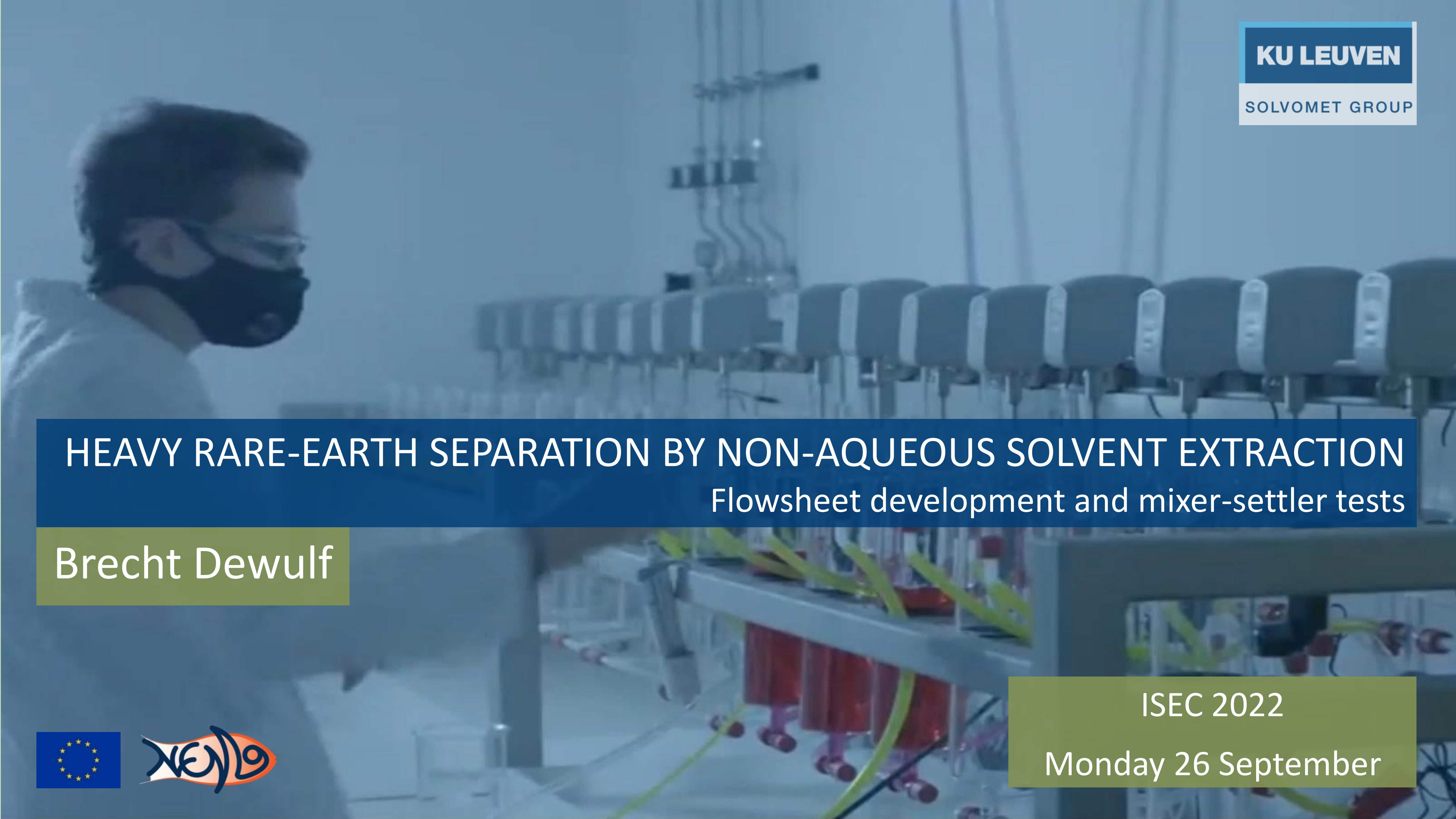


# HEAVY RARE-EARTH SEPARATION BY NON-AQUEOUS SOLVENT EXTRACTION

## Flowsheet development and mixer-settler tests

Brecht Dewulf

KU LEUVEN
SOLVOMET GROUP

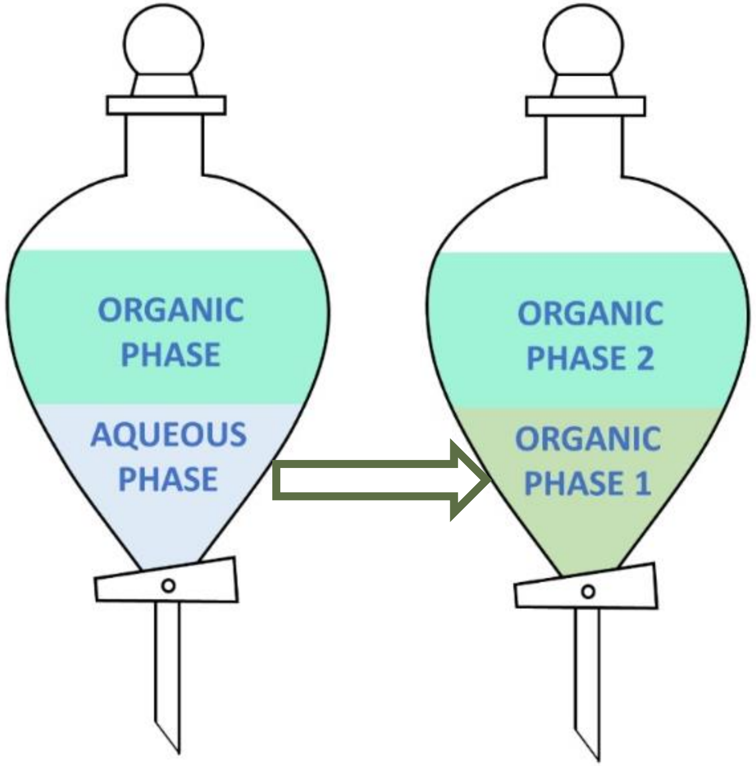
ISEC 2022

Monday 26 September

# Solvometallurgy

## Non-aqueous solvent extraction (NASX)

- Distribution of a solute between two immiscible organic phases
- Expands scope of conventional SX
- Can offer enhanced selectivity and treat water-sensitive compounds




