BAUXITE RESIDUE VALORISATION AND BEST PRACTICES CONFERENCE

Leuven 5-7 October 2015

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Rare earths: essential elements for the transition to a low-carbon economy

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Fossil carbon CO_2 emission

Source: http://ec.europa.eu

Source: www.ucsusa.org

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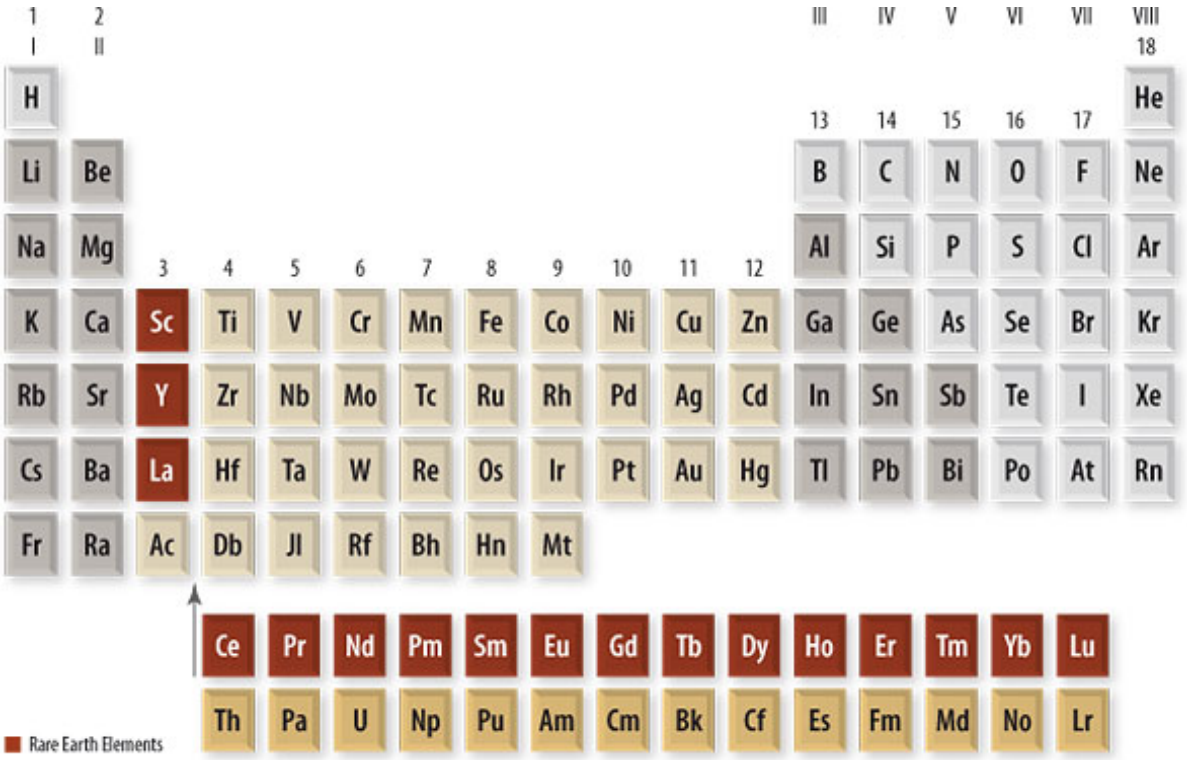
How can rare earths help to reduce fossil carbon CO_2 emission?

- Strong permanent magnets for electric motors
  - Electric and hybrid electric cars
  - Electric bikes
- Lamp phosphors for efficient lighting
- Generation of electricity
  - Magnets in generators of wind turbines
  - Solid oxide fuel cells
- Energy storage
  - Nickel metal hydride batteries
  - Redox flow batteries
- Cooling: magnetic refrigeration

Rare earths in the periodic table



Lanthanides = series of elements La-Lu
Rare earths = lanthanides + Y + Sc
REEs = rare-earth elements
LREE = La-Sm HREE = Eu-Lu, Y

