Precipitation of Rare Earth Element Salts of High Quality

Kerstin Forsberg, professor

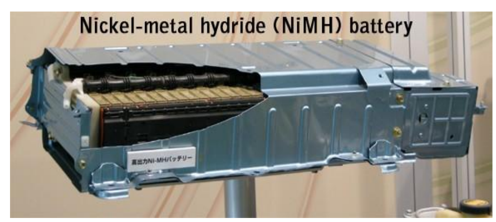
KTH Royal Institute of Technology, *Stockholm*

Dept. of Chemical Engineering

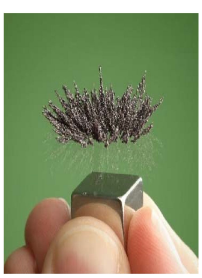
Rare Earth Elements (REE)

Sc (Al alloy)

Sc (SOFC)



La, Ce, Pr, Nd, Sm

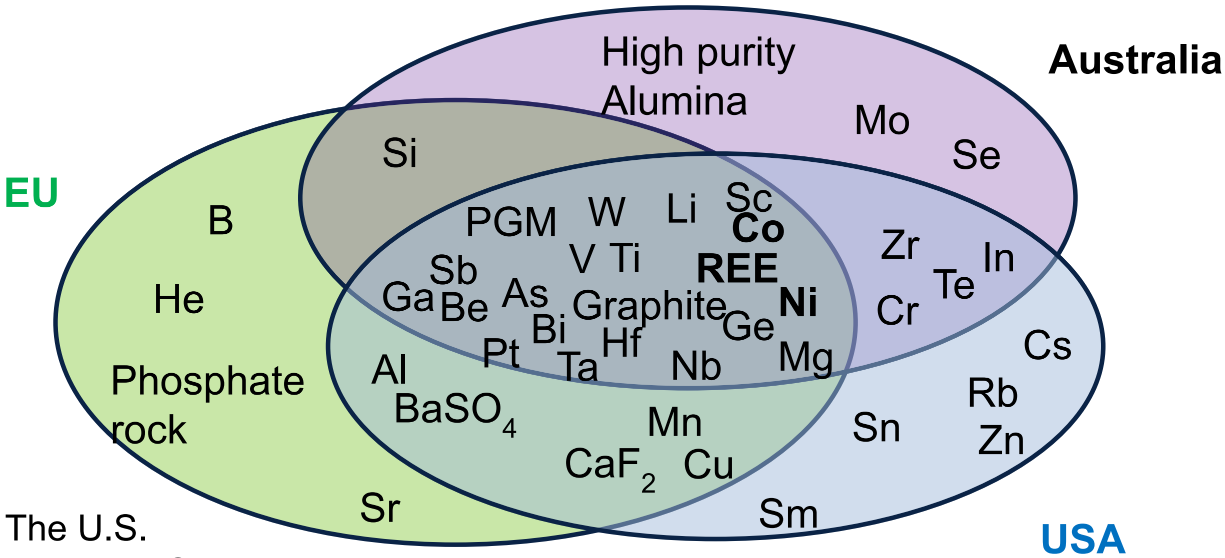


Nd, Pr, Dy, Sm

Ce, Eu, La, Y, Tb

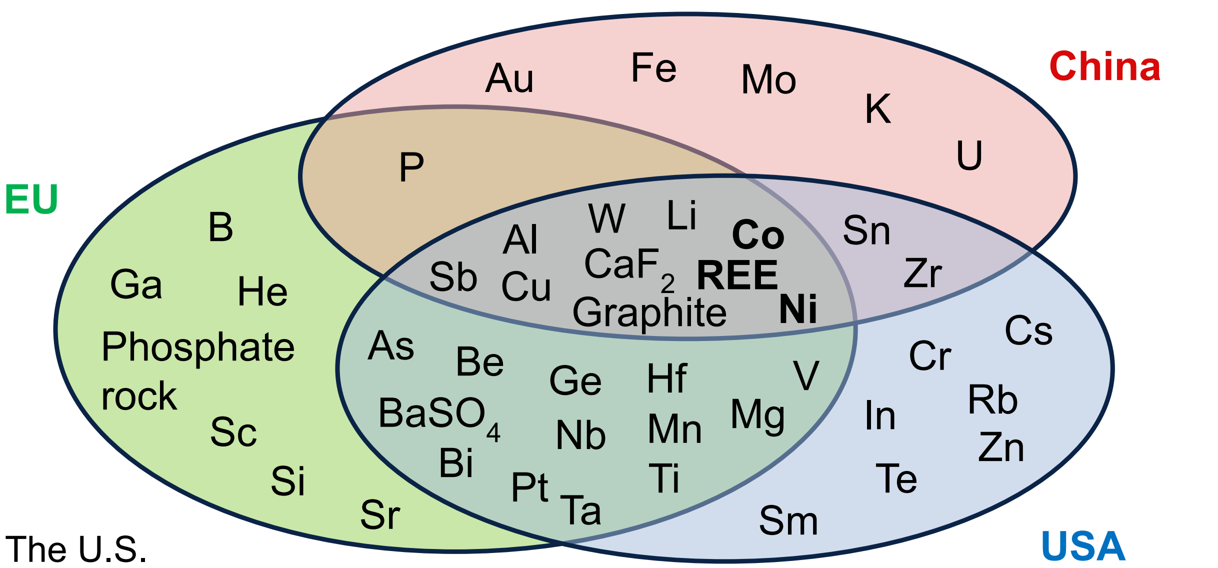
Magnets (25%), catalysts (22%), batteries (14%), polish (14%), metallurgy (9%), glass (6%), luminescence (6%)

Critical Raw Materials

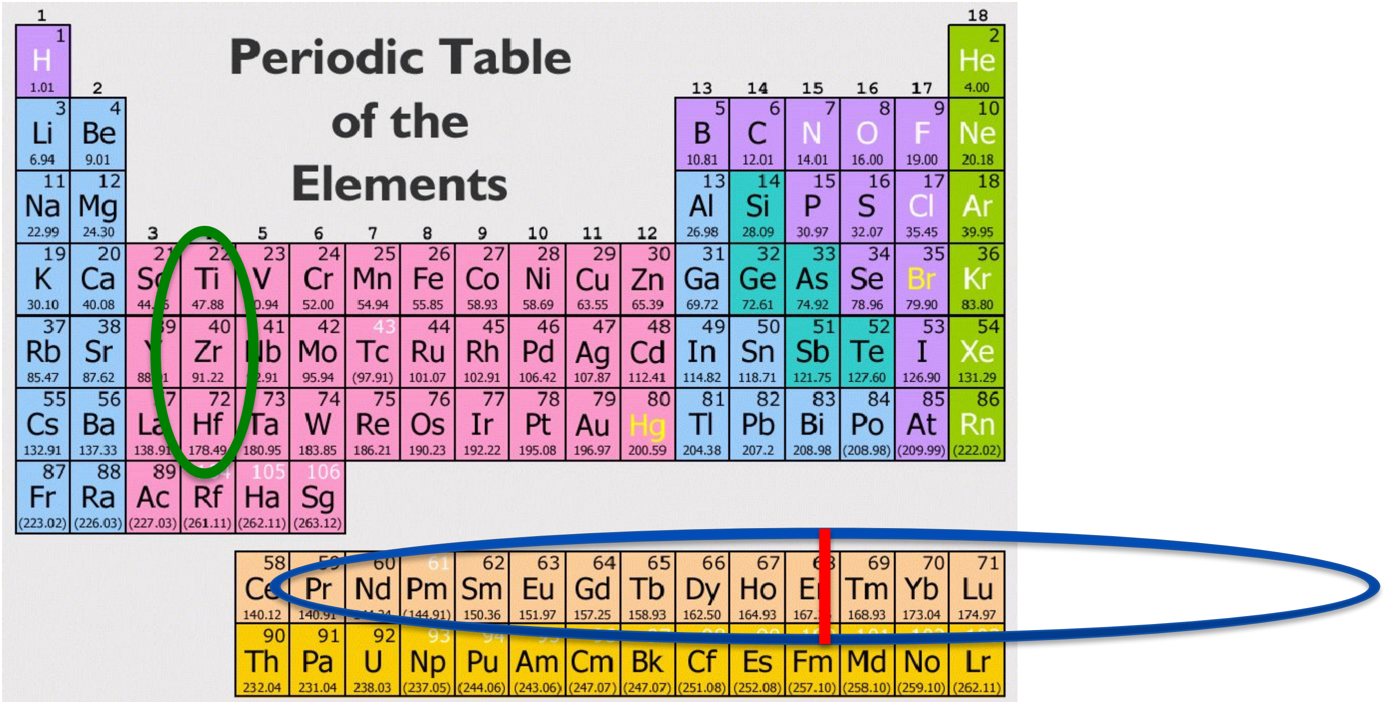


Source: Irena, The U.S. Department of Energy, EC, Australian Gov.