## Requirements

- Low mutual solubility of two phases
- Fast phase separation
- Extractant is soluble in less polar (LP) phase, not in more polar (MP) phase
- Starting metal compound is soluble in the MP phase
- Metal compounds should not react with the organic solvents

Binnemans and Jones, **2017**, J. Sustain. Met. 3, 570–600

# Non-aqueous solvent extraction for rare-earth separation

**Solvometallurgy & rare earths**

H2020 NEMO

Equipment & Materials

Mixer-settler pilot

Conclusions

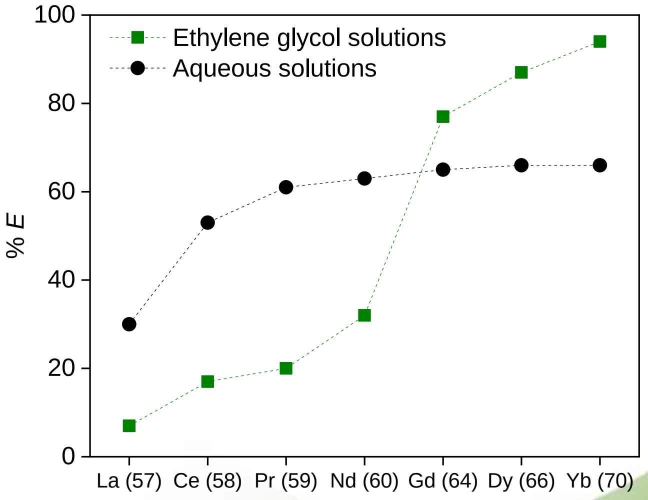
## Rare-earth elements (REEs) and their application

- 15 lanthanides + Sc and Y
- Critical raw material: highest supply risk (EU: 98% imported from China)
- Economic importance: hard-disk drives, catalysts, abrasives, fluorescent phosphors, permanent magnets
- Importance in energy transition and green technologies

## Group separation and purification of individual REE

- Conventional process: 1000s of stages comprising numerous extraction-scrubbing-stripping cycles
- Non-aqueous SX: higher separation factors → more efficient separation process

Batchu *et al.*, **2017**, Sep. Purif. Technol. 174, 544–553

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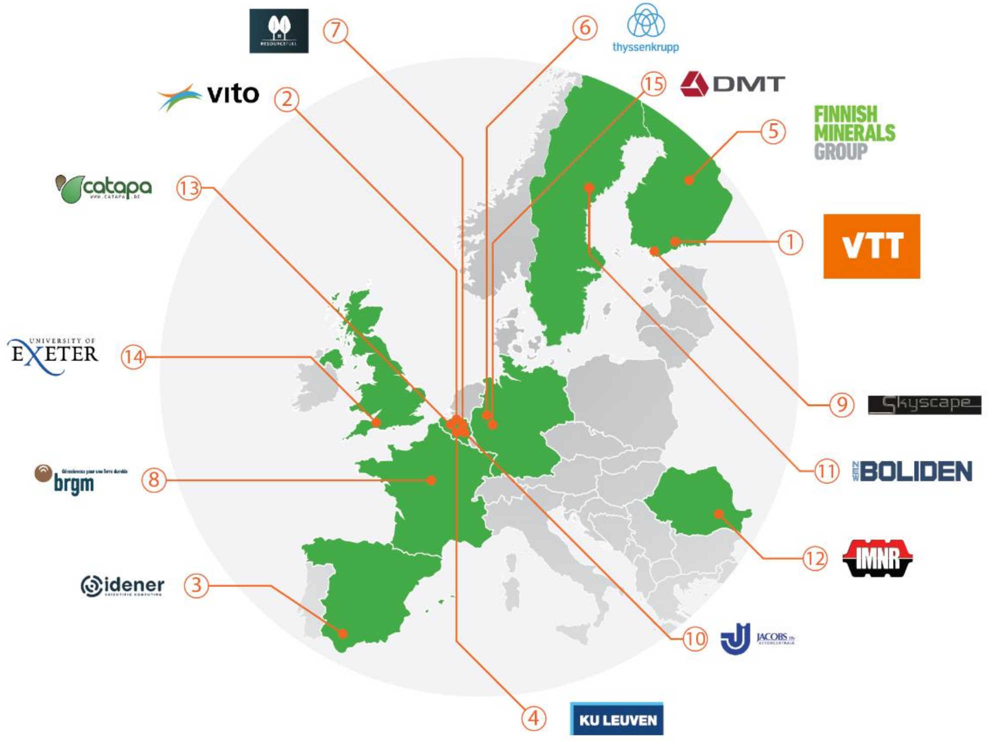
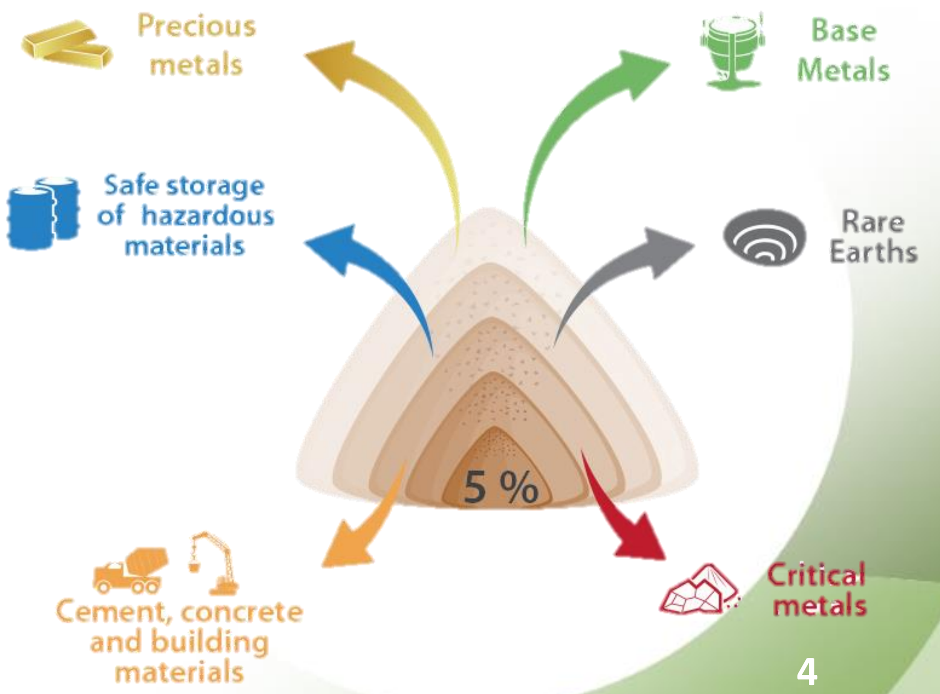
# EU H2020 NEMO

