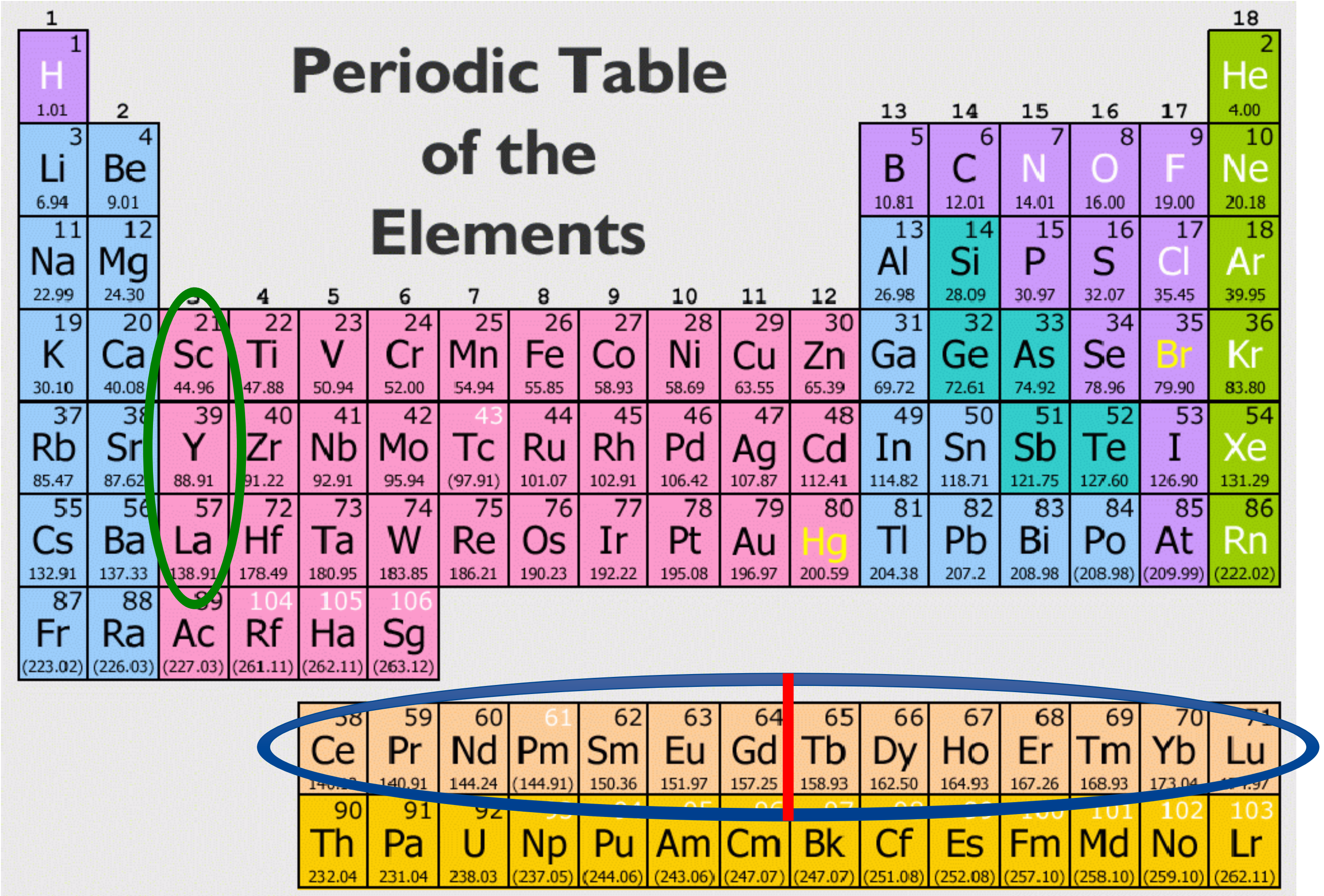
Sällsynta jordartsmetaller användning och återvinning

Prof. Kerstin Forsberg, KTH

Rare earth elements (REE)



The electrons are placed in the 4f shell, which has little effect on bonding.

The lanthanide contraction is due to poor shielding of nuclear charge by the electrons in the 4f shell.

The significant difference between two lanthanides is often only their atomic or ionic radius.

Typically, trivalent ions.

Unique magnetic, phosphorescent, and catalytic properties.

Rare earth elements (REE)

Unique magnetic, phosphorescent, and catalytic properties.

- Used in everyday technologies like **LED lights**, **mobile phones** and **computers** (e.g. screens, magnets in speakers and hard discs etc.).
- Critical in several **green technologies**, especially those that support net zero carbon emissions goals, like **wind turbines** and **electric vehicles** (e.g. magnets and batteries).
- Advanced **medical technologies** like MRIs, laser scalpels and cancer drugs.
- In **defence applications**, they are used in satellite communications, guidance systems and aircraft structures.

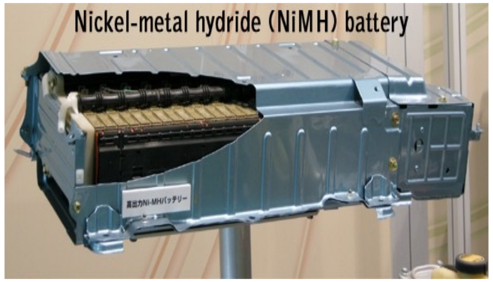
Substitutes are available for many applications but generally are less effective: REE free organic LEDs and halogen incandescent lights, catalysts with reduced amount of Ce, REE-free strong magnets (FePt, MnBi, FeNi, Co-carbide, Fe-nitride, $ZrCo_{11}$, and $HfCo_7$, nanostructuring).

Rare Earth Elements (REE)

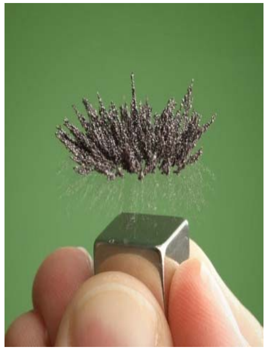
- ➢ **Design for recycling**
- ➢ **Products from recycling**

Sc (Al alloy)

Sc (SOFC)

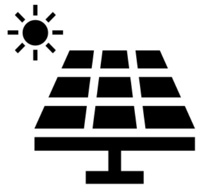


La, Ce, Pr, Nd, Sm



Nd, Pr, Dy, Tb, Sm ($Nd_2Fe_{14}B$, Sm_2Co_{17}, ...)