Critical Raw Materials



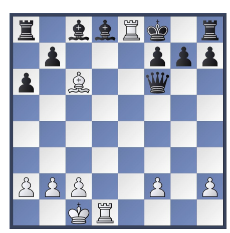
Source: Irena, The U.S. Department of Energy, EC



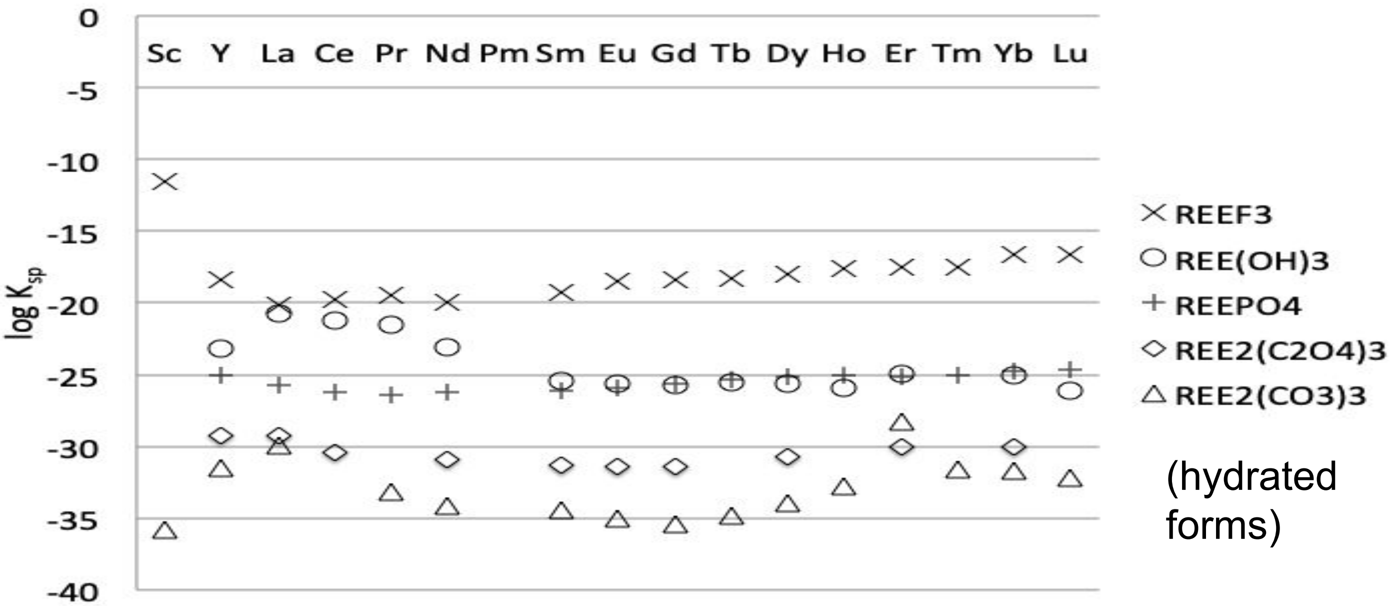
Separation of REE

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

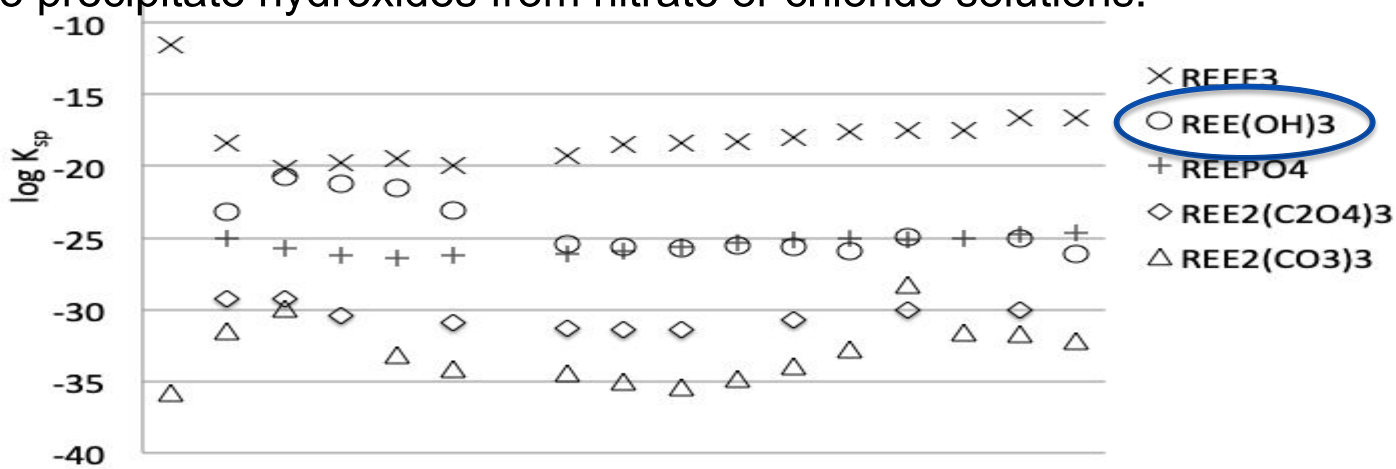


(hydrated forms)

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

Sparingly soluble REE salts

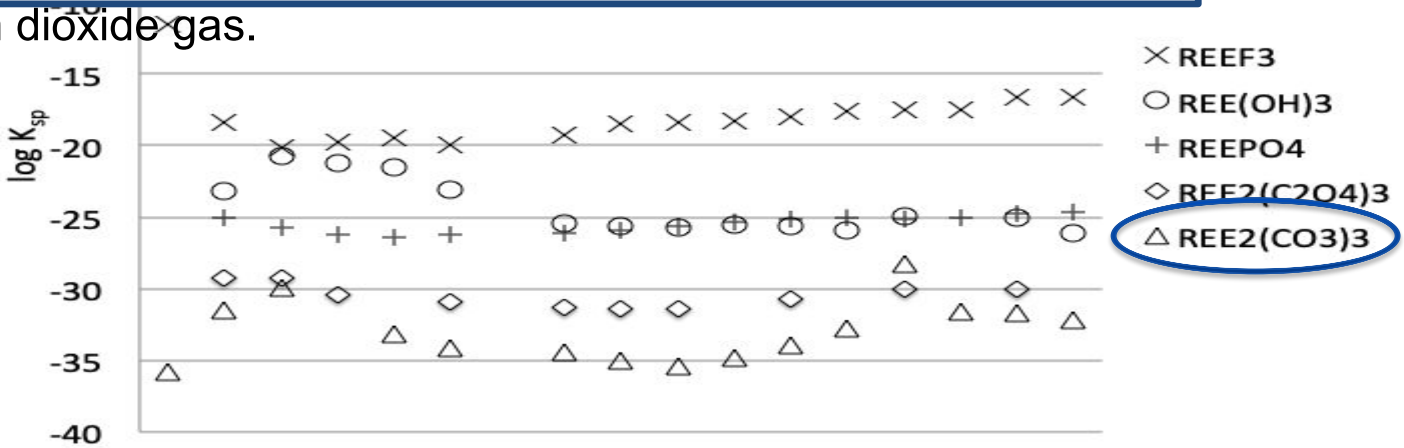
Basicity precipitation (*e.g.* using magnesia or caustic soda) is widely used in industry. Ammonia has also been used in large scale to precipitate hydroxides from nitrate or chloride solutions.



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

Sparingly soluble REE salts

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 – closing the loop

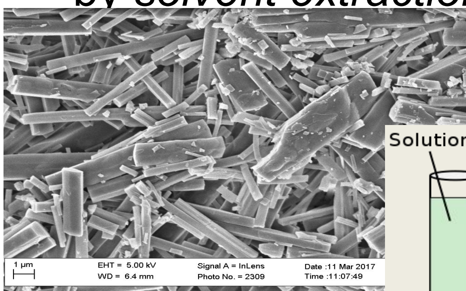
- **Reuse** – Large PM can be dismantled and reused, *e.g.* those in generators in wind turbines and potentially those in vehicle electric motors.
- **Direct recycling** – PM are harvested and used to make new PM, like in-house recycling of materials from production.
- **Indirect recycling** – due to 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.