Source: www.tre-ag.com

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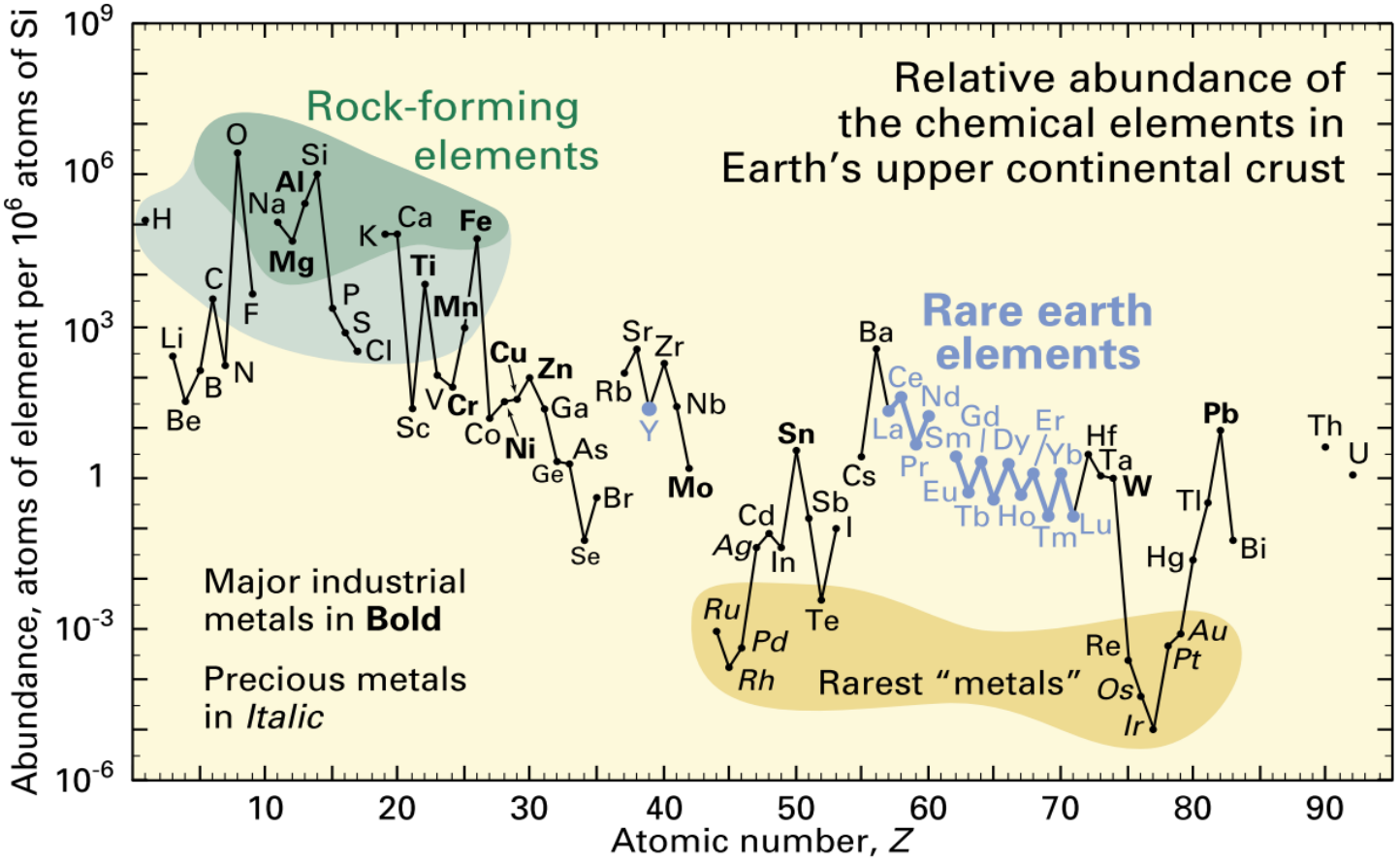
Rare earths: names and symbols

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

Abundance of rare earths



Source: US Geological Survey

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Rare earths in bauxite residue (BR)

- Enrichment of REEs by a factor of 2 compared to bauxite
  - bauxite from Greece: 506 ppm of REEs (on average)
  - BR from Greek bauxite: 1040 ppm of REEs
- BR is rich in scandium
  - Greece: 120 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

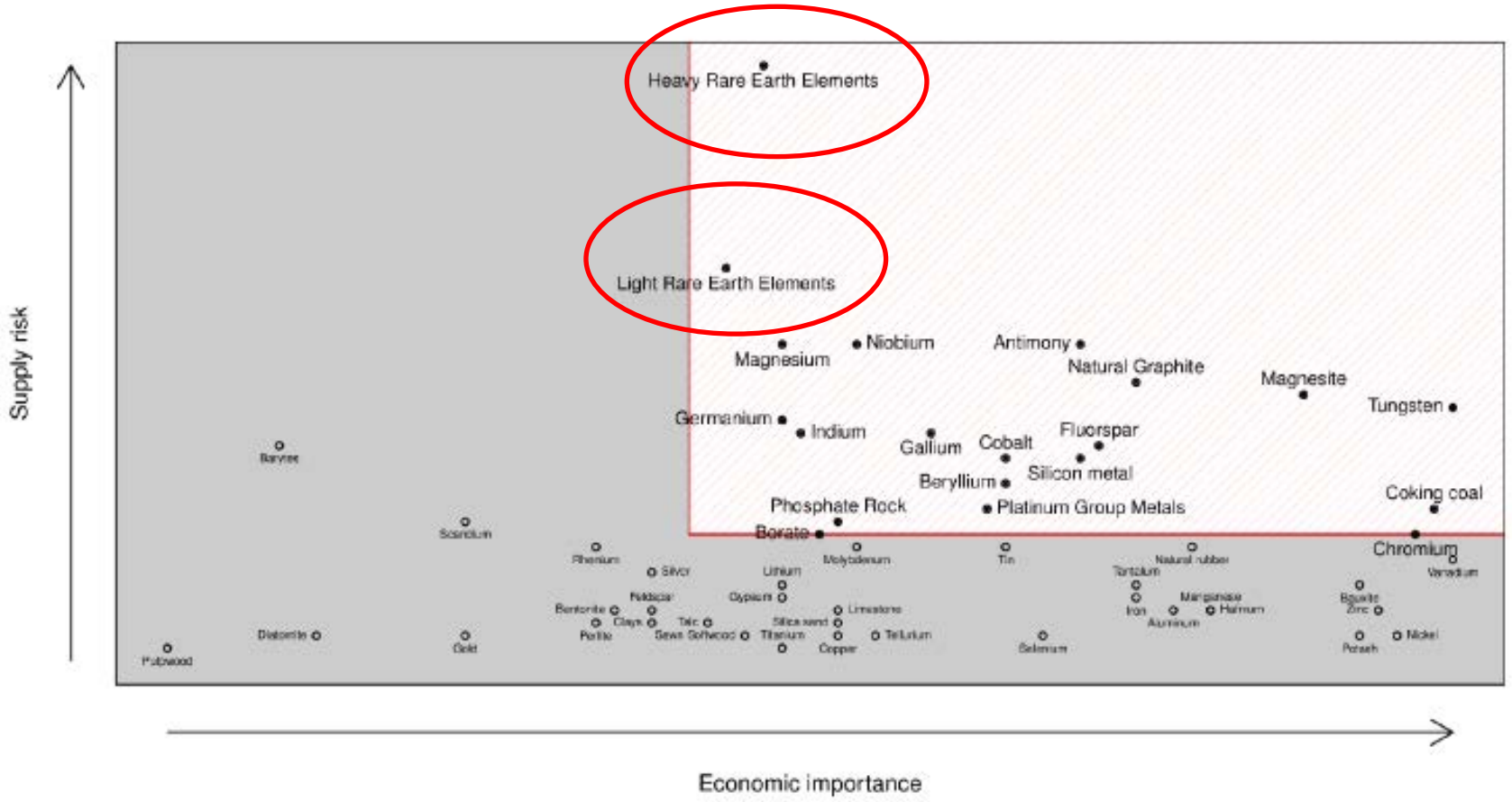
Source: K. Binnemans et al., *J. Clean. Prod.* 99 (2015) 17–38.