Ce, Eu, La, Y, Tb



Nd, Dy, Pr, Ce

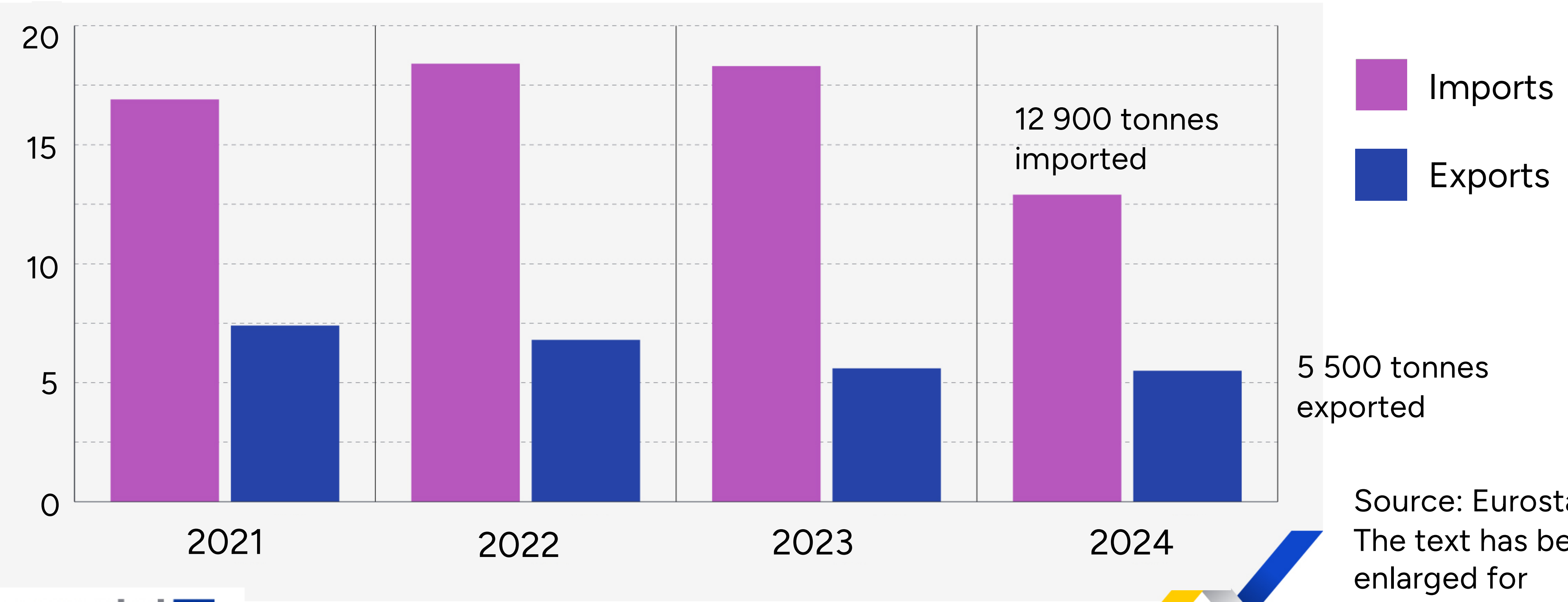
Magnets (25%), catalysts (22%), batteries (14%), polish (14%), metallurgy (9%), glass (6%), luminescence (6%)

30% drop of EU REEs imports in 2024

- Unclear if recycling or domestic production contributed to offsetting import needs.
- Yet no data on price shifts or industry stock levels.

EU trade in REE, 2021- 2024

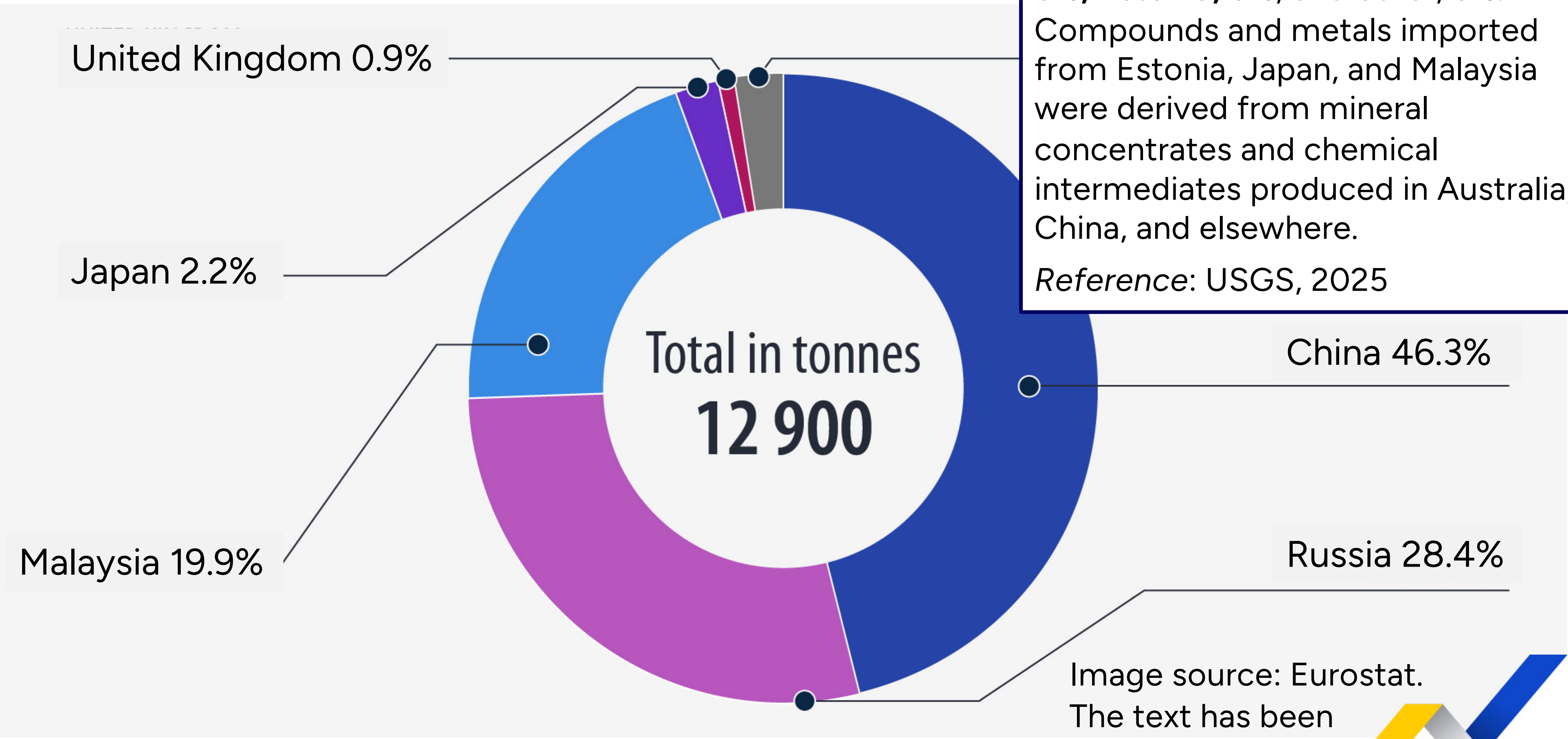
(*1 000 tonnes*)



Source: Eurostat
The text has been enlarged for better visibility

https://ec.europa.eu/eurostat

REE imports to the EU, 2024 (% of total weight)