- Valorization of low-grade sulphide mining waste: 600 Mtonne/yr + historic stockpile 28,000 Mtonne in Europe
- 15 partners across Europe, 3 case studies, 4 pilots
- REE recovery from Sotkamo heap leaching PLS: study of solvometallurgical routes




https://h2020-nemo.eu/

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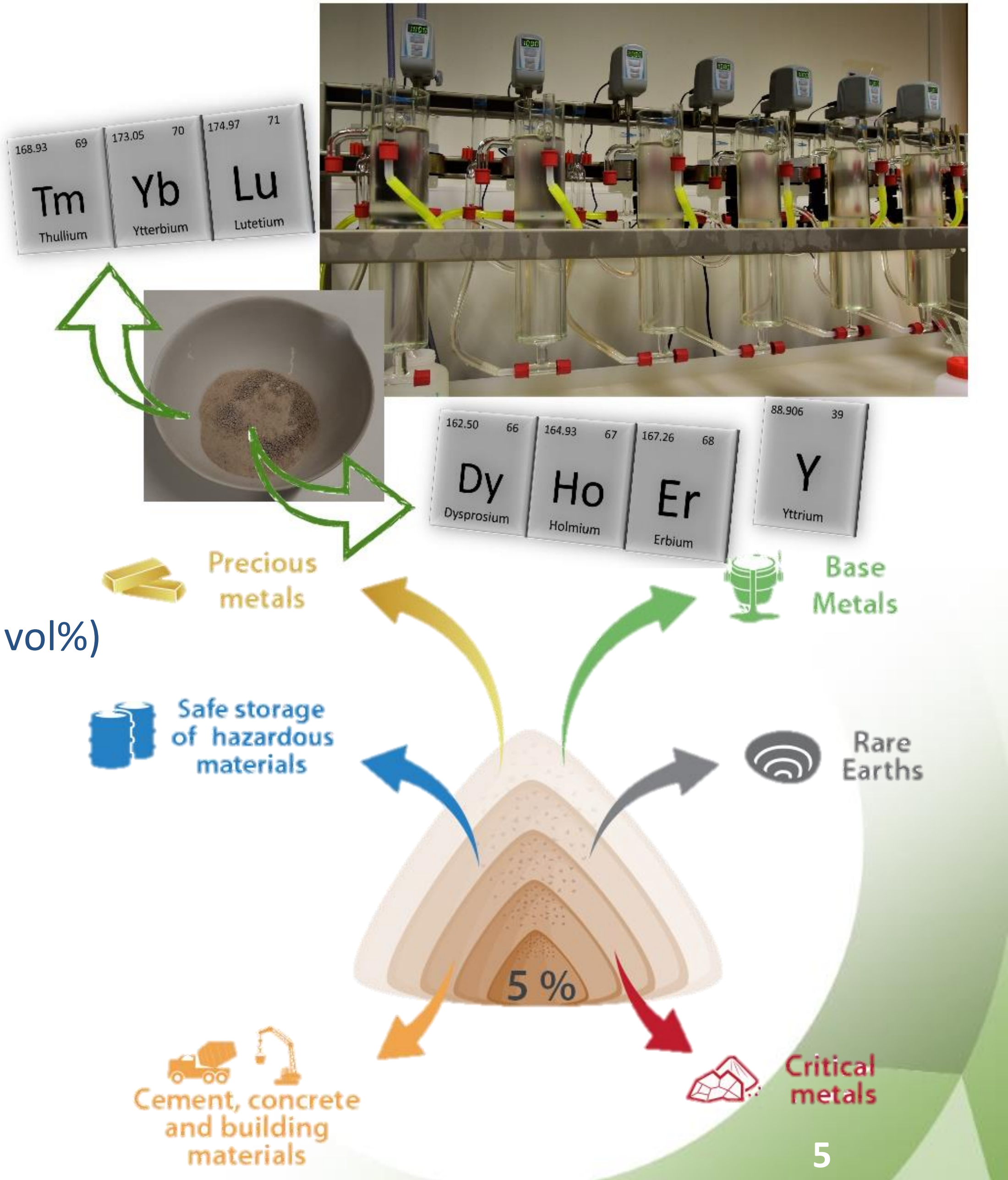
# Goals