Rare earths in Greek bauxite residue

Element	Concentration (g/tonne)
Sc	121 ± 10
Y	75.7 ± 9.6
La	114 ± 15
Ce	368 ± 68
Pr	28.0 ± 3.9
Nd	98.6 ± 7.0
Sm	21.3 ± 2.3
Eu	5.0 ± 0.9
Gd	22.0 ± 1.9
Tb	3.5 ± 0.6
Dy	16.7 ± 0.7
Ho	3.9 ± 0.6
Er	13.5 ± 1.8
Tm	1.9 ± 0.3
Yb	14.0 ± 1.9
Lu	2.4 ± 0.3

Source: C.R. Borra et al., *Minerals Engineering* 76 (2015) 20–27.

Rare earths as critical raw materials



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

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Applications of rare earths

Metallic state

20%

Motors and generators, HD Drives, Microphones and Speakers, MRI, Defence applications, Magnetic refrigeration

Nd, Pr, Sm (Tb, Dy)

5%

Fertilizer
Pigments
Nuclear
Medical Tracers

Magnets

Other

Metal Alloys

La, Ce, Pr, Nd, Y

NimH batteries
Superalloys
Al – Mg alloys
Steel

18%

REE

Polishing media
UV resistant glass
Thermal glass
Capacitors
Sensors
Colorants
Refractories
Fuel Cells
Superconductors

Ce, La, Pr, Nd, Gd, Er, Ho

30%

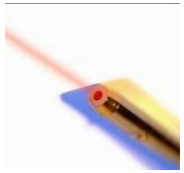
Ceramics & Glass

Phosphors

Eu, Y, Tb, Nd, Er, Gd (Ce, Pr)

LED,
LASER
Flat Panel Display
Fluorescent lamps
Xray imaging
Optical sensors
Fibre Optics

7%



Catalysts & Chemical Process

La, Ce, (Pr, Nd)

Petroleum Refining, Automotive Catalysts, Diesel Additive, Water treatment

20%

Oxidized state

Source: www.eurare.eu

Breakdown of estimated rare-earth consumption by sector in 2012

- Magnets **20%**
- Batteries **8%**
- Other metallurgy **10%**
- FCCS **13%**
- Autocatalysts **6%**
- Other Catalysts **1%**
- Polishing **15%**
- Glass **7%**
- Phosphors **7%**
- Ceramics **5%**
- Other **7%**

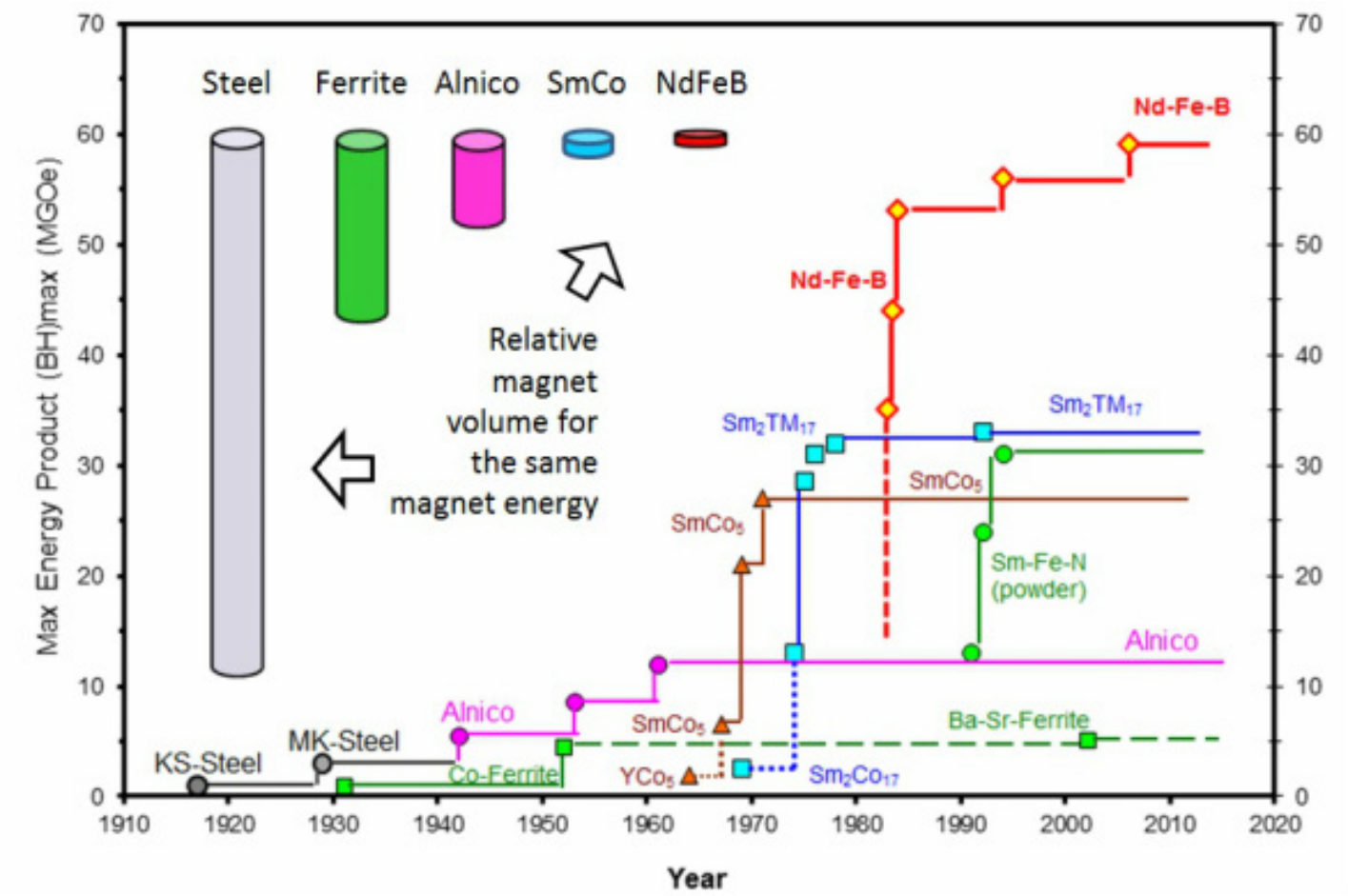
Total REO production: 120,000 tonnes/year