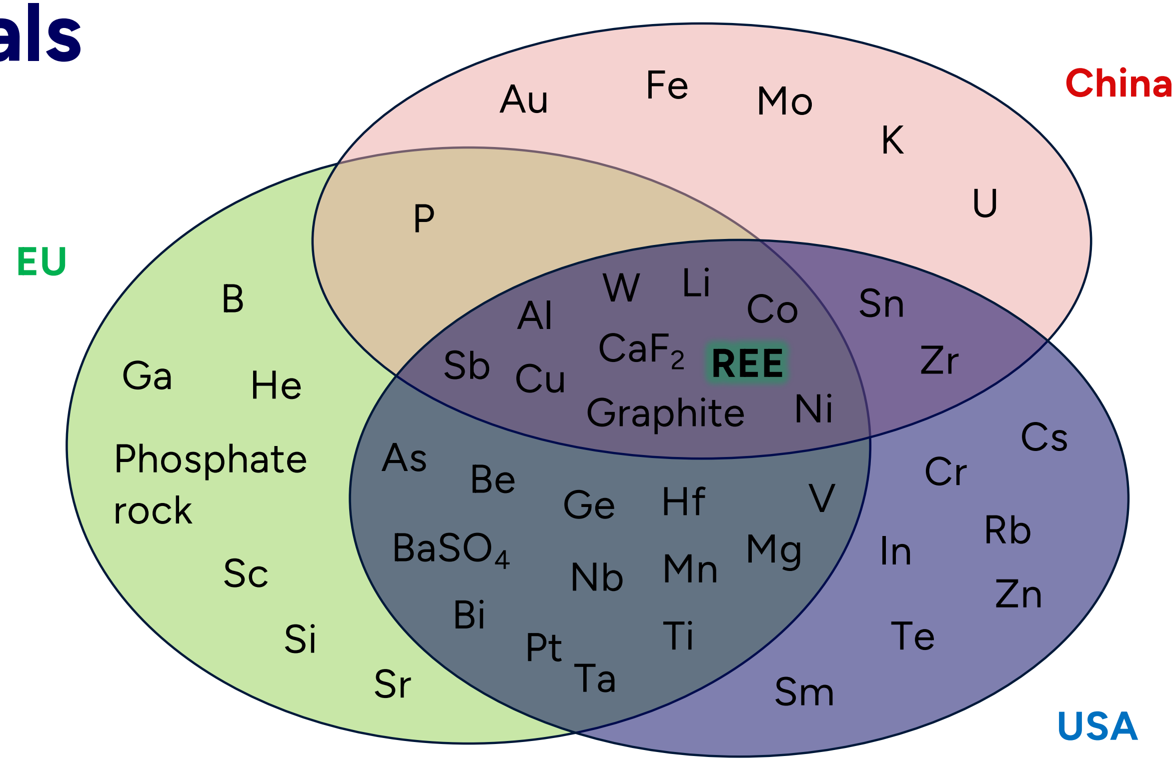
USA import Sources (2020–23): Rare-earth compounds and metals: **China, 70%; Malaysia, 13%; Japan, 6%; Estonia, 5%**; and other, 6%. Compounds and metals imported from Estonia, Japan, and Malaysia were derived from mineral concentrates and chemical intermediates produced in Australia, China, and elsewhere.

Reference: USGS, 2025

eurostat https://ec.europa.eu/eurostat

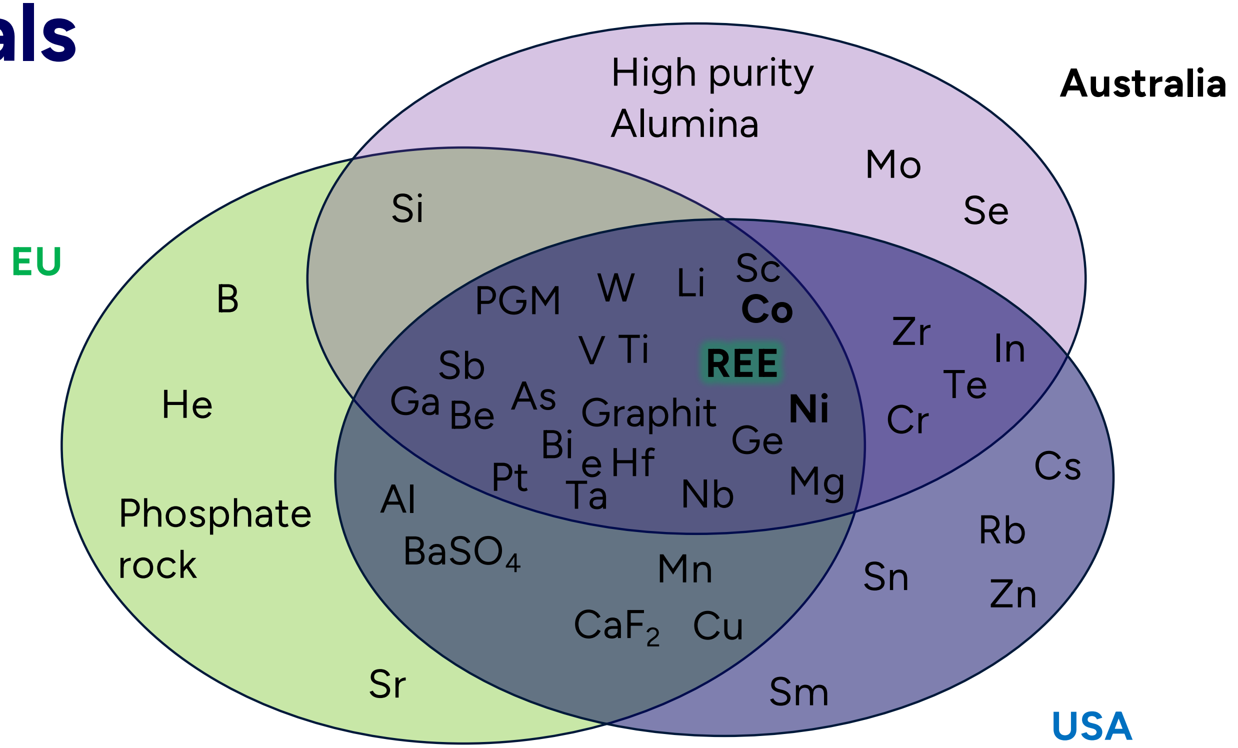
Image source: Eurostat. The text has been enlarged for better visibility

Critical Raw Materials



Source: Irena, The U.S. Department of Energy, EC

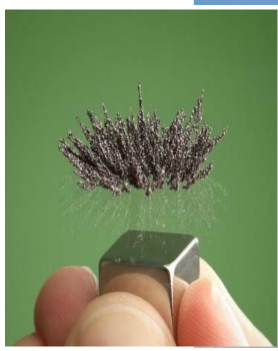
Critical Raw Materials



Source: Irena, The U.S. Department of Energy, EC, Australian Gov.

Permanent magnets

- Green and smart technologies need magnets for use in *e.g.* sensors, motors and generators
- Permanent magnets (PM) are very strong allowing the magnets to be smaller and the items lighter
- PM are crucial for wind turbines, computer hard disc drives, motors in cordless tools, hybrid and electric vehicles etc.
- The strongest type (NdFeB) contain boron and the rare earth elements (REE) Nd, Pr and Dy, (Gd, Tb), (Co)
- REE are defined as Critical Raw Materials for the EU



Recycling of magnets – closing the loop

- **Reuse** – Large PM can be dismantled and reused, *e.g.* those in generators in wind turbines and potentially those in vehicle electric motors.

- **Direct recycling** – PM are harvested and used to make new PM, like in-house recycling of materials from production.

- **Indirect recycling** – due to the complexity of the products, oxidation or other contamination and varying alloy composition the PM might need to undergo metallurgical processes to extract and recover the metals separately.

Yang et al. *J. Sustain. Metall.* (2017); Zhang et al. Metals (2020), www.urbanminingco.com

Recycling of magnets – closing the loop

- Hydrogen Decrepitation (HD) is a process used in the recycling of rare-earth magnets, e.g., neodymium-iron-boron (NdFeB) magnets.

- Hydrogen Decrepitation refers to the controlled exposure of magnets to hydrogen hydrogen gas at elevated temperatures. The absorption of hydrogen causes the magnet material to become brittle and fracture into fine powders.

- The powder can be further processed to make new magnets by sintering at high temperature followed by compaction under a magnetic field.