Within H2020 NEMO project, recovery of REEs from PLS originating from primary heap leaching at Sotkamo (Zn, Cu, Ni, Co) → near-zero waste strategy

Use advantages of NASX for efficient group separation of HREEs and individual REE purification with REE starting material based on real industrial concentrate:

- Dissolution in ethylene glycol + aqueous HCl (10 vol%)
- Non-aqueous SX with Cyanex 923
- Entire process will be tested on lab-scale pilots

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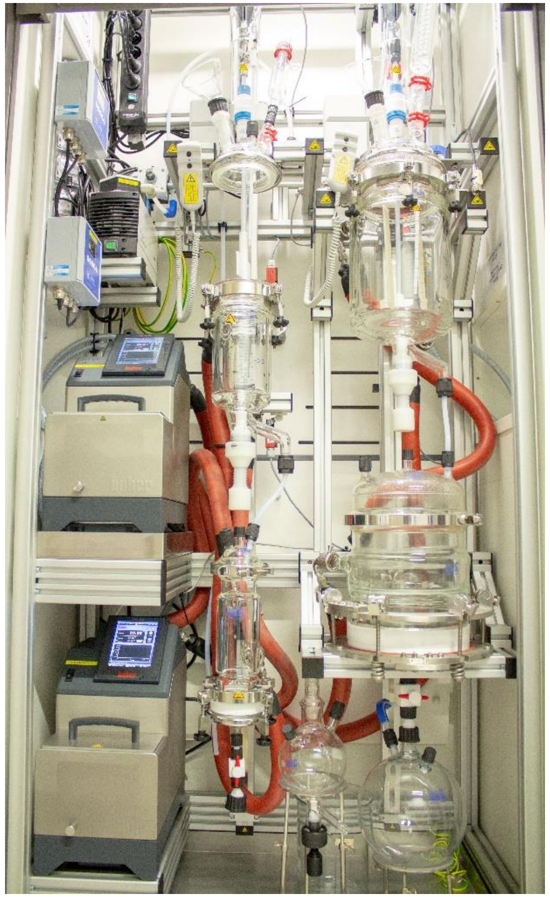
# Experimental setup - equipment



Batch Leaching platform (HiTec-Zang)
- Jacketed 1 L and 5 L reactors
- Jacketed filtration units
- Borosilicate glass
- Optimized for viscous liquids

Mixer-settler setup (SX Kinetics)
- 16 stages
- Mixer: 0.270 L; settler: 1.050 L
- Pumps: Cole-Parmer Masterflex L/S: max 10 L/h



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# Starting material & dissolution

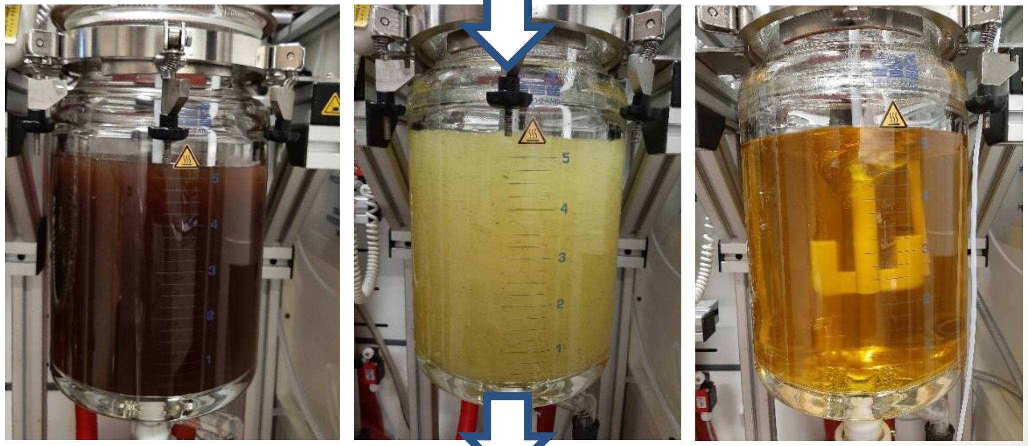
## Starting material

- Obtained via selective precipitation → hydroxide
- High REE content (50 wt%)
- Impurities < 4 wt%

## Dissolution

- Preparation of SX MP feed: 10 g $L^{-1}$ REE
- Increase of temperature to 60 °C was needed to enhance dissolution kinetics
- 10 vol% water as optimum during SX lab-scale tests:
  - Allows bridging gap between hydro- and solvometallurgy
  - Allows the use of NaCl
  - Reduced mutual solubility

| Impurities | | Rare-earth elements | |
|---|---|---|---|
| element | Concentration (wt%) | element | Concentration (wt%) |
| Al | 1.48 | Dy | 0.36 |
| Ca | 0.20 | Ho | 0.23 |
| Fe | 0.11 | Er | 2.16 |
| Mg | 0.12 | Tm | 1.29 |
| Mn | 0.86 | Yb | 14.27 |
| Ni | 0.25 | Lu | 2.64 |
| Zn | 0.77 | Y | 28.77 |



| Impurities | | Rare-earth elements | |
|---|---|---|---|
| element | Concentration (ppm) | element | Concentration (ppm) |
| Al | 297 | Dy | 75 |
| Ca | 207 | Ho | 46 |
| Fe | 34 | Er | 400 |
| Mg | 23 | Tm | 252 |
| Mn | 166 | Yb | 2595 |
| Ni | 49 | Lu | 536 |
| Zn | 142 | Y | 5135 |

