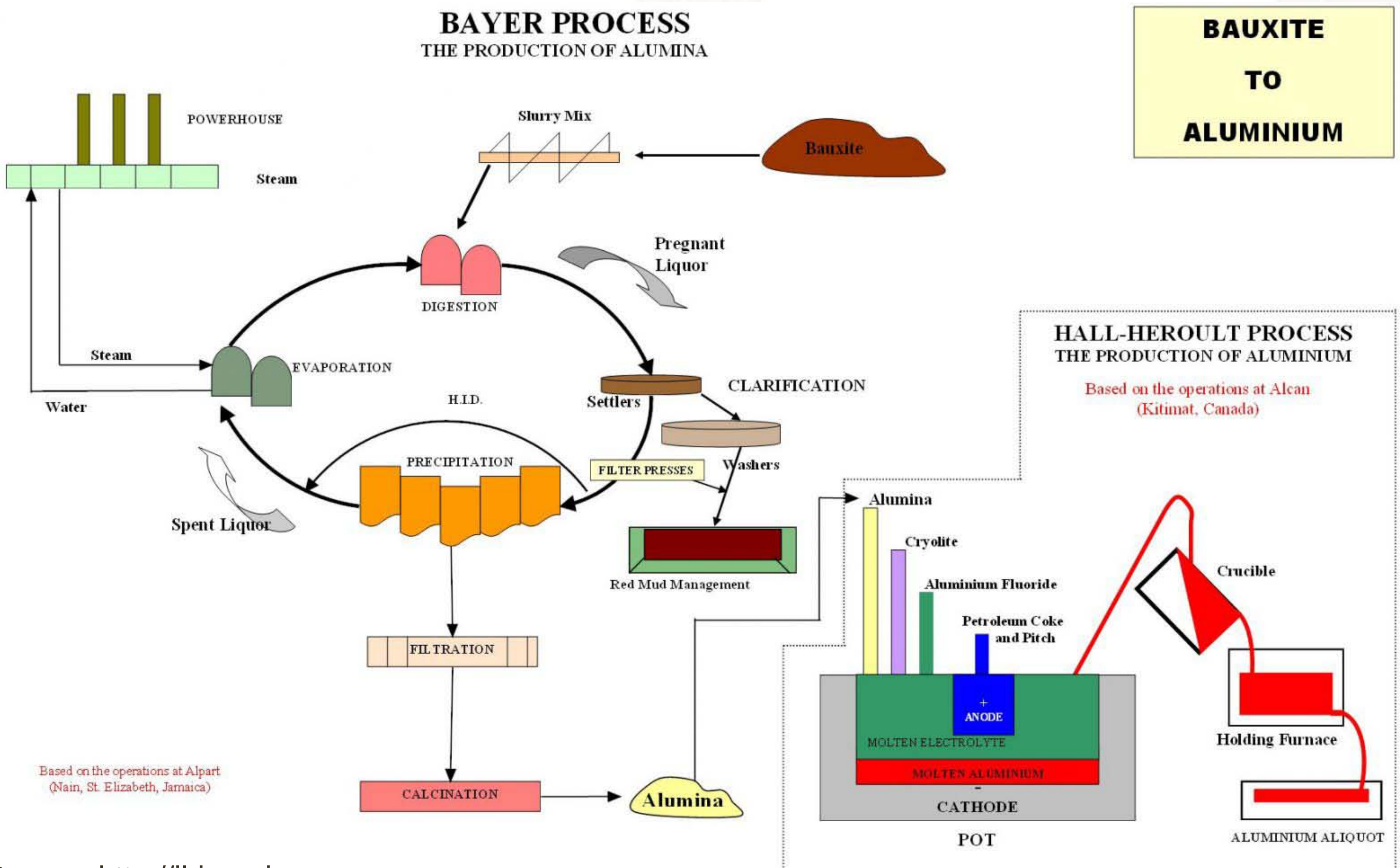


Source: Maurits van Camp (Umicore)

Bauxite residue (red mud)

- Bauxite: most important aluminium ore
  Mixture of impure hydrated aluminium oxides
- Alumina purified by Bayer process
  (digestion in hot concentrated NaOH)
- Solid impurities of Bayer process: bauxite residue or red mud
- pH ≈ 12
- Annual production: 120 million tonnes

Bauxite residue (red mud)



Source: http://jbi.org.jm

Red mud

Rare earths in red mud

- Bauxite contains 30–50% Al_2O_3, the rest being SiO_2, various Fe oxides, TiO_2, but also Ca, Na, Zm, Ga, Ni, V, Zr, Nb, Th, U and REEs
- Enrichment of REEs by a factor of 2 compared to bauxite
  - bauxite from Greece: 506 ppm of REEs (on average)
  - red mud from Greek bauxite: 1040 ppm of REEs

Ref.:

- M. Ochsenkühn-Petropoulou et al. *Anal. Chim. Acta*, **315** (1-2), 231-237, 1995.
- D. I. Smirnov and T. V. Molchanova, *Hydrometallurgy*, **45** (3), 249-259, 1997.
- M. Ochsenkühn-Petropoulou, et al., *Anal. Chim. Acta*, **296** (3), 305-313, 1994.