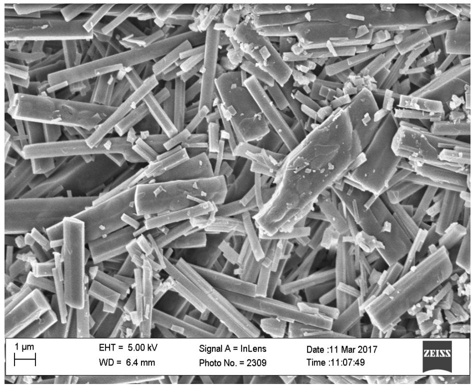
- The HD process can also be applied as a pre-treatment step for further so called long-loop recycling processes.

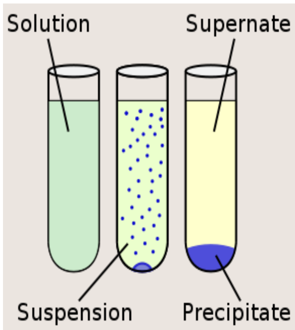
Stankovic N., Jourdan J. Marin J., Chagnes A., Quatravaux T. Kinetic study of rare earth elements extraction from decrepitated magnet powder using liquid magnesium. RSC Adv., 2023,13, 32824-32832

Hydrometallurgical recycling

Leaching (with or without roasting) followed by separation

by *solvent extraction*, *ion exchange*, ***crystallization/ precipitation***



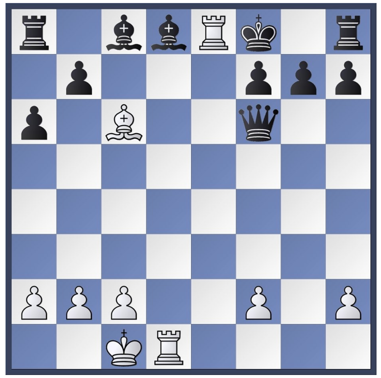


- The REE (Nd, Pr, Dy, Gd, Tb) are obtained as a mixture or as individual salts
- The final REE product is often the oxides or fluorides

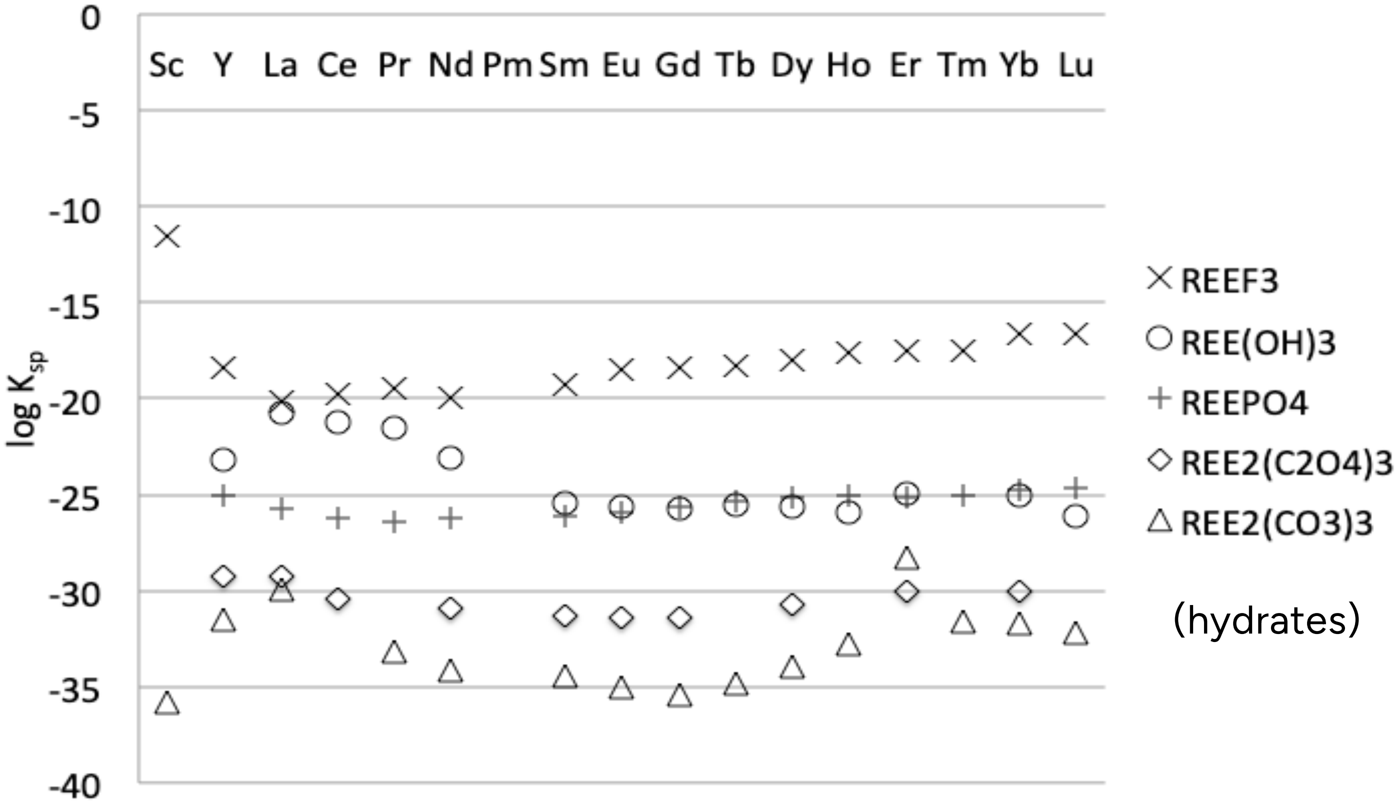
Separation of REE

Callow, 1967:

"Discussing lanthanon separation is like discussing chess. There are a limited number of opening moves, which can be analysed in detail. As the game develops, possibilities multiply enormously…"