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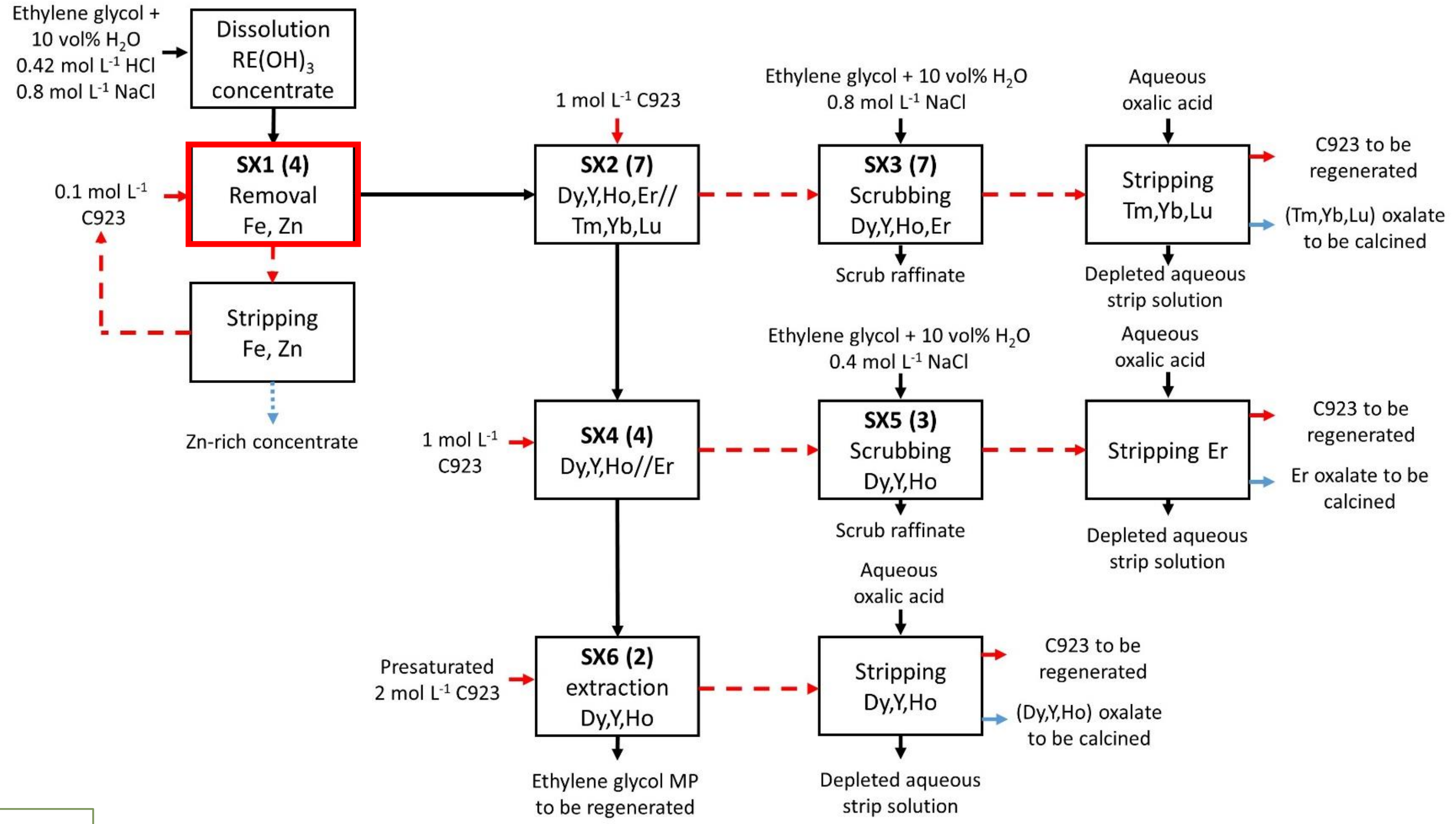
# Flowsheet overview: Dy, Y, Ho // Er // Tm, Yb, Lu



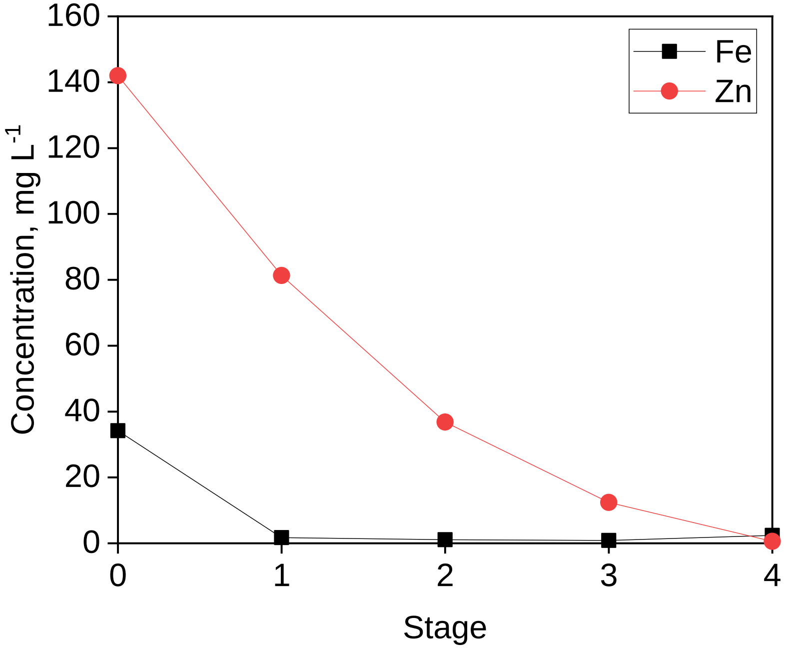
## Step 1: removal of Zn and Fe (SX1)




Scale:
- 60 L of original MP feed solution → purification & separation
- 2* 30 L of scrub solution
- > 100 L of LP phase, with various [Cyanex 923]