Source: ERECON report (2015)

Rare-earth permanent magnets

- samarium-cobalt alloys: $SmCo_5$ and Sm_2Co_{17}
  - maximum energy product $(BH)_{max}$:130 to 260 kJ/m^3
  - good corrosion resistance
  - high operating temperatures
  - expensive (Co)
  - small part of REE magnet market (2-5%): niche applications
- neodymium-iron-boron alloy: $Nd_2Fe_{14}B$
  - strongest commercially available permanent magnets
  - maximum energy product $(BH)_{max}$:512 kJ/m^3
  - poor corrosion resistance (surface plating required)
  - lower operating temperatures (Dy addition)

Evolution of permanent magnets



Source: http://www.magnetnrg.com

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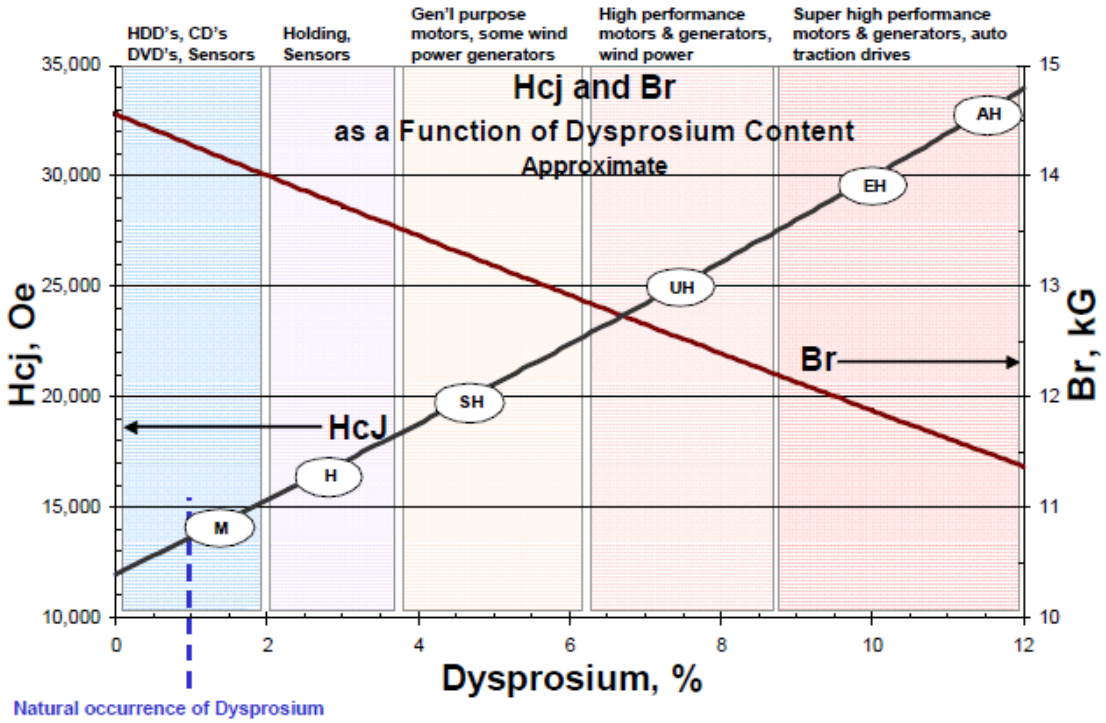
Dysprosium in NdFeB magnets



- Dysprosium is required to allow NdFeB magnets to be used at elevated temperatures (>80 ºC), especially in the presence of demagnetizing stress such as in motors and generators.
- Hcj is a measure of a magnet's resistance to demagnetization. Br is a measure of a magnet's field strength.

Source: Arnold Magnetics

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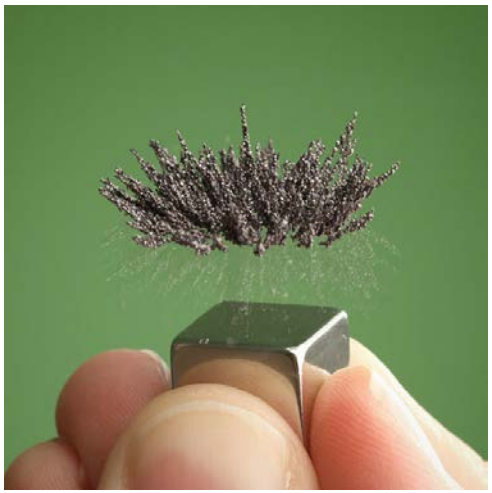
Strong NdFeB magnets