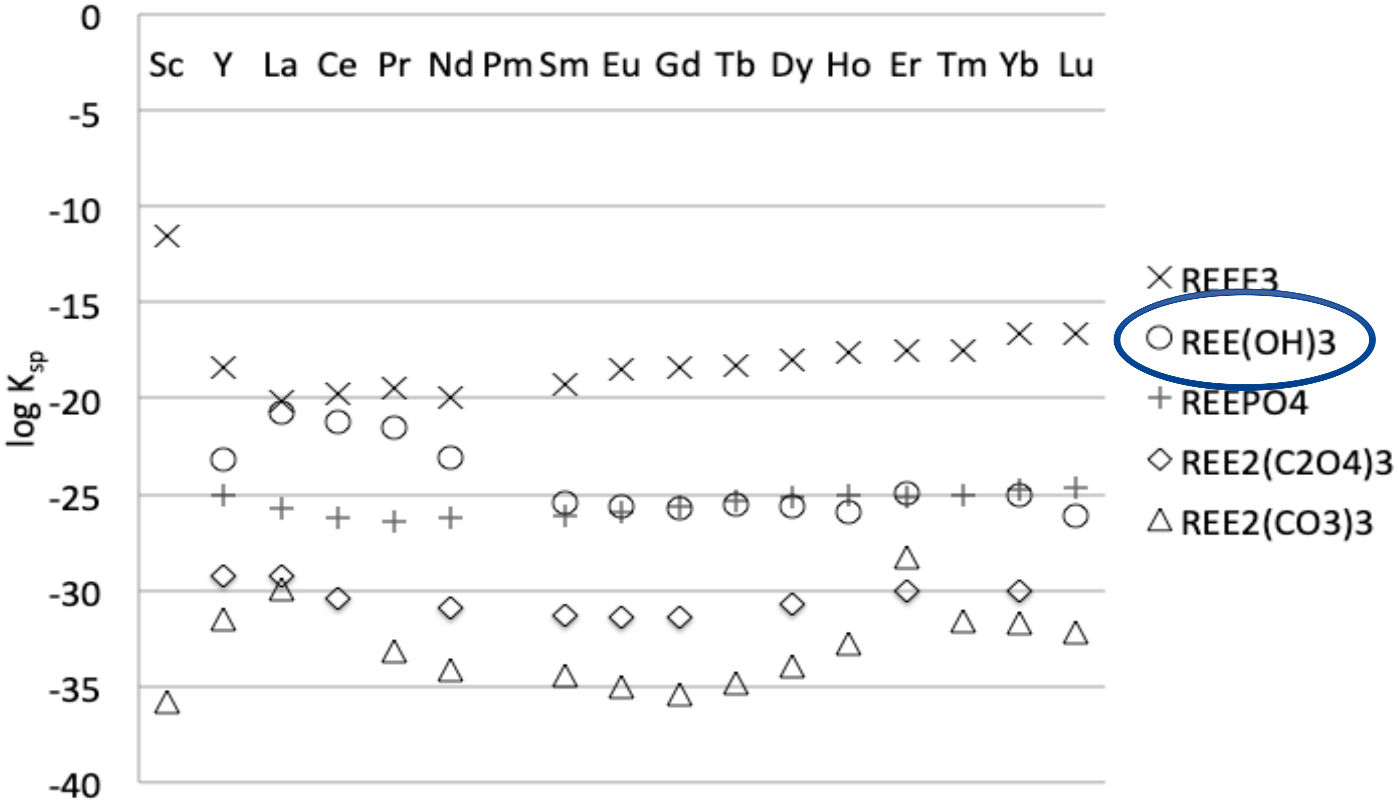


Sparingly soluble REE salts



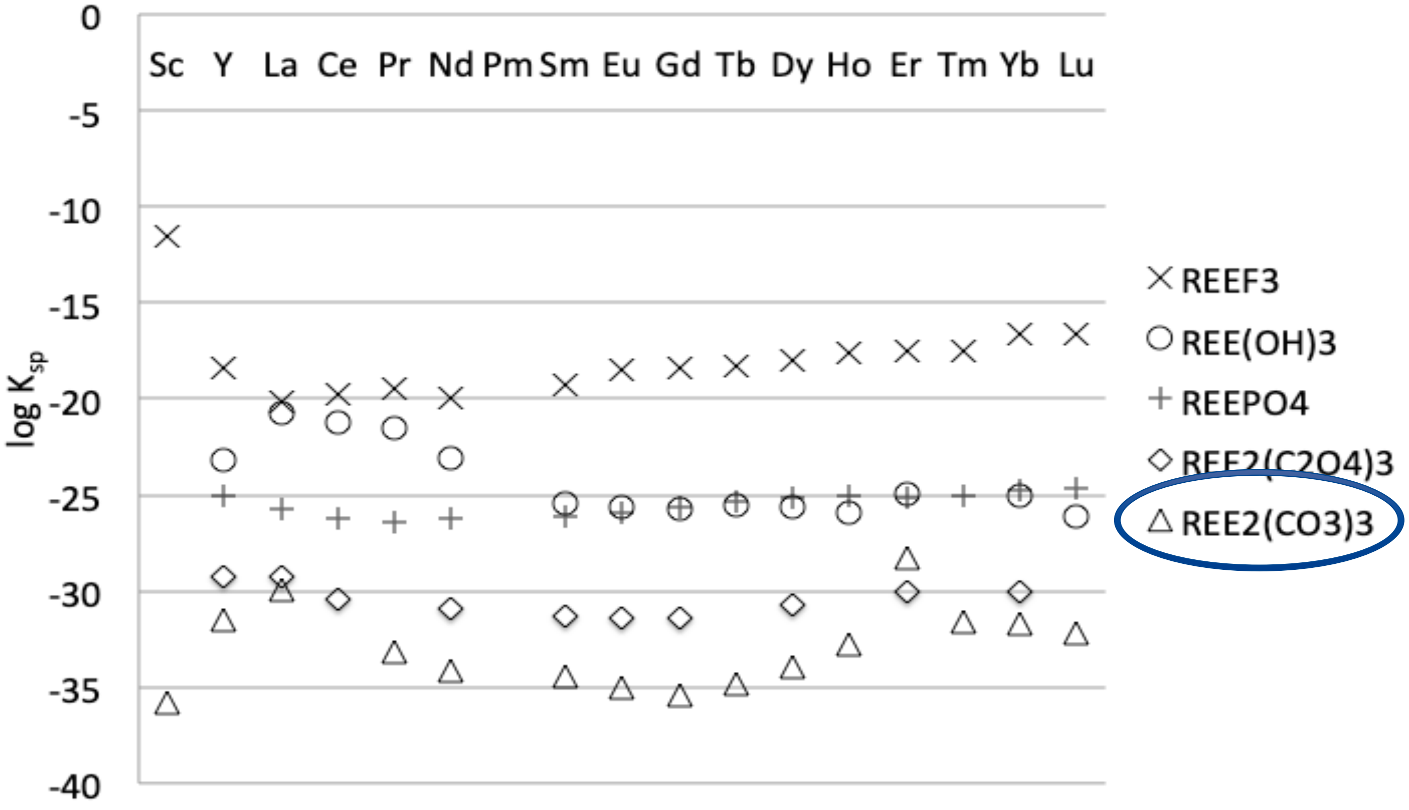
Solubility products, valid at 25°C and zero ionic strength.

Basicity precipitation (*e.g.* using magnesia or caustic soda) is widely used in industry. Ammonia has also been used in large scale to precipitate hydroxides from nitrate or chloride solutions.



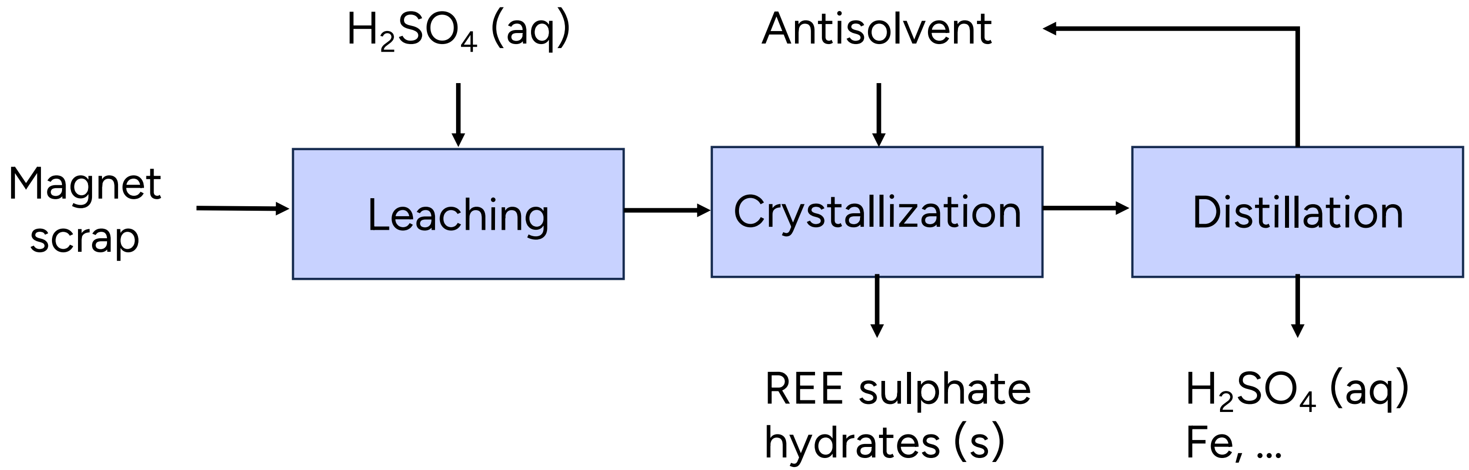
Solubility products, valid at 25°C and zero ionic strength.