# Removal of Fe, Zn




**MP:** 10 g $L^{-1}$ REE, 0.14 g $L^{-1}$ Zn, 0.4 g $L^{-1}$ Fe, 0.8 M NaCl, 10 vol% $H_2O$, EG
**LP:** 0.1 M Cyanex 923, petroleum ether

- Retention time 6 min
- Ni and Mg not extracted by Cyanex 923; Ca, Mn limited extraction at higher Cyanex 923 concentration
- Good phase separation, limited yet visible entrainment of LP in MP phase

3 stages:

- *%E* Fe 85% (6 ppm) - Zn 96% (6 ppm)
- No loss of REE

4 stages:

- *%E* Fe 95% (2 ppm) - Zn 99.95% (< 1 ppm)
- Limited loss of REE (1-3 %)

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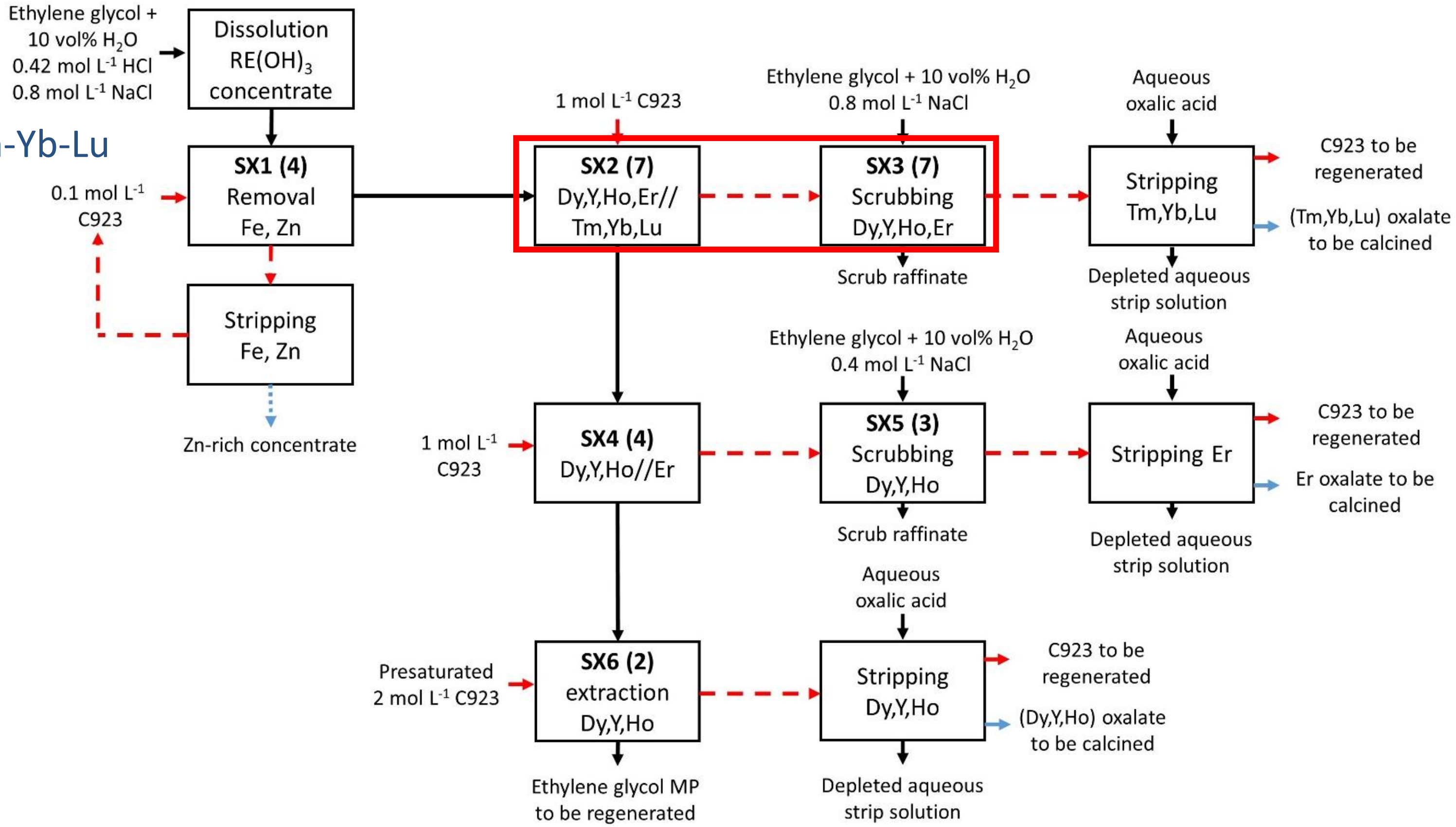
# Flowsheet overview: Dy, Y, Ho // Er // Tm, Yb, Lu



Step 1: removal of Zn and Fe (SX1)

Step 2: separation Dy-Ho-(Y)-Er// Tm-Yb-Lu

- Extraction 7 stages (SX2)
- Scrubbing 7 stages (SX3)

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# Separation Dy, Y, Ho, Er // Tm, Yb, Lu