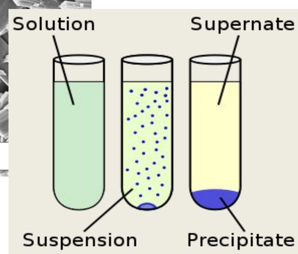
Yang et al. *J. Sustain. Metall.* (2017); Zhang et al. Metals (2020), www.urbanminingco.com

Hydrometallurgical recycling

Leaching (with or without roasting) followed by separation

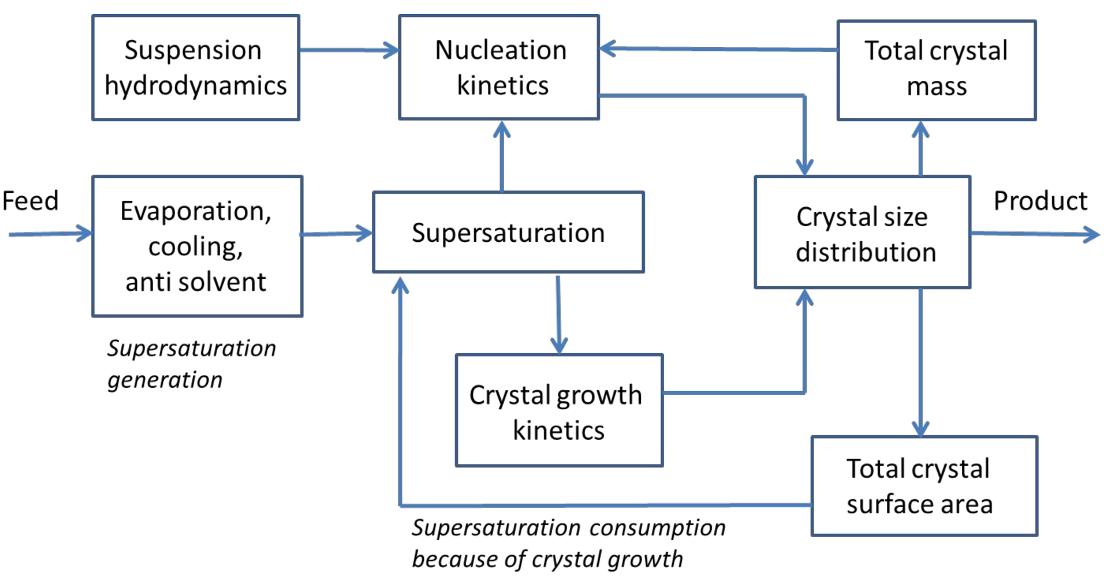
by *solvent extraction*, *ion exchange*, ***crystallization/ precipitation***



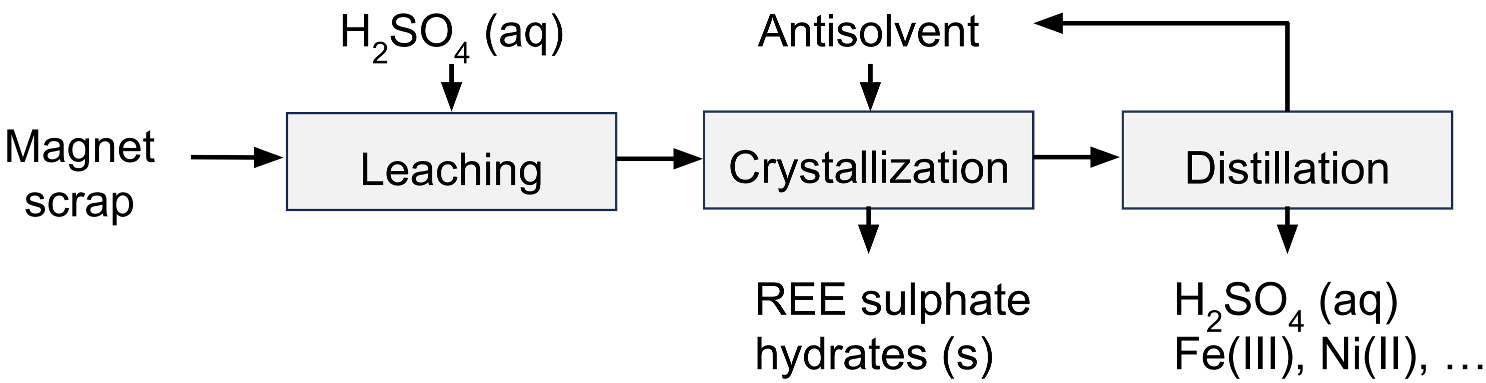


- The REE (Nd, Pr, Dy, Gd, Tb) are obtained as a mixture or as individual salts
- The final REE product is often the oxides or fluorides

Principles of Crystallization



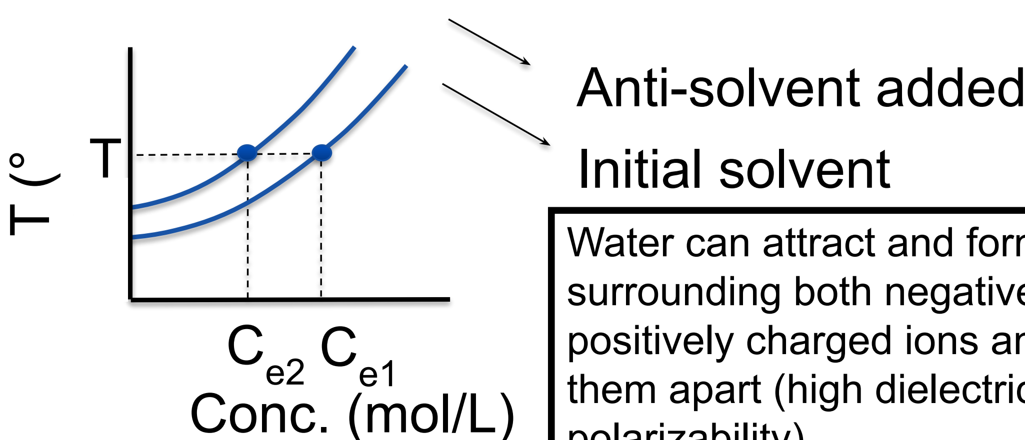
Recycling of magnets



- 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

Antisolvent crystallization

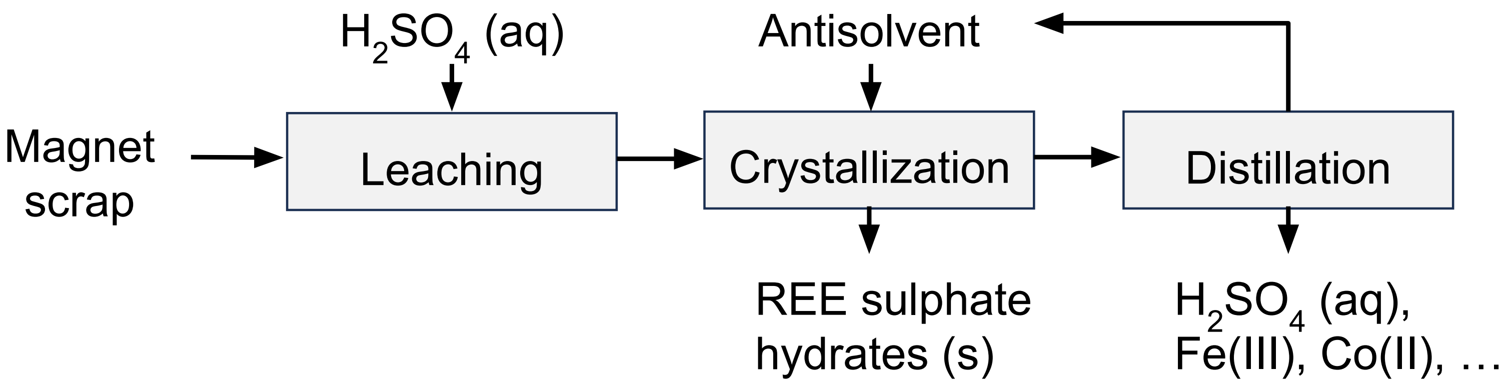
- By adding an antisolvent the solubility of the salt decreases



Water can attract and form layers surrounding both negatively and positively charged ions and thus keep them apart (high dielectric constant/ polarizability).