Carbonates are almost insoluble in water but readily soluble in dilute acids. Carbonates can be precipitated from aqueous solutions *e.g.* by addition of alkali carbonates, bicarbonates or carbon dioxide gas.



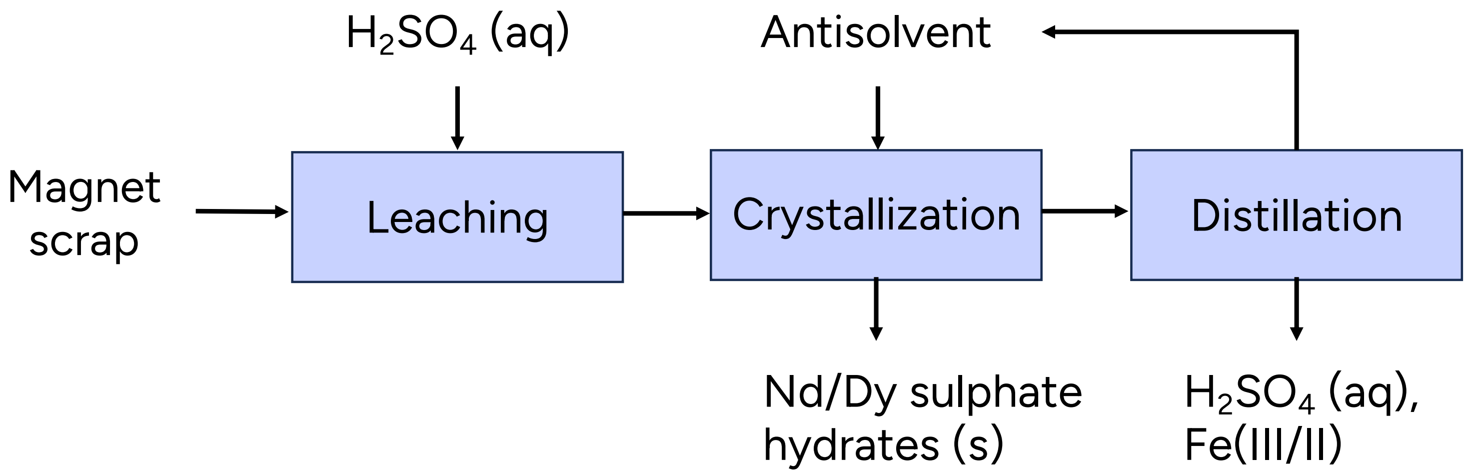
Solubility products, valid at 25°C and zero ionic strength.

Recycling of magnets



- The REE can be selectively separated from the leach liquor
- The REE sulfate hydrates have a high solubility in water
- The solvents can be recovered by distillation
- Choice of antisolvent: economy, availability, safety, recovery

Recycling of magnets



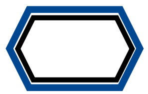
Synthetic solutions

- Nd(III) (8 g/kg) and Dy(III) (0.9 g/kg) in H_2SO_4
- Iron (25 g/kg) in the form of either Fe(II) or Fe(III)

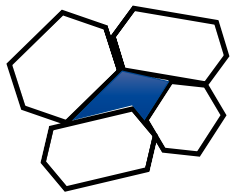
➢ Crystallization of either $Nd_2(SO4)_3 \cdot 8H_2O$ or $(Nd/Dy)_2(SO4)_3 \cdot 8H_2O$

Mechanisms of impurity incorporation

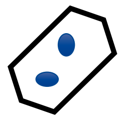
- Solution adhering to the surface
  “Interfacial tension and viscosity”
  Washing and centrifuge



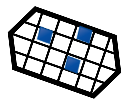
- Macroscopic inclusion
  “Surface irregularity”
  Crushing, reslurrying, and washing



- Microscopic inclusion
  “Step behaviour”
  Sweating, reslurrying



- Lattice incorporation
  “Molecular resemblance”
  Sweating, fractional crystallization



Mechanisms of impurity incorporation

Kinetically controlled non-equilibrium lattice impurity incorporation and incorporation by 3D inclusion or by adhesion to mother liquor can all be influenced by modifying the crystallization conditions or downstream processes.

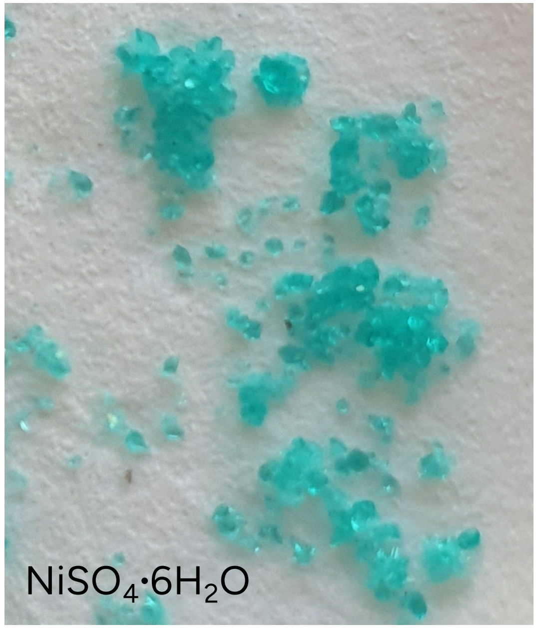
- Slow growth rate enhances purity (- productivity)
- Effective mixing enhances purity (> 10- 20μm)
- Avoid agglomeration
- Suitable CSD and shape gives shorter washing and filtration times which in turn leads to improved product quality, e.g. better purity

The formation of a solid solution is a thermodynamically controlled process. Thus, the purity from a single step crystallization is limited; higher purities can be obtained by fractional crystallization.