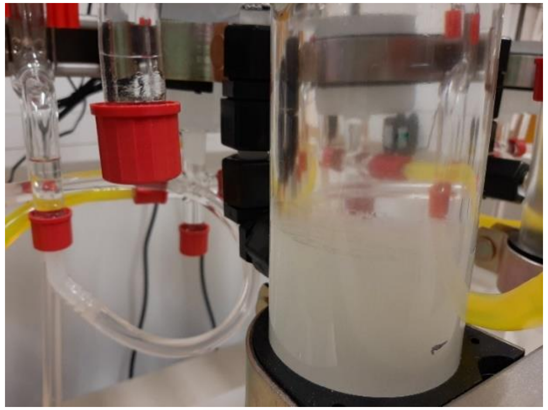
LP phase flow: 1.65 L/h

MP phase flow: 2.48 L/h

- Retention time 4 min
- Quasi complete extraction of Tm, Yb, Lu
- Emulsion might pose a problem – adapt design of mixer-settlers

| element | %E | Conc MP (ppm) | Conc LP (ppm) |
|---|---|---|---|
| Y | 24 | 3411 | 1743 |
| Dy | 11 | 59 | 11.6 |
| Ho | 25 | 26.5 | 16.0 |
| Er | 49 | 123 | 274 |
| **Tm** | **95.4** | 11.9 | 355 |
| **Yb** | **99.4** | 15.5 | 3905 |
| **Lu** | **99.4** | 3.1 | 919 |

**MP:** raffinate ~10 g $L^{-1}$ REE, 0.8 M NaCl, 10 vol% $H_2O$, EG
**LP:** 0.1 M Cyanex 923, petroleum ether



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# Scrubbing of Y, Dy, Ho, Er

MP phase flow: 2.48 L/h

LP phase flow: 1.65 L/h

| element | *%Scr* | Conc MP (ppm) | Conc LP (ppm) |
|---|---|---|---|
| **Y** | **99.98** | 1204 | 0.3 |
| **Dy** | **100** | 7.9 | 0 |
| **Ho** | **98.5** | 7.4 | 0.2 |
| **Er** | **100** | 184 | 0 |
| Tm | 78 | 173 | 77 |
| Yb | 44 | 1634 | 2285 |
| Lu | 42 | 296 | 566 |

**MP:** 0.8 M NaCl, 10 vol% $H_2O$, EG
**LP:** loaded 1 M Cyanex 923, petroleum ether

- Retention time 4 min
- REE in MP scrub raffinate → recycled to extraction
- Scrubbing very efficient: only 0.5 ppm impurities left

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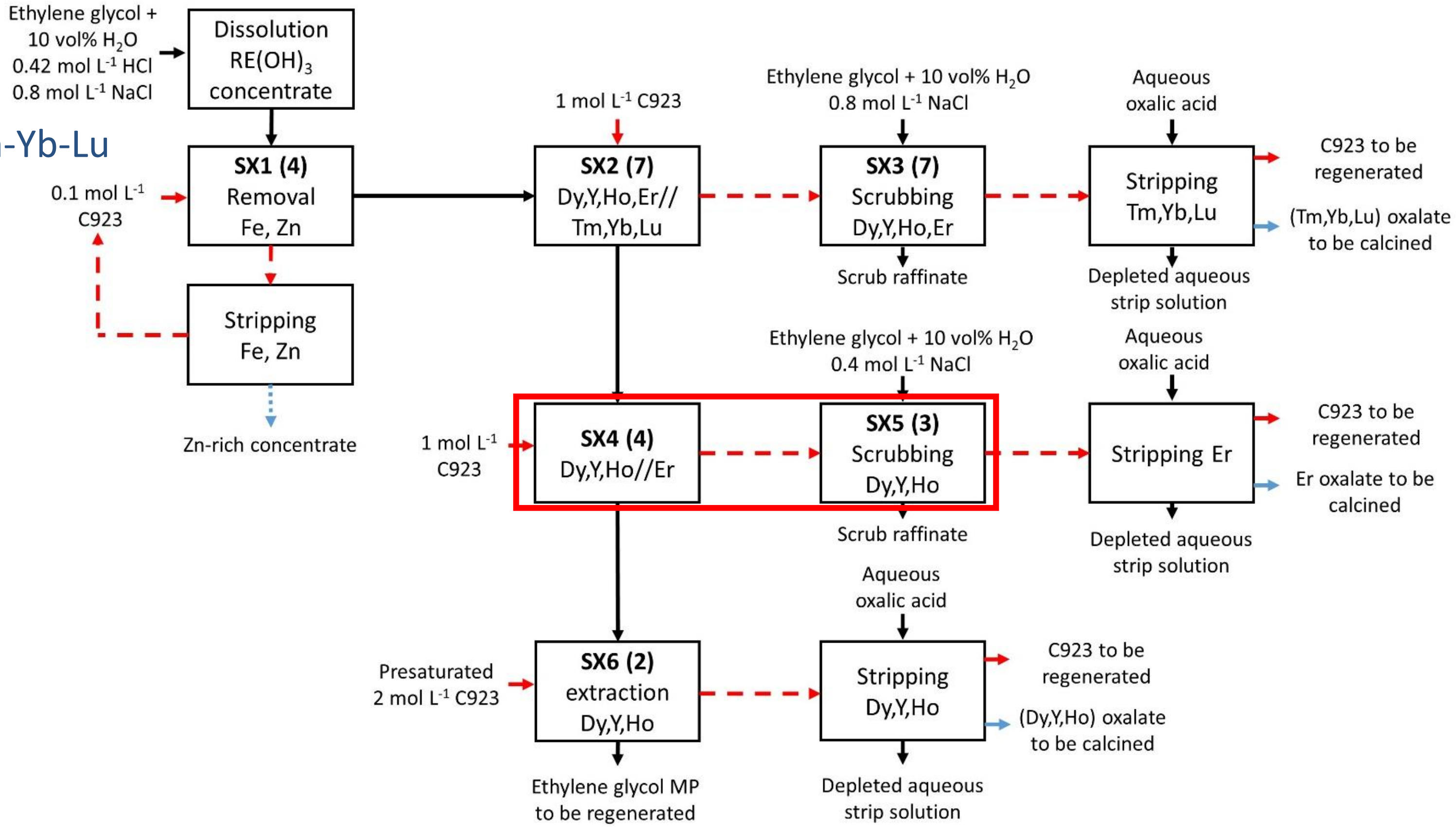
# Flowsheet overview: Dy, Y, Ho // Er // Tm, Yb, Lu