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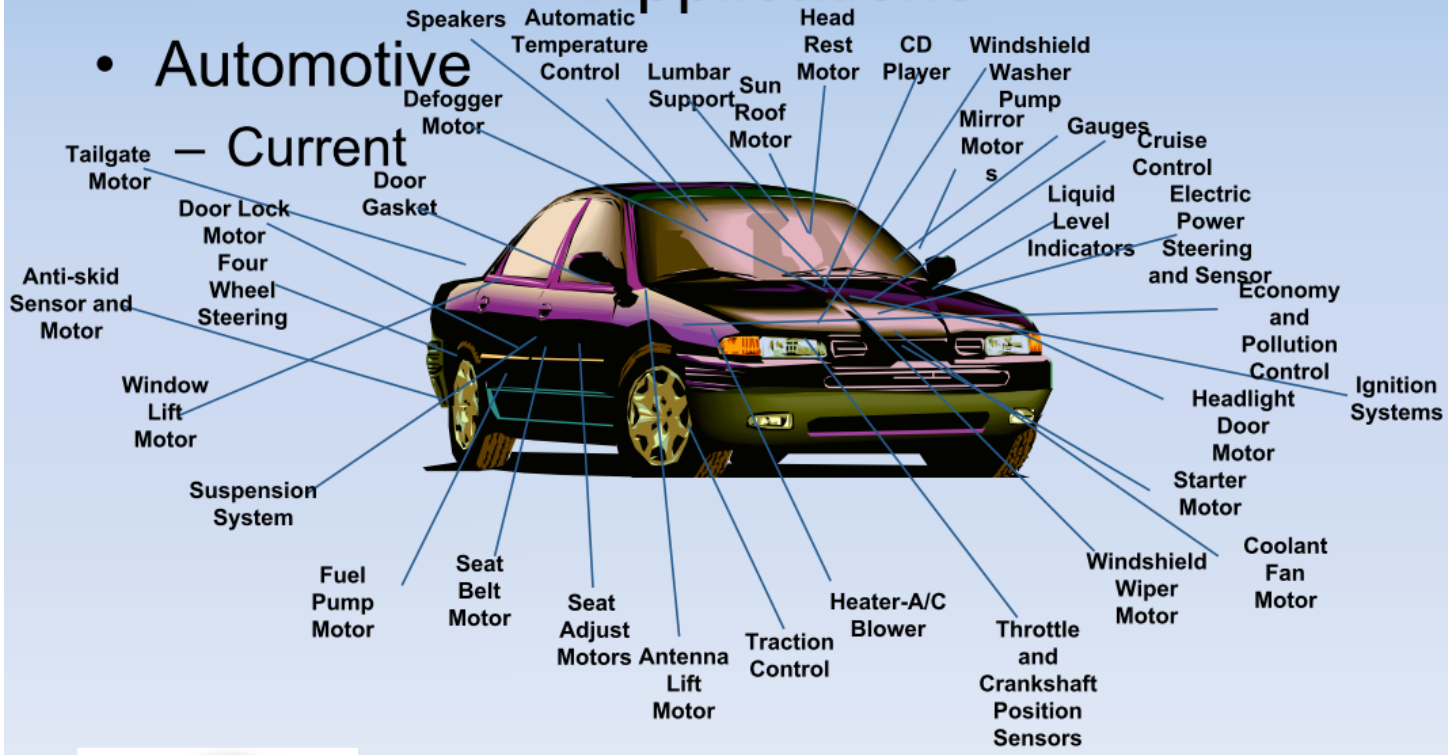
Rare Earth Magnets

Applications

- Automotive
  - Current



Source: Magnequench

Spontaneous Materials

Electric and hybrid electric cars

- Hybrid and full electric cars are becoming increasingly more common in the US and Europe
- High dysprosium (10-12 wt%) is required due primarily to the higher temperature of the application
- Each electric car requires on average 1.25 kg of NdFeB magnets (not in Tesla)

Source: www.arnoldclark.com

Electric bikes

- Electric bikes are a fast-fast growing market, not only in Asia but also in Europe
- Small-sized performant magnets are essential
- 300-600 g of NdFeB magnets per e-bike (intermediate Dy)
- Although the amount of magnet material per unit is small, the quantities are large (> 10,000 tonnes/year)

Source: www.fietsenpagina.nl

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Wind power

Source: www.telegraph.co.uk

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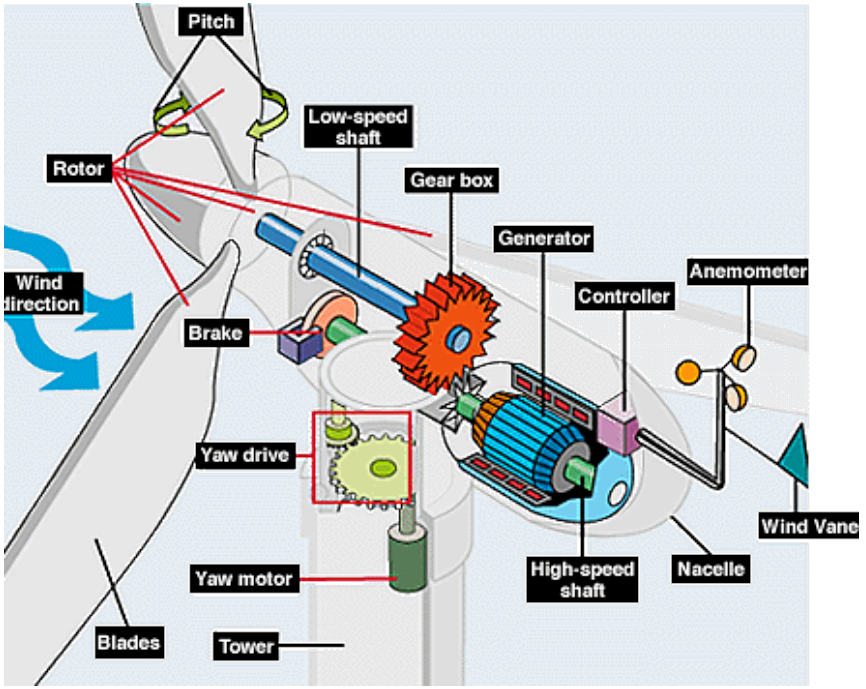
Wind turbines: induction generator