Antisolvent crystallization

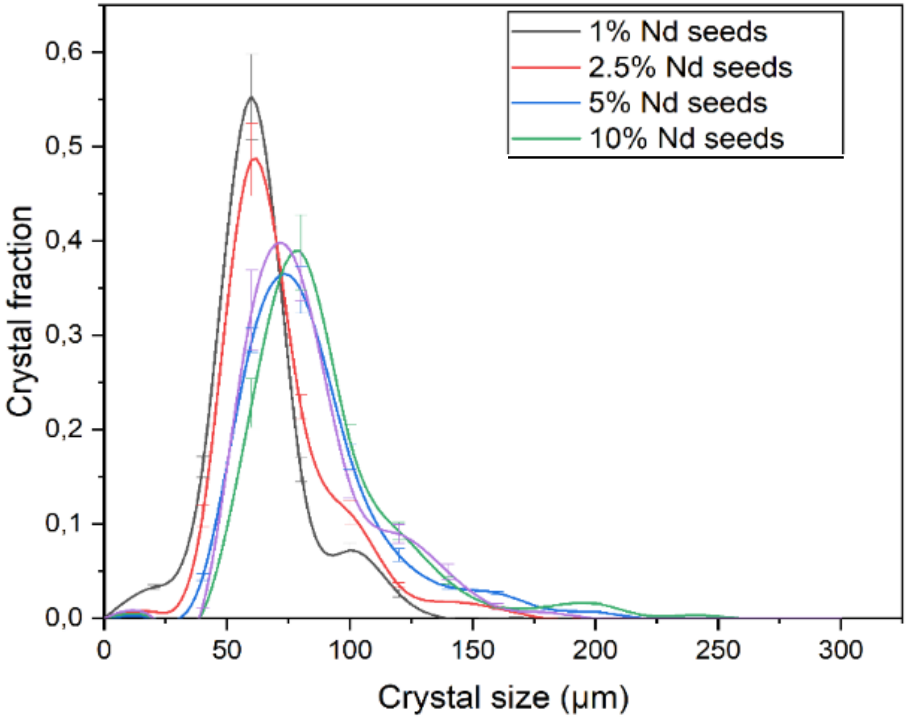
Which parameters are important?

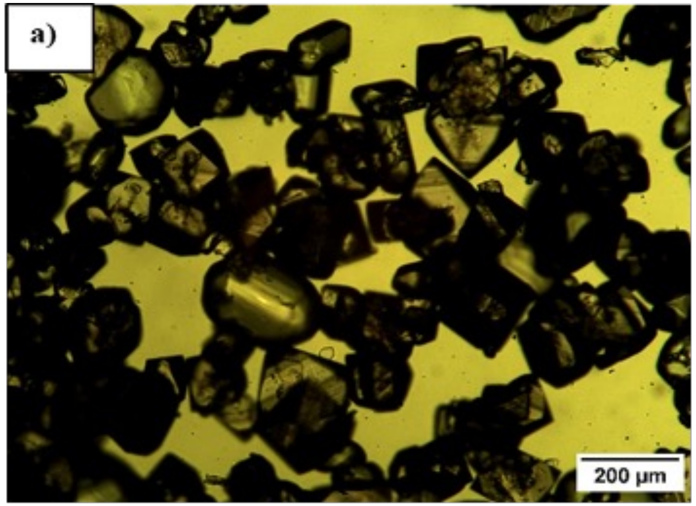
- Choice of antisolvent (solubility of impurities, shape)
- Dosing of antisolvent (amount, concentration and rate)
- Operation and mixing techniques (micro/macro)
- Study aging and agglomeration
- Seeding



Thermodynamics and kinetics are important

Recycling of magnets



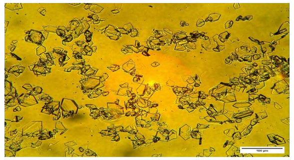


25 g/kg of Fe(II) and 10% Nd seed loading

Optimal
10% seed loading

Recycling of magnets

Antisolvent Crystallization of
REE sulphates



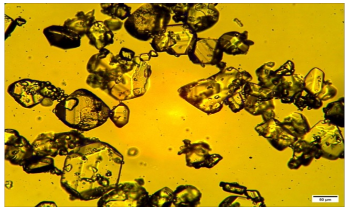
Seed crystals
$Nd_2(SO_4)_3 \, 8H_2O$

100 µm (all images)

Seeds

Antisolvent
0.1 mL/min

H_2SO_4 (aq)
Nd(III), **Fe(II)**

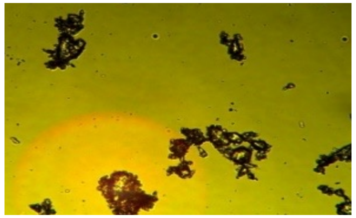


$Nd_2(SO_4)_3 \, 8H_2O$
Larger crystals
Nd purity >99%

Seeds

Antisolvent
0.1 mL/min

H_2SO_4 (aq)
Nd(III), **Fe(III)**



$Nd_2(SO_4)_3 \, 8H_2O$
Smaller crystals
Agglomerates
Nd purity >99%

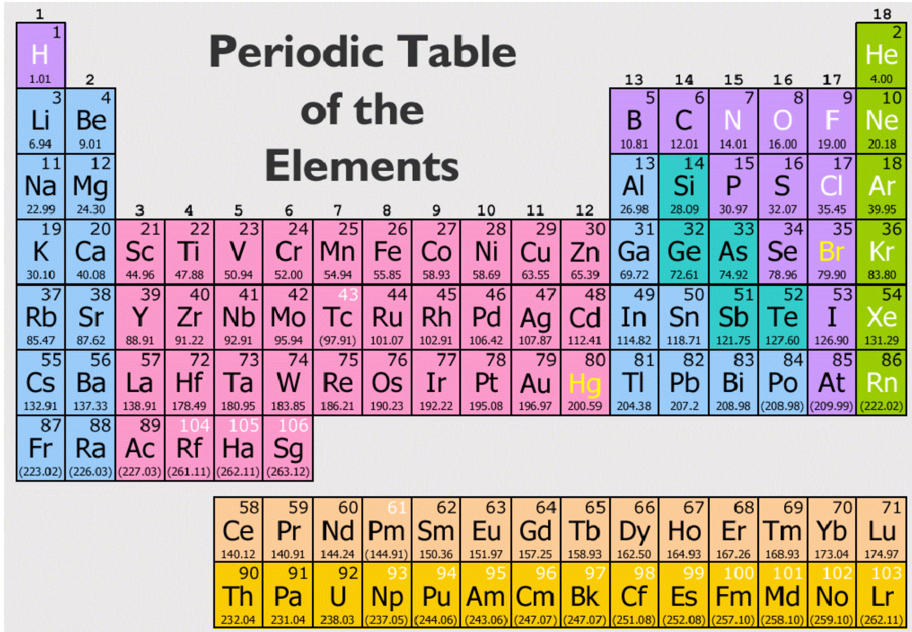
Co-funded by the Horizon 2020
programme of the European Union

ANTISOLVO
Nd-Fe-B

Individual separation of REE

Methods for REE separation

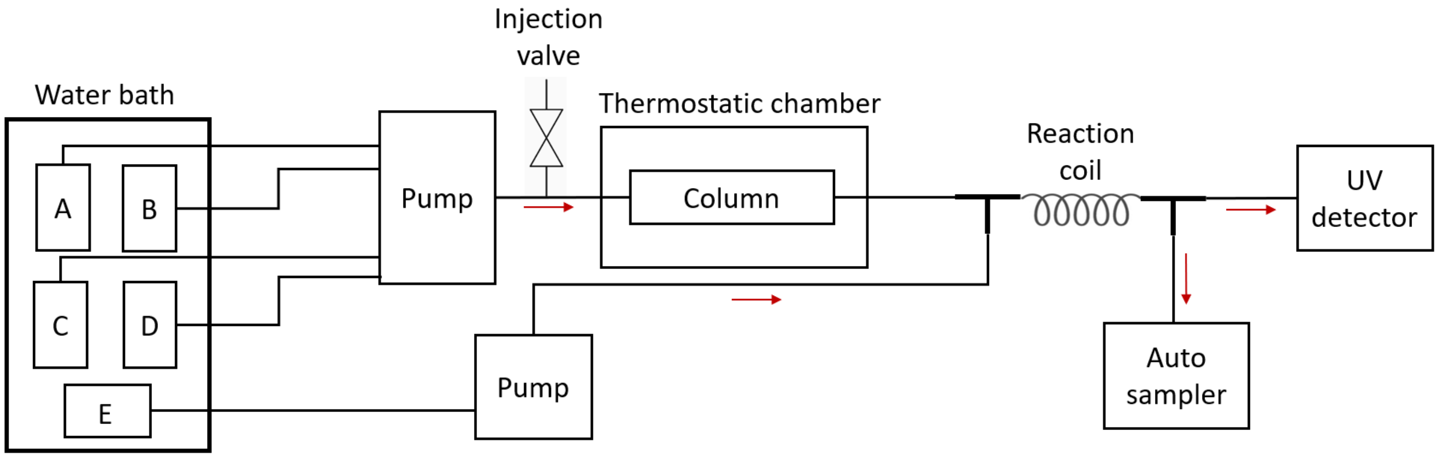
- Solvent Extraction (mixer settlers)
- Chromatographic Separation