Scandium in red mud

- Red mud is rich in scandium
  - Greece: 130 ppm
  - Jamaica: 390 ppm
  - Moengo (Suriname): 1700 ppm
  - average abundance of scandium: 22 ppm
- Scandium represents > 95% of the economic value of rare earths in red mud

Ref.:

- Logomerac, V. G., *Res. Inst. Non-Ferrous Metals*: 1971; pp 383-393.
- A. S. Wagh, W. R. Pinnock, *Econ. Geol.*, **82** (3), 757-761, 1987 .
- M. Ochsenkühn-Petropoulou, et al., *Anal. Chim. Acta*, **296** (3), 305-313, 1994.

Recovery of rare earths from red mud

- Hydrometallurgical processes
  - to selectively leach minor metals from red mud, leaving behind major components such as iron oxides
  - REEs are readily leachable from red mud by diluted mineral acids, other elements not
  - Best leachant: dilute HNO_3

    Recovery: Y 96%, Sc 80%, light lanthanides 30-50%
  - After leaching, REEs can be recovered from leachate by selective precipitation (oxalate) or solvent extraction

Ref.:

• M. Ochsenkühn-Petropoulou, et al., *Anal. Chim. Acta*, **319** (1-2), 249-254, 1996.

• M. Ochsenkühn-Petropoulou, et al., *Ind. Eng. Chem. Res.*, **41** (23), 5794-5801, 2002.

Recovery of rare earths from red mud

- Combination of pyrometallurgical and hydro-metallurgical processes
  - to first recover iron from red mud and to subsequently concentrate REEs in an oxide slag
  - red mud is treated in a blast furnace in the presence of a reducing agent, generating pig iron and a titanium-rich slag (containing REEs)
  - problems with high sodium content and water
  - hydrometallurgical step consists of leaching REEs from slag with diluted mineral acid

Ref.:
- V. G. *Trav. Com. Int. Etude Bauxites, Alumine Alum.*, **15**, 279-285, 1979.
- V. G. Logomerac *CIM Spec. Vol.*, **21** (2, Proc. Int. Solvent Extr. Conf., 1977), 516-520, 1979.
- W. C. Liu, J. K. Yang and B. Xiao, *Int. J. Miner. Process.*, **93** (3-4), 220-231, 2009.

Scandium-rich minerals are rare

- Thortveitite $(Sc,Y)_2Si_2O_7$
- Bazzite $Be_3Sc_2(Si_6O_{18})$
- Kolbeckite $ScPO_4 \cdot 2H_2O$
- Ixiolite-Sc $(Nb,Ta,Ti,Sc,Fe,Mn)_4O_8$
- Perrierite-Sc
  $(Ce,Ca,Th)_4(Fe^{2+},Sc)Fe_2^{3+}(Ti,Fe^{3+})_2(Si_2O_7)_2O_8$
- Magbasite $KBa(Al,Sc)Fe^{2+}Mg_5F_2Si_6O_{20}$

- Scandium occurs in many ores in trace amounts, but is not found in sufficient concentrations to be mined for scandium alone.

Applications of scandium

- Al-Sc alloys for minor aerospace industry components (Russian military aircraft, MiG-21 and MiG-29) 0.1% and 0.5% Sc
- Al-Sc high-strength light weight alloy is used in bicycle frames, golf clubs, and baseball bats
- yttrium-scandium-gallium garnet (Er,Cr:YSGG) lasers for use in dentistry
- ScI_3 in high-intensity discharge lamps
- $Sc(CF_3SO_3)_3$: water-stable Lewis acid catalyst for use in organic synthesis

Applications of scandium

Phosphogypsum

- Main by-product of phosphoric acid production
- Formed by acidic digestion of phosphate rock
- Phosphate rock (phosphorite) contains mainly apatite, $Ca_5(PO_4)_3(OH,F,Cl)$
- Digestion is mainly done by H_2SO_4, although also HNO_3 can be used.
- Depending on the production method, phosphogypsum consists primarily of either $CaSO_4{\cdot}2H_2O$ (gypsum) or $CaSO_4{\cdot}\frac{1}{2}H_2O$
- 4.5 to 5.5 tonnes of phosphogypsum are generated per tonne of P_2O_5