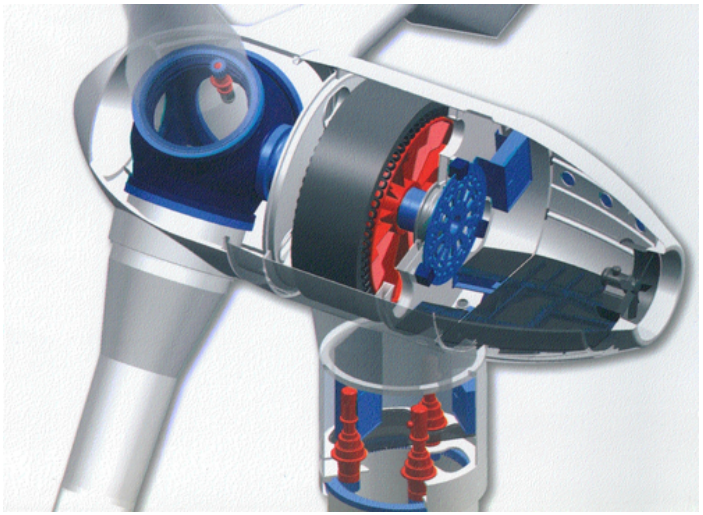
- Older types of wind turbines use **induction generators**
  - Induction generators must spin fast (> 1800 rpm)
  - Turbine rotor turn at 10-12 rpm, so that a 170:1 **gearbox** is required to increase the shaft rotational speed
  - Gearboxes are expensive, heavy, noisy, and require frequent maintenance



Source: http://www.daviddarling.info/images/wind_turbine.gif

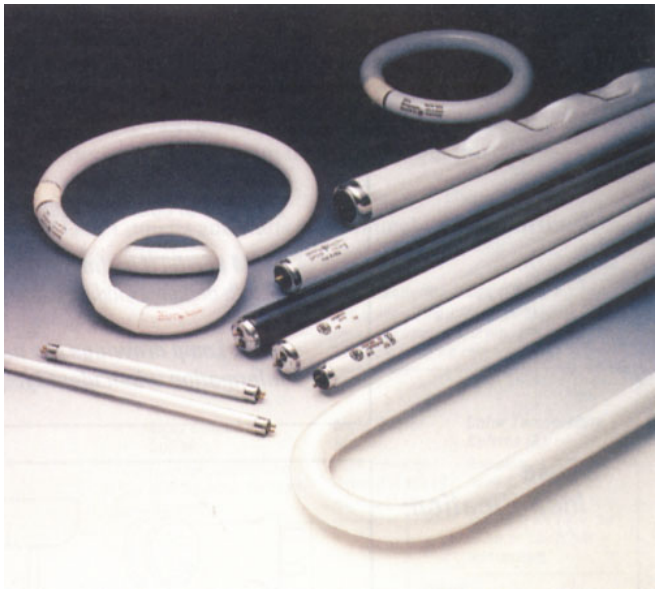
Wind turbines: direct drive

- New generations of wind turbines use permanent magnets (**direct drive wind turbines**); no gearbox
- Low maintenance: ideal for off-shore applications or for use at difficult accessible locations
- 250 to 600 kg of NdFeB magnets per MW of output
- Replacement of 1 GW coal-fired power plant requires 400 tonnes of NdFeB magnets
- Wind power boosts NdFeB magnet usage