Individual separation of REE

Criteria	Chromatographic Separation	Solvent Extraction
Selectivity and Precision	High, precise separation	Lower, less selective
Speed and Throughput	Slow, low throughput	Fast, high throughput
Cost	High equipment and operating costs	Lower capital costs for large scale
Environmental Impact	Low chemical waste	High chemical waste and solvents
Scalability	Moderate, limited by column size	Highly scalable for large quantities
Established Technology	Relatively new in industry	Long-established in industry

Extraction Chromatography

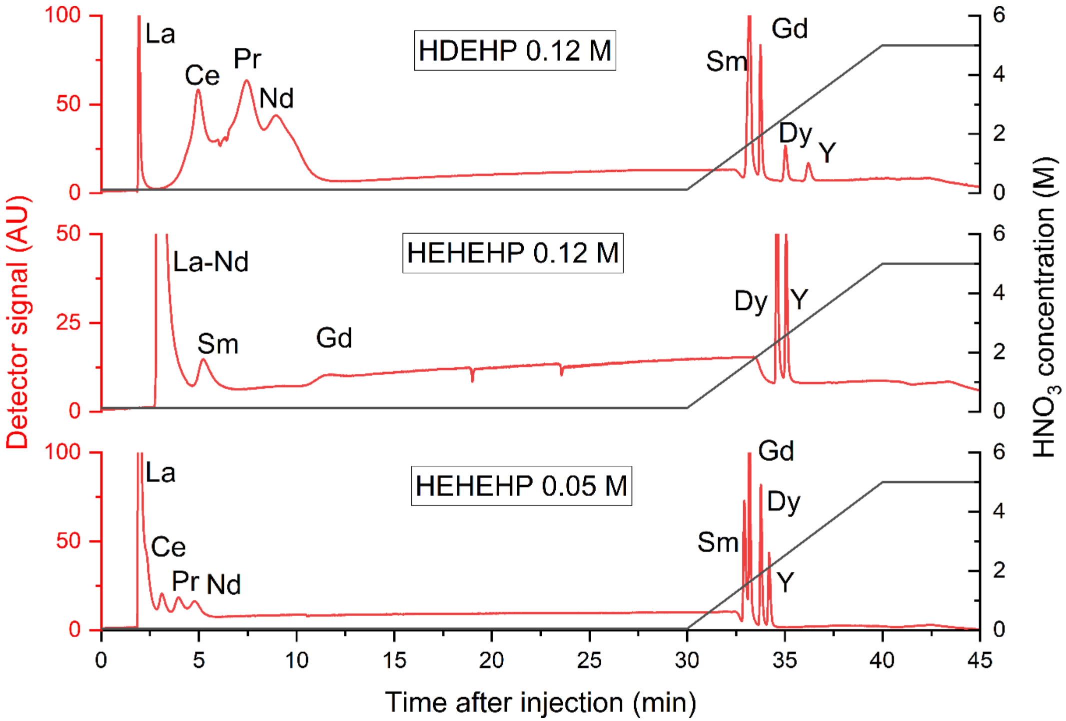


Schematic of the HPLC setup used in this work. The solutions used at the different channels in the water bath vary with the purpose. For column preparation: A – column conditioner, B – acidic organophosphorus solution, C – ethanol, and D – Milli-Q water. For REE separation: A – Milli-Q water, B – 2 M HNO_3, C – 5 M HNO_3 and E – Arsenazo III solution.

Co-funded by the European Union

We acknowledge
funding from Formas

Extraction Chromatography



Chromatograms

C18 column functionalized with 0.5 mmol of HDEHP (top) and HEHEHP (middle and bottom)

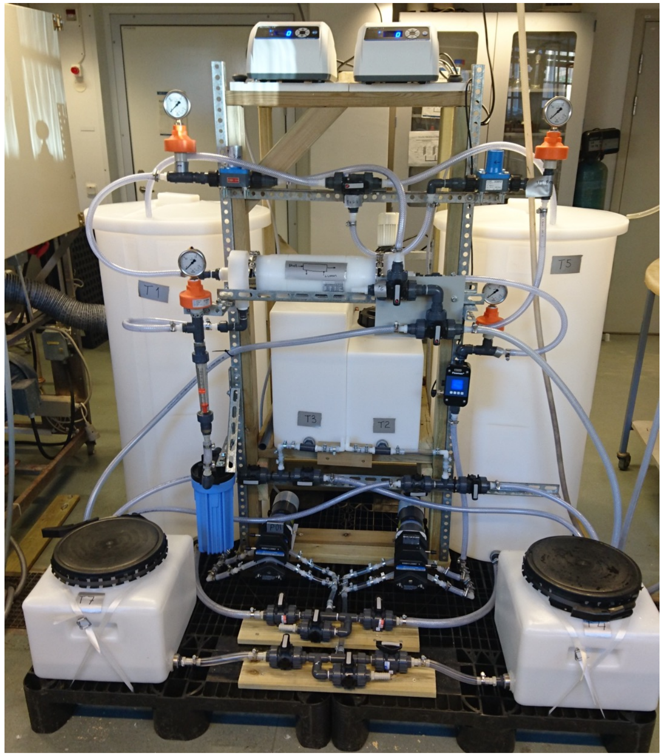
30 min isocratic elution at the concentration specified in the legend followed by

10 min gradient elution to 5 M HNO_3 (elution profiles shown as black lines on second axis).

Geetika Sanku M., Forsberg K. and Svärd M. (2022). Preparation of Extraction Chromatography Columns by Organophosphorus Acid Compounds. Journal of Chromatography A, vol. 1676, 463278.

Supported liquid membrane extraction

Exp. setup at KTH



Mini pilot at IVL

Thank you for your attention

Kerstin Forsberg, *professor*

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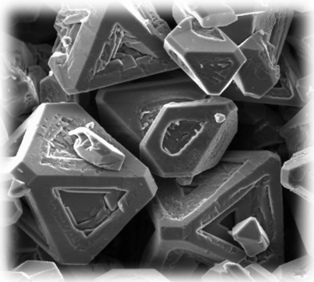
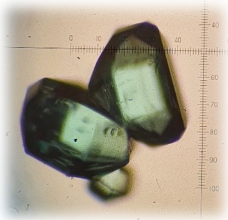
Dept. of Chemical Engineering





Acknowledge funding: Formas, Vinnova/ ERA-MIN (ANTISOLVO), STEM, EIT Raw Materials (DysCovery) and SSF.