Alcohols have lower dielectric constants than water, which means that they have

Recycling of magnets



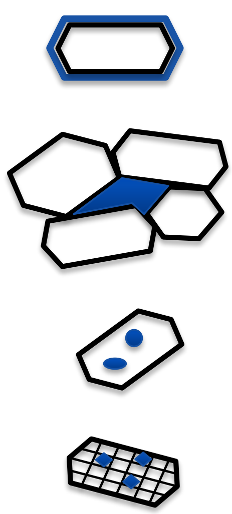
Synthetic solutions

- 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



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.

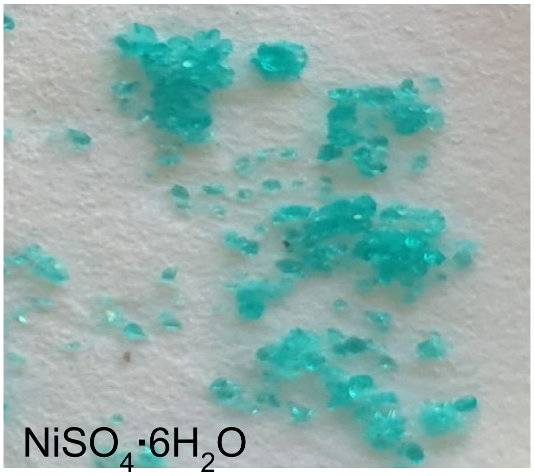
- Slow growth rate enhances purity (- productivity)
- Effective mixing enhances purity (> 10- 20µm)
- Avoid agglomeration
- Suitable CSD and shape gives shorter washing and filtration times which in turn leads to improved product quality, e.g. better purity

The formation of a solid solution is a thermodynamically controlled process. Thus the purity from a single step crystallization is limited;

Antisolvent crystallization

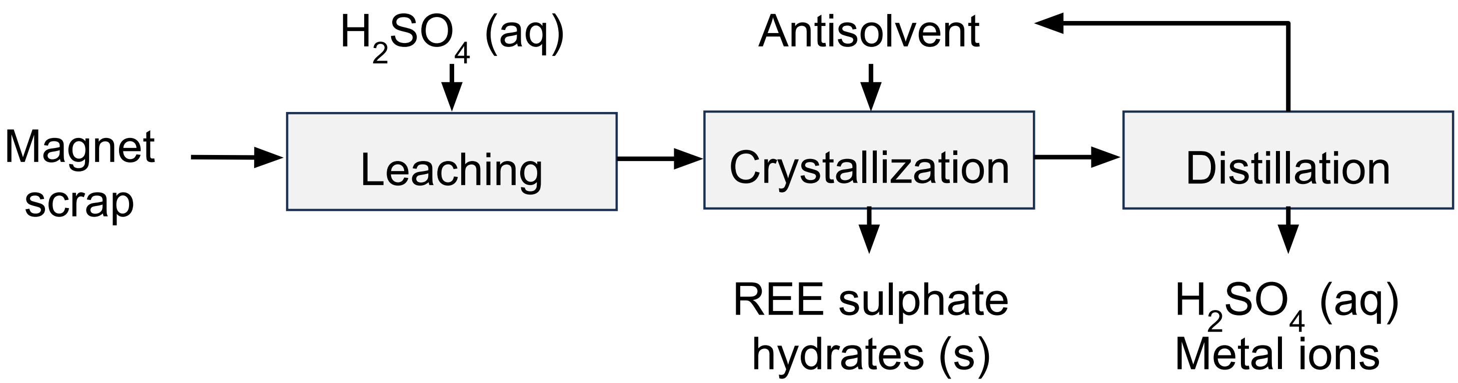
Which parameters are important?

- 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 °C
- 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 $(Nd/Dy)_2(SO4)_3 \cdot 8H_2O$

Recycling of magnets

Balance the generation and consumption of supersaturation

Promote growth and avoid secondary nucleation

- Antisolvent addition rate (generation of supersaturation)
- Seed loading (higher seed loading -> lower linear growth rate)

Addition rate (mL/min)	Seed loading
0.25	10%
0.1	1%
0.1	2.5%
0.1	5%
0.1	10%

Antisolvent crystallization

8 g/kg of Nd(III)

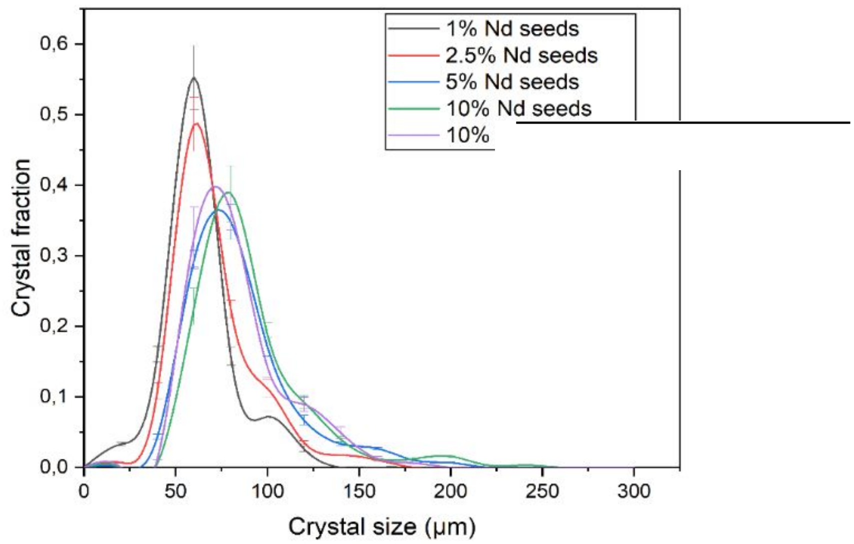
25 g/kg Fe(II)

Seeding with $Nd_2(SO_4)_3 \cdot 8H_2O$

Antisolvent: Ethanol (100%)

25 °C

Recycling of magnets



Optimal
10% seed loading

Recycling of magnets

Purity of $Nd_2(SO_4)_3 \cdot 8H_2O$ (c)

Addition rate (mL/min)	Seed loading	Fe (II) (g/kg)	Purity[1] (%)
0.1	1%	9± 2	97.1 ± 0.6
0.1	2.5%	7± 2	98.3 ± 0.4
0.1	5%	4 ± 3	98.9 ± 0.5
0.1	10%	2± 1	**99.5 ± 0.2**
0.25	10%	17± 4	95.6 ± 0.8

Optimal
10% seed loading
0.1 mL/min addition rate

- The systematic change in purity with seed loading and antisolvent addition rate indicate that the Fe(II) is primarily introduced into the sample during the crystallization process rather than during the washing stage.
- It is not possible to determine to which extent the iron is present as separate crystals or incorporated into the neodymium phase respectively.

Recycling of magnets

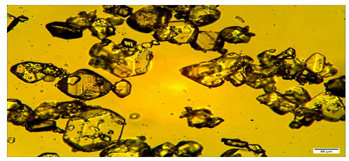
Antisolvent Crystallization of REE sulphates

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

100 µm (all images)

Seeds

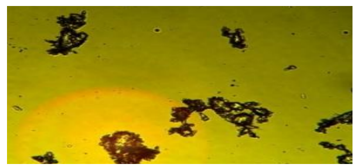
Antisolvent 0.1 mL/min → H_2SO_4 (aq) Nd(III), Fe(II) →