Phospogypsum

Rare earths in phosphate rock

- On average: 0.01 and 0.1 wt% of REOs
- Phosphate rock of Kola Peninsula (Russia): up to 1.0 wt% of REOs
- Ce, La, Nd: 80% of the total REE content

Ref.:

- F. Habashi, *J. Chem. Technol. Biot. A*, **35** (1), 5-14, 1985.
- C. Koopman, G. J. Witkamp, *Hydrometallurgy*, **58** (1), 51-60, 2000.
- H. El-Didamony et al., *J. Radioanal. Nucl. Chem.*, **291** (3), 907-914, 2012.
- S. Zielinski et al., *J. Chem. Technol. Biot.*, **56** (4), 355-360, 1993.
- D. I. Skorovarov et al., *J. Alloys Compd.*, **180**, 71-76, 1992.
-

Rare earths in phosphogypsum

- REEs concentrated in phosphogypsum during phosphoric acid production
- 70 to 85% of REEs originally present in phosphate rock end up in phosphogypsum; rest remains dissolved in leaching solution.
- Average concentration of REEs in phosphogypsum: 0.4 wt%
- Phosphogypsum contains lower concentrations of scandium than red mud

Ref.:

• F. Habashi, *J. Chem. Technol. Biot. A*, **35** (1), 5-14, 1985

Recovery of REEs from phosphogypsum

- About 50% of rare earths present in phosphogypsum can be recovered by leaching at ambient temperature with 0.1 to 0.5 M H_2SO_4
- Impossible to quantitatively recover rare earths without destruction of phosphogypsum lattice
- Leaching efficiencies can be increased by gravity flow of H_2SO_4 solution through column packed with phosphogypsum
- Enhanced leaching after mechanical activation of phosphogypsum by ball-milling

Recovery of REEs from phosphogypsum

- Higher leaching efficiencies by leaching with HNO_3 solution instead of H_2SO_4
- Rare earths recovered from leaching solution by precipitation (sodium rare-earth double sulphates) or solvent extraction
- Possible to leach metals from phosphogypsum with organic extraction agents dissolved in kerosene

Ref.:

- F. Habashi, *J. Chem. Technol. Biot. A*, **35** (1), 5-14, 1985.
- H. El-Didamony, et al., *J. Radioanal. Nucl. Chem.*, **291** (3), 907-914, 2012.
- A. Jarosinski, et all., *J. Alloys Compd.*, **200**, 147-150, 1993.
- E. P. Lokshin et al., *Russian J. Appl. Chem.*, **84** (9), 1461-1469, 2011.
- D. Todorovsky et al., *Hydrometallurgy*, **45** (1-2), 13-19, 1997

Mine tailings

- Older processing methods of rare-earth ores were not efficient
- During flotation process of ground rare-earth ores large losses occurred
- Large volumes of solid waste with significant concentrations of rare earths
- Mountain Pass mine tailings still contain between 3 to 5% REOs
- Large amounts of REEs in tailings of uranium mines in Queensland (Australia), Kazachstan and Kyrgyzstan

Mountain Pass mine (Molycorp)

Source: http://webservices.itcs.umich.edu

Waste water

- Waste water produced during the extraction and separation of rare earths
- Acid mine drainage (AMD)
- Gadolinium from MRI contrast agents in waste water of hospitals

- Low concentrations of REEs
- Recovery by ion-exchange resins and chelating resins to be preferred
- Biosorption

Conclusions

- Waste streams have in common that they contain relatively low REE concentrations (<1% REOs)
- Large volumes are available
- Could become economically attractive secondary sources of rare earths
- Bauxite residue (red mud): source of scandium
- Phosphogypsum: source of light rare earths
- Dilution of rare earths in most types of slags remains a problem
- Recovery of rare earths from mine tailings and waste water is not well investigated

FP7 EURARE project

"Development of a sustainable exploitation scheme for Europe's Rare Earth ore deposits"

Project coordinator: Prof. Ioannis Paspaliaris (NTUA, Greece)
Start date: 2013-01-01 End date: 2017-12-31
Project Funding: 9,000,000 EURO
Subprogramme Area:New environmentally friendly approaches in minerals processing
Contract type:Large-scale integrating project
Website: www.eurare.eu

rare3

Research Platform for the
Advanced Recycling and Reuse of Rare Earths

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www.kuleuven.rare3.eu/

Thank you !