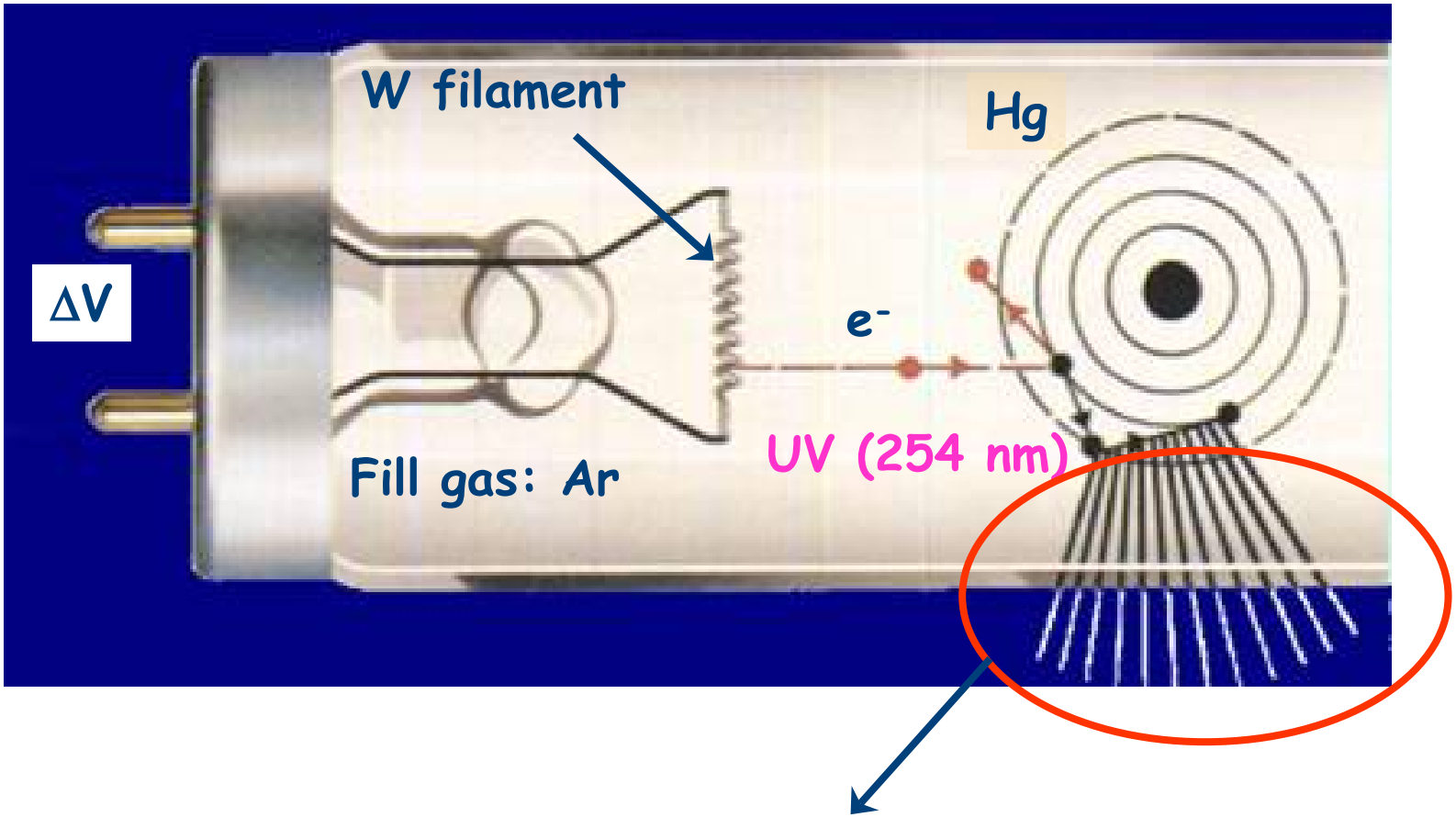


Source: MTorres

Fluorescent lamps



Fluorescent lamps



UV photons excite phosphor coating. White light is emitted.

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)

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Nickel metal hydride batteries

Positive electrode:

$Ni(OH)_2 + OH^- \leftrightarrows Ni(OOH) + H_2O + e^-$

$\rightarrow$: charging

$\leftarrow$: discharging

Negative electrode:

$M + xH_2O + e^- \leftrightarrows MH_x + xOH^-$

$\rightarrow$: charging

$\leftarrow$: discharging

$M = LaNi_5$ or similar alloy

Overall reaction:

$M + xNi(OH)_2 \leftrightarrows xNiOOH + MH_x$

$\rightarrow$: charging

$\leftarrow$: discharging

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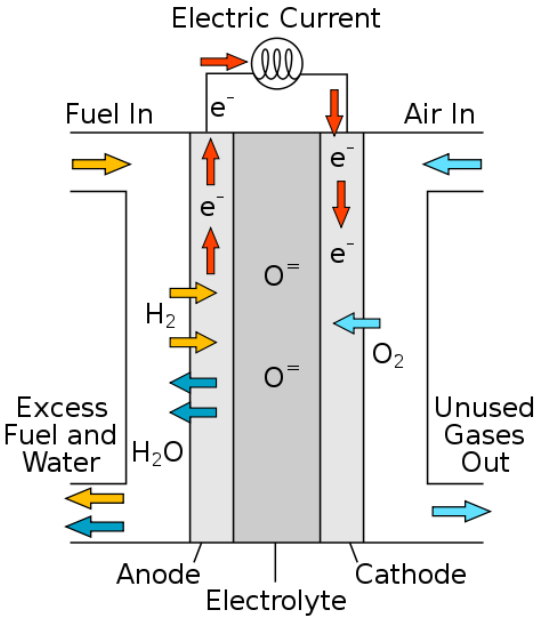
Solid oxide fuel cells (SOFCs) - scandium

- SOFCs are used to generate electricity from natural gas or from renewable fuels
- Sc_2O_3 can replace Y_2O_3 in yttria-stabilized zirconia (YSZ) for SOFCs applications
- ScSZ has a higher conductivity than YSZ
- Incorporation of scandium in SOFCs enables lower operating temperatures resulting in longer lived equipment and less costly materials of construction
- SOFCs could lead to a major increase in scandium consumption



Source: wikipedia

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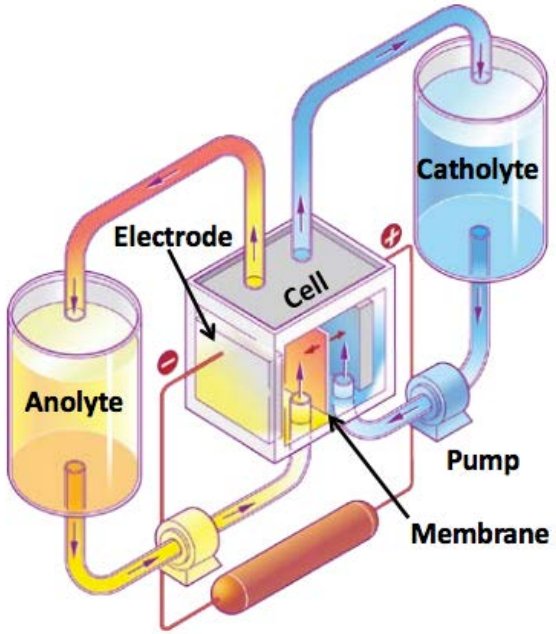
Cerium redox flow batteries