$Nd_2(SO_4)_3\,8H_2O$
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

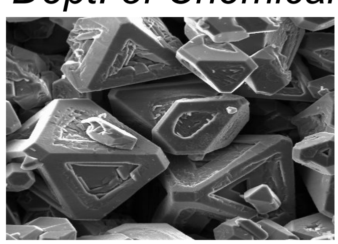
Thank you for your attention

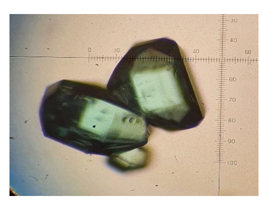
Kerstin Forsberg, *professor*

M. Svärd, N. Pawar, T. Punt, M. Geetika Sanku

***KTH Royal Institute of technology**, Stockholm*

Dept. of Chemical Engineering

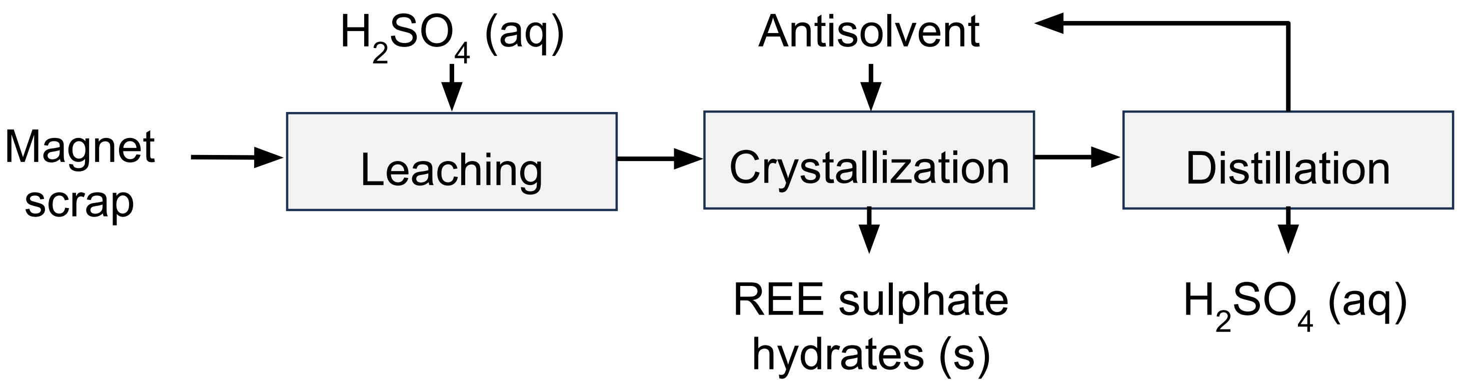




Co-funded by the European Union

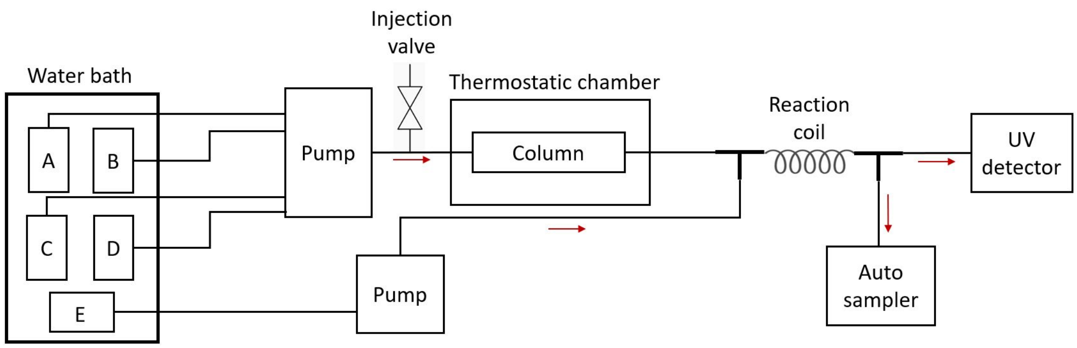
Acknowledge funding: Formas, Vinnova (ERA-MIN), H2020, EIT Raw and TÜBİTAK.

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
- **What to do with the REE concentrate?**

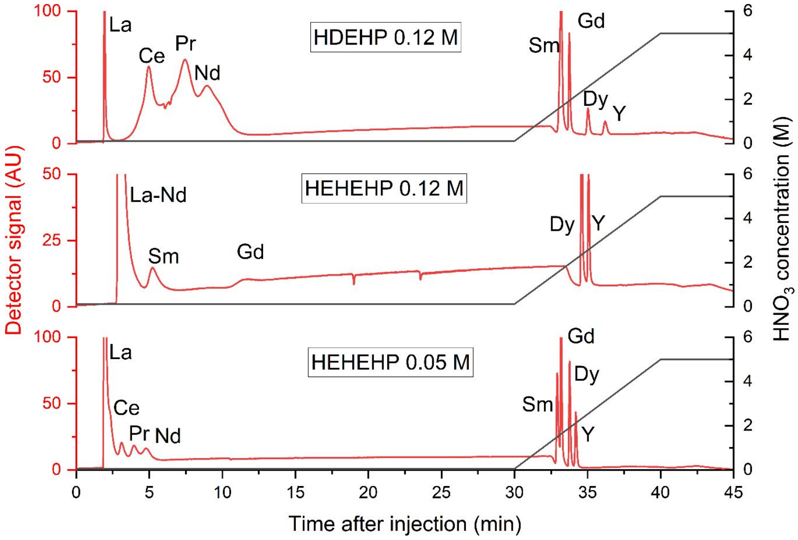
Extraction Chromatography



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.

eit RawMaterials Connecting matters
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

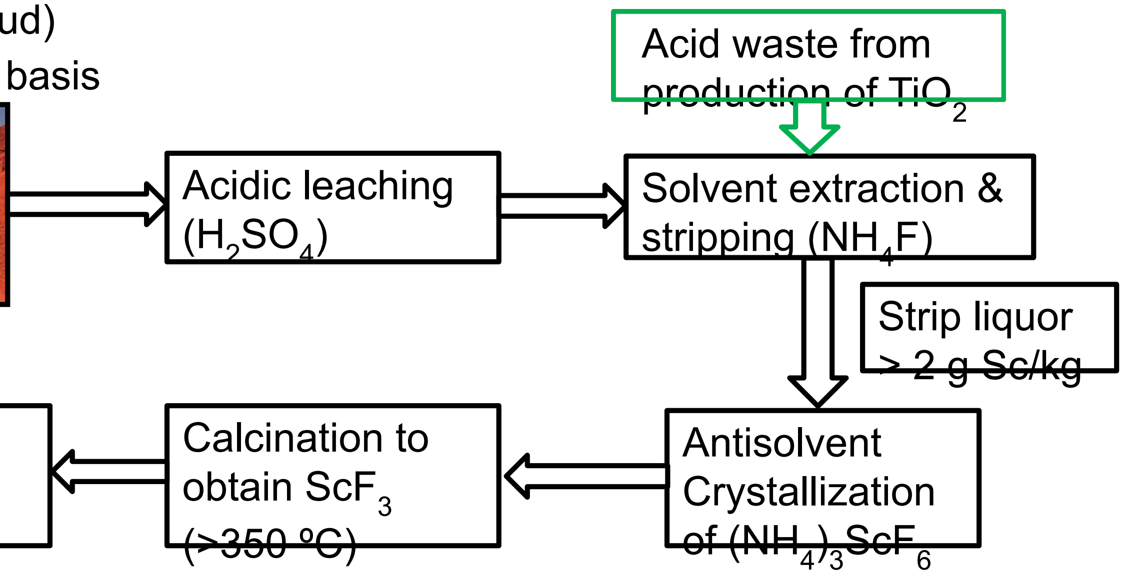
10 min gradient elution to 5 M HNO_3 (elution profiles shown as black lines on second axis).

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.

Recovery of Sc

Bauxite residue (red mud)

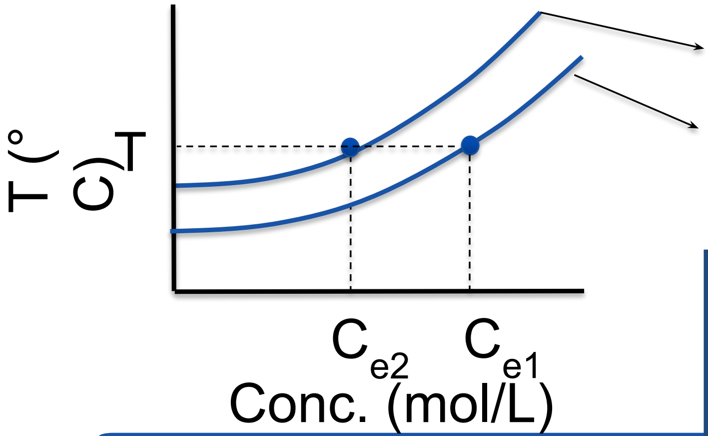
50 – 150 mg Sc/kg dry basis



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 730105.