Step 1: removal of Zn and Fe (SX1)

Step 2: separation Dy-Ho-(Y)-Er// Tm-Yb-Lu
- Extraction 7 stages (SX2)
- Scrubbing 7 stages (SX3)

Step 3: separation Dy-Ho-(Y) // Er
- Extraction 4 stages (SX4)
- Scrubbing 3 stages (SX5)



# Separation Dy, Y, Ho // Er



LP phase flow: 1.20 L/h

MP phase flow: 0.84 L/h

| element | %E | Conc MP (ppm) | Conc LP (ppm) |
|---|---|---|---|
| Y | 90 | 766 | 2147 |
| Dy | 57 | 30 | 20 |
| Ho | 92 | 6 | 17 |
| **Er** | **98.5** | 8 | 112 |
| Tm | 100 | 0 | 15 |
| Yb | 100 | 0 | 18 |
| Lu | 100 | 0 | 3 |

**MP:** 59 ppm Dy, 32 ppm Ho, 130 ppm Er, 3927 ppm Y, 0.8 M NaCl, 10 vol% $H_2O$, EG
**LP:** 1 M Cyanex 923, petroleum ether

- Retention time 7 min
- Efficient Er extraction (> 98%)
- Significant co-extraction of Y (90%) and Ho (92%)
  → main issue is scrubbing Y

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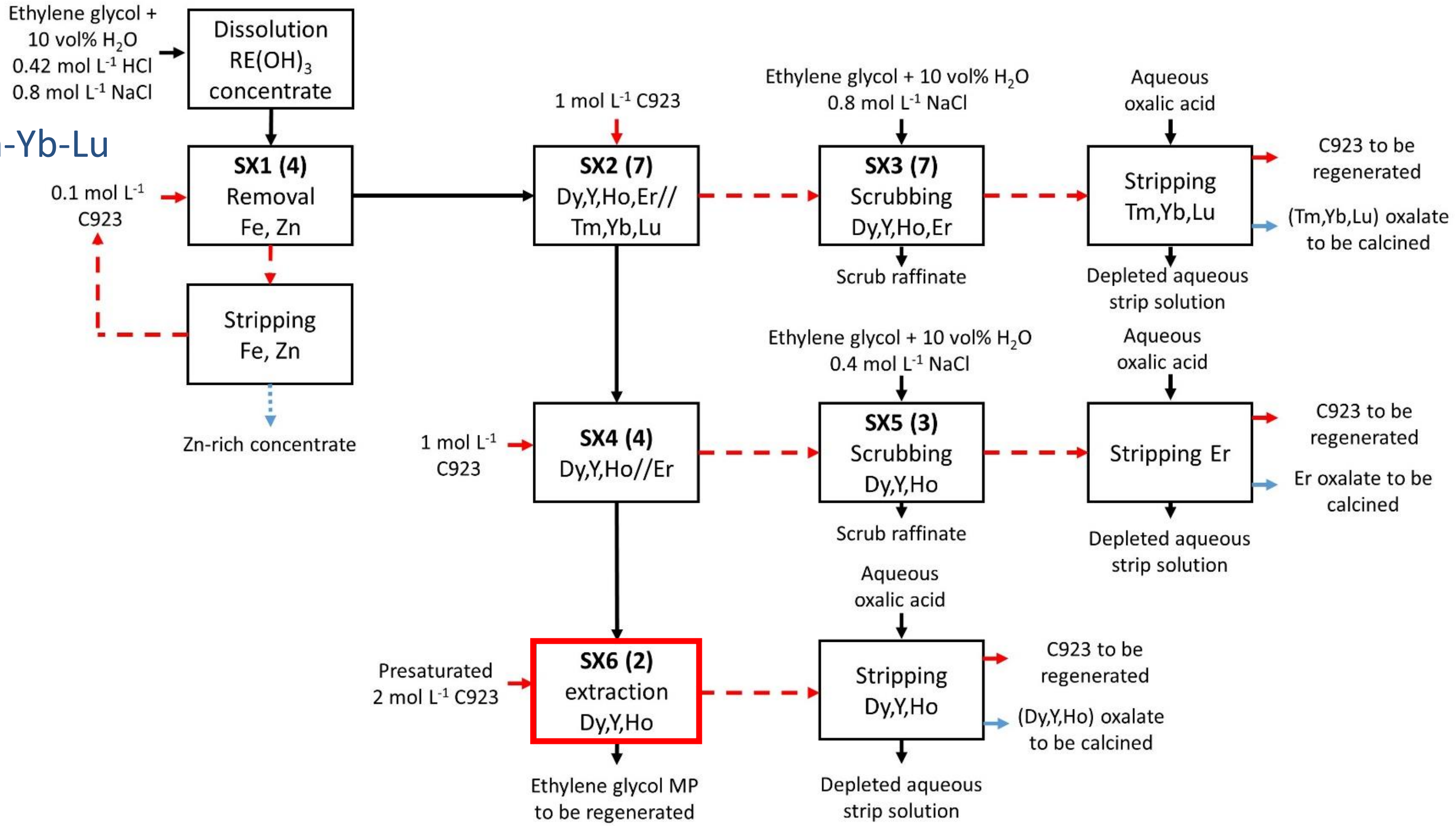
# Flowsheet overview: Dy, Y, Ho // Er // Tm, Yb, Lu

Step 1: removal of Zn and Fe (SX1)

Step 2: separation Dy-Ho-(Y)-Er// Tm-Yb-Lu
- Extraction 7 stages (SX