- 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

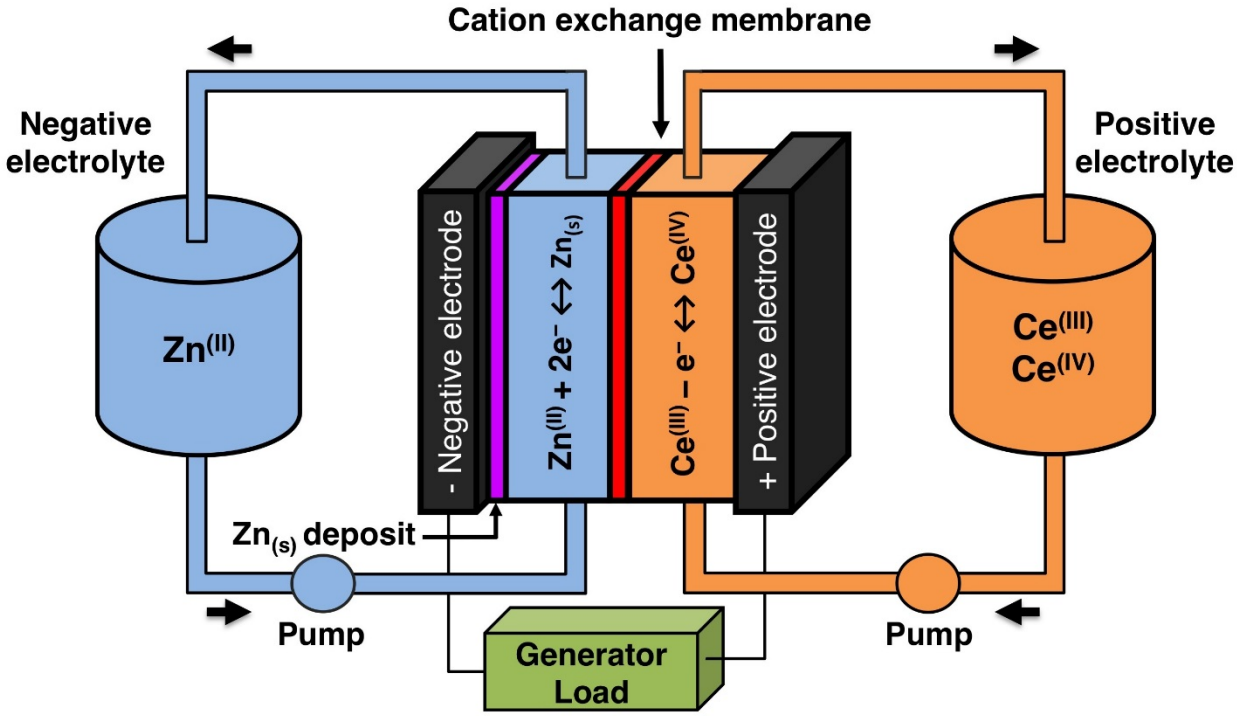


Diagram of the Divided Zinc-Cerium Flow Battery

Source: wikipedia

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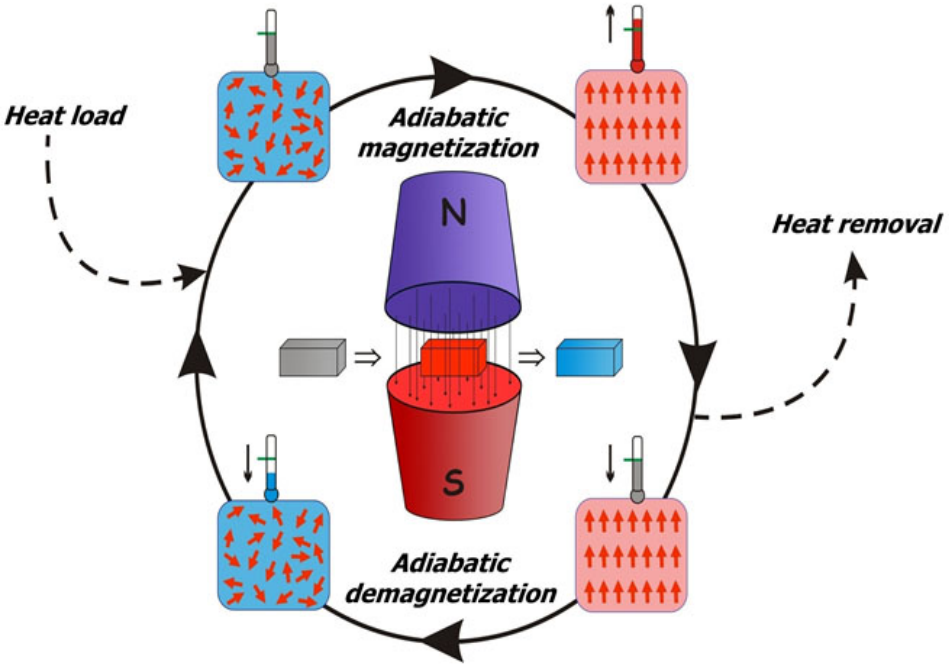
Magnetic refrigeration



- Based on the **magnetocaloric effect**
- A temperature change of a suitable material is caused by exposing the material to a changing magnetic field.
- REE alloys

  $Gd_5(Si_xGe_{1-x})_4$,

  $La(Fe_xSi_{1-x})_{13}H_x$

Source: refrigerationnew.blogspot.com

Conclusions

- Rare earths are essential for green-tech applications
  - Nd, Dy for (H)Evs, e-bikes and wind turbines
  - Eu, Tb, Y for fluorescent lamps
  - Ce, Y for LEDs
  - La for nickel metal hydride batteries
  - Y, Sc for solid oxide fuel cells
  - Ce for redox flow batteries
  - Gd, La for magnetic refrigeration
- Bauxite residue is an interesting source of rare earths, and especially of scandium

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Research Platform for the
Advanced Recycling and Reuse of Rare Earths

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http://www.kuleuven.rare3.eu/

Thank you !

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