Antisolvent precipitation

- By adding an antisolvent the solubility of the salt decreases

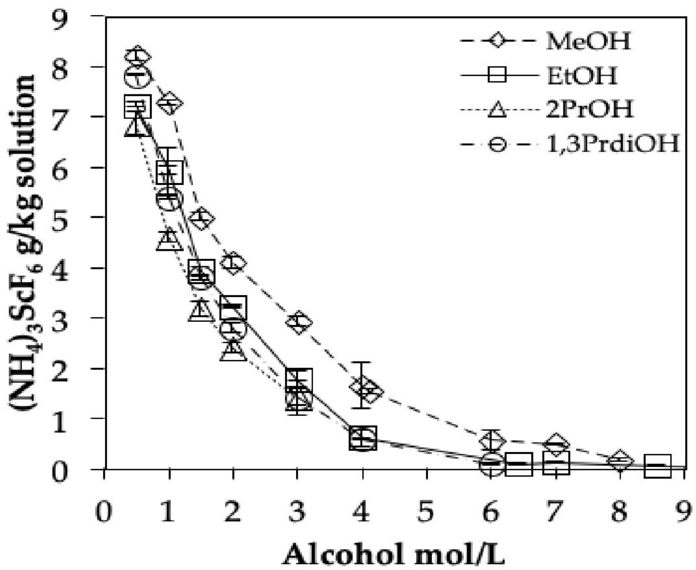


- Water polarizes and can keep charged ions apart.
- Alcohols have a lower ability to keep charged ions apart

(dielectric constant/ polarizability)

Antisolvent crystallization of $(NH_4)_3ScF_6$

Choice of antisolvent



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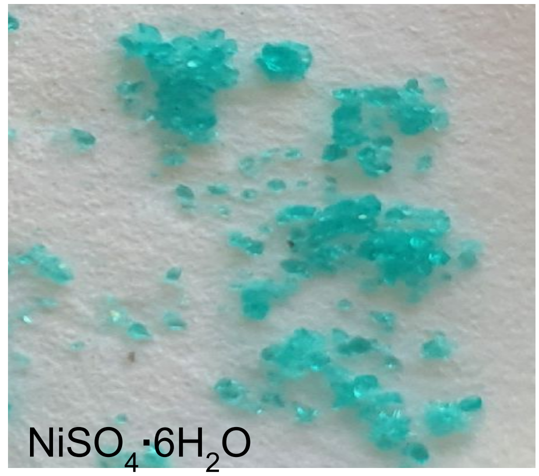
Antisolvent crystallization

Which parameters are important?

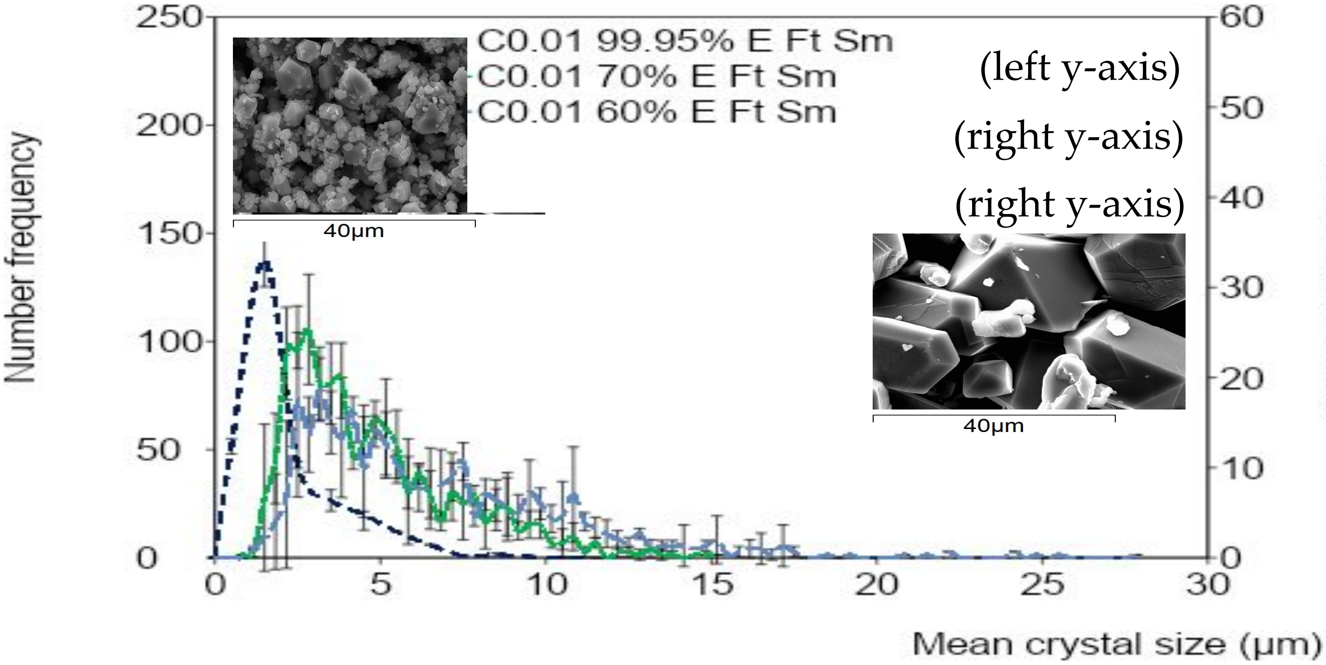
- Choice of antisolvent (solubility of impurities, shape)
- Dosing of antisolvent (amount, concentration and rate)
- **Operation and mixing techniques** (micro/macro)
- Study aging and agglomeration
- Seeding



Thermodynamics and kinetics are important

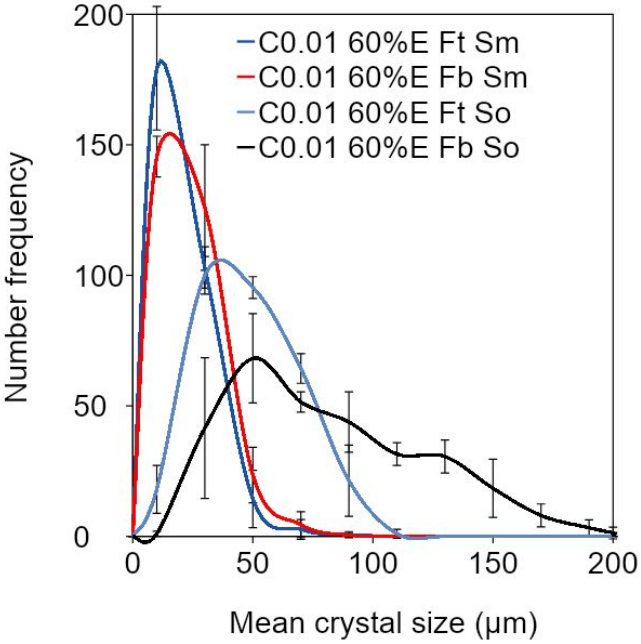
Antisolvent crystallization of $(NH_4)_3ScF_6$

Dosing of antisolvent (concentration)

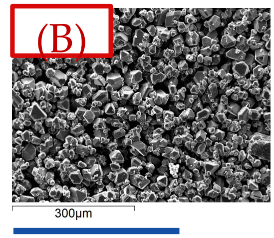


Antisolvent crystallization of $(NH_4)_3ScF_6$

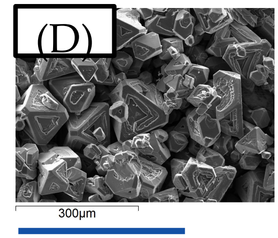
Operation and mixing techniques



(A)
(B)
(C)
(D)

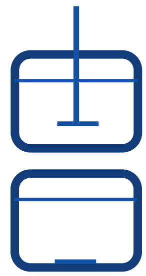


300 µm



300 µm

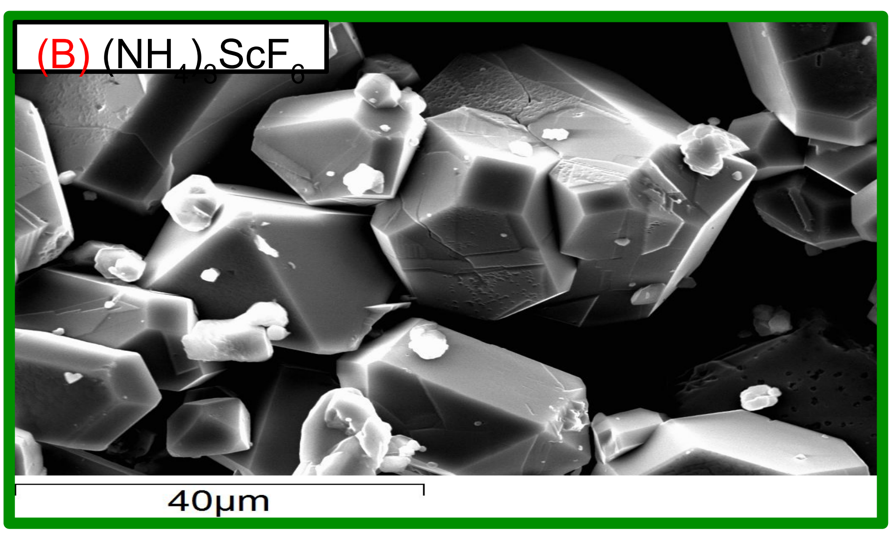
Ft: Top feed
Fb: Bottom feed
So: Overhead stirring
Sm: Magnetic stirring



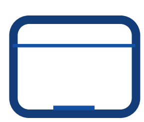
So

Sm

Antisolvent crystallization of $(NH_4)_3ScF_6$



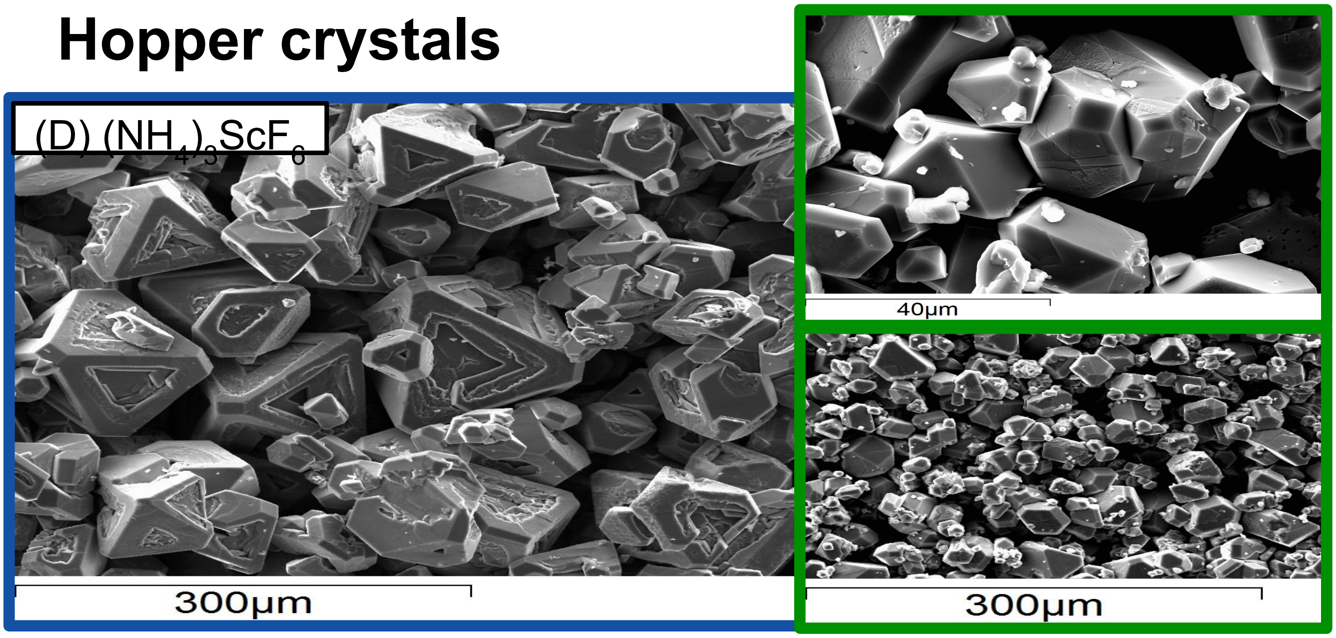
- Dosing 0.01 mL/s
- 60% EtOH
- Magnetic Stirring
- Top feed



Sm

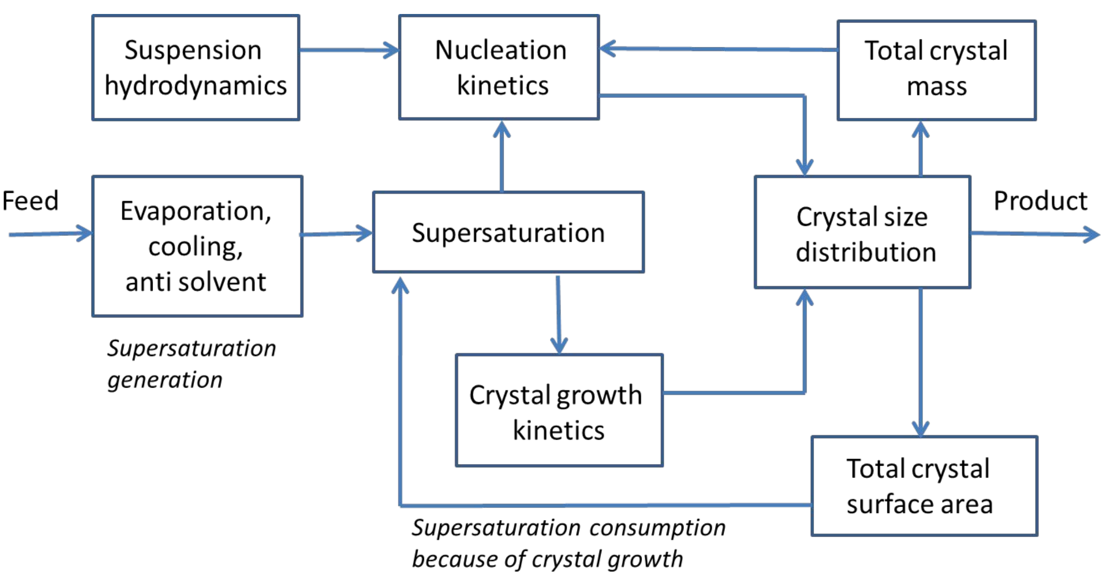
Antisolvent crystallization of $(NH_4)_3ScF_6$

Hopper crystals



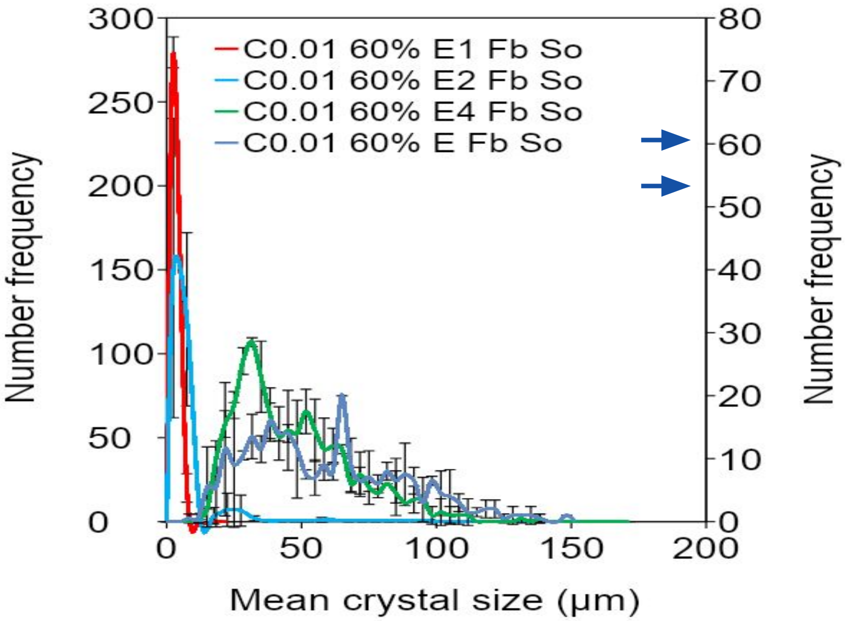
Peters E., Svärd M., Forsberg K. (2022). Impact of process parameters on product size and morphology in hydrometallurgical antisolvent crystallization, CrystEngComm, 24, 2851- 2866.

Principles of Crystallization



Antisolvent crystallization of $(NH_4)_3ScF_6$

Seeding (internal)



Research Activities

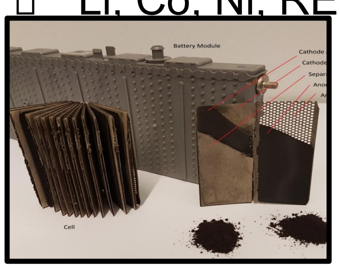
Hydrometallurgy, separation processes

Magnet recycling

- REE, Co

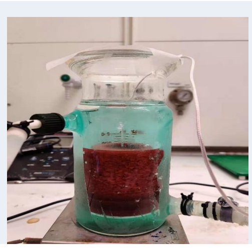
Battery recycling

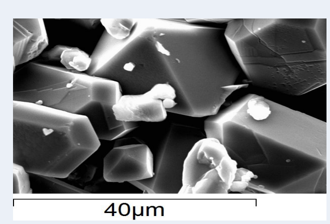
- Li, Co, Ni, REE



Mining waste

- V and Sc





We acknowledge funding from: the Swedish Energy Agency, the Swedish Foundation for Strategic Research, Formas, the Swedish Radiation and Safety Authority, the Swedish Nuclear Fuel and Waste Management

Critical Raw Materials

Critical and strategic Raw Materials for the EU

2023 CRMs (5^{th} list)			
Aluminium/Bauxite	Coking Coal	Lithium	Phosphorous
Antimony	**Feldspar**	Light REE	Scandium
Arsenic	Fluorspar	Magnesium	Silicon metal
Baryte	Gallium	**Manganese**	Strontium
Beryllium	Germanium	Natural Graphite	Tantalum
Bismuth	Hafnium	Niobium	Titanium metal
Boron/Borate	**Helium**	Platinum group metals	Tungsten
Cobalt	Heavy REE	Phosphate Rock	Vanadium
		Copper*	**Nickel***

New materials added to the list in 2023 in **bold**

* Cu and Ni are included only as strategic raw materials (CRMs Act)

Critical and Strategic Raw Materials

Critical Raw Materials (CRMs)**:**

Economic importance - importance for the EU economy regarding end-use applications and value added of corresponding EU manufacturing. Corrected by the substitution index related to technical and cost performance of the substitutes for individual applications.

Supply risk - reflects risk of a disruption in the EU supply. Based on primary supply from countries, considering governance performance and trade aspects. Measured at the 'bottleneck' stage of the material (extraction or processing), presenting the highest supply risk. Substitution and recycling are considered risk-reducing measures.

Strategic Raw Materials (SRMs):

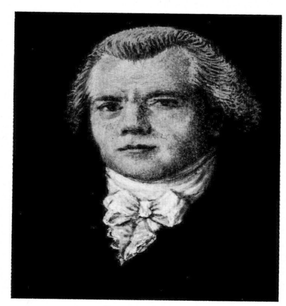
Raw materials important for technologies that support the twin green and digital transition and defence and aerospace objectives

Ref: http://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en

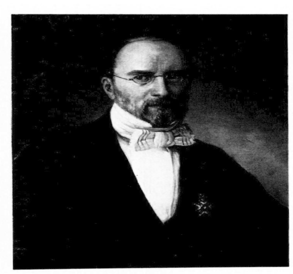
Naturhistoriska addera…

Discovery of REE

Year	Element	Origin of Name	Discovery	Nationality
1794	Yttrium	Ytterby mine, Sweden	Johan Gadolin	Finnish
1803	Cerium	After the asteroid Ceres	Baron Jöns Jakob	Swedish
1839	Lanthanum	From Greek lathano = concealed	Carl Gustav Mosander	Swedish
[illegible]	Erbium	Derived from Ytterby mine, Sweden	Carl Gustav Mosander	Swedish
1878	Terbium	Derived from Ytterby mine, Sweden	Carl Gustav Mosander	Swedish
[illegible]	Ytterbium	Derived from Ytterby mine, Sweden	Jean Charles de Marignac	French
1879	Samarium	After the mineral samarskite	Paul E. Lecoq de Boisbaudran	Swedish
1879	Scandium	After Scandinavia	Lars Fredrik Nilson	Swedish
1879	Holmium	After the Latin for Stockholm	Per Teodor Cleve	Swedish
1879	Thulium	Ancient name for Scandinavia	[illegible]	Swedish



J. Gadolin



C.G. Mosander

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)
- China supplies Europe with 100% of HREE and 85% LREE

Study on the Critical Raw Materials for the EU 2023

Recycling of magnets – closing the loop

- In the short term recycling of PM can only satisfy a small part of the total REE demand globally
- In the long term, by 2100, recycling is estimated to be able to satisfy almost 50% of the Nd and Dy demand

How can the magnets from EOL products be recycled and how do they age?

The magnets vary in size in different applications and small magnets are not dismantled.

Different items reach their EOL at different times.

Yang et al. *J. Sustain. Metall.* (2017); Habib and Wenzel *J. Clean Prod.* (2014)

Hydrometallurgy for Resource Recovery

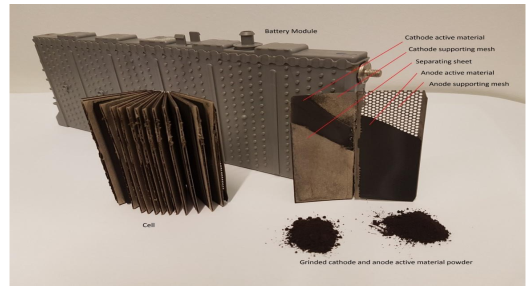
Bauxite residues and acid waste from TiO_2 pigment production

- Recovery of Sc

Scale-Up, EIT Raw Materials

Apatite concentrate $Ca_{10}(PO_4)_6(OH,F,Cl)_2$

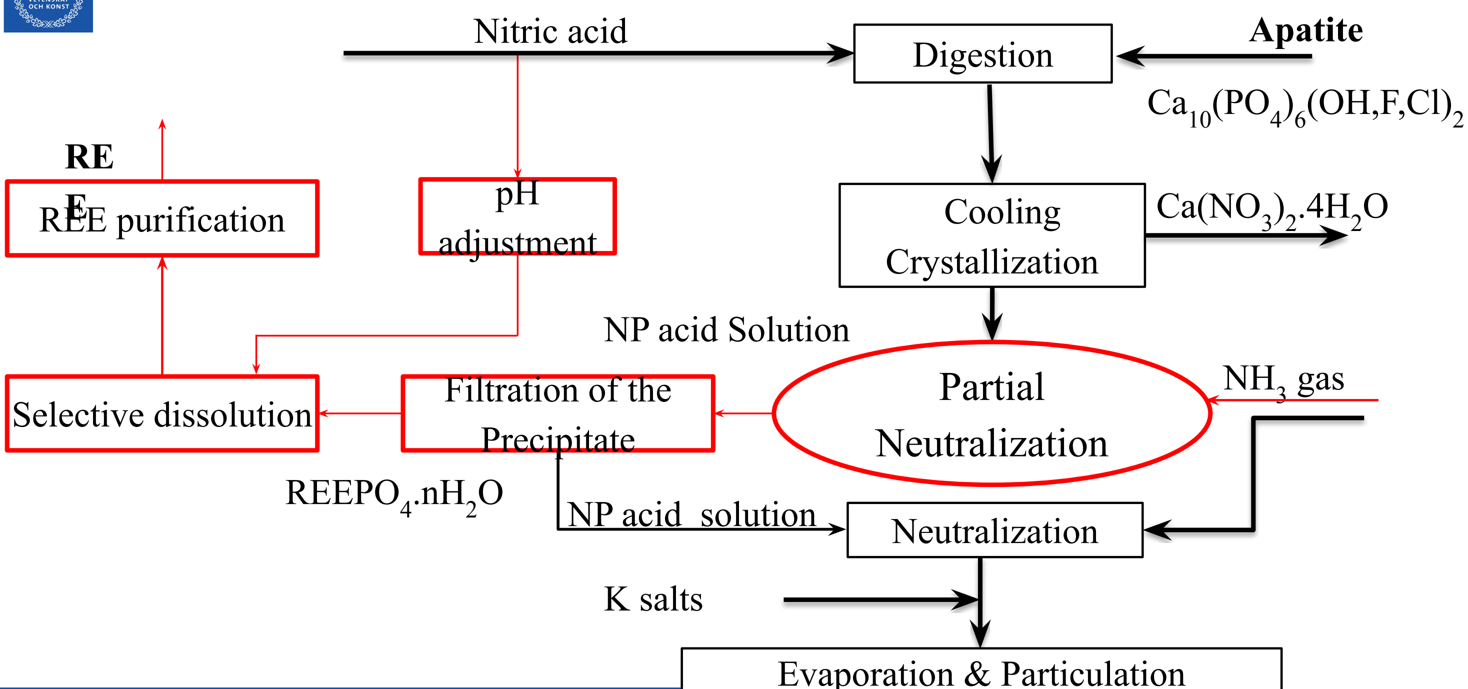
- Recovery of P and Ce, Nd, Y, La, Pr, Dy…



HEV NiMH batteries

- Recovery of Ni, Co, La, Ce, Nd, Pr and Y

REE separation integrated with the NP process



M. Alemrajabi et al., "Upgrading of a rare earth phosphate concentrate within the nitrophosphate process," Journal of Cleaner Production, vol. 198,

Recycling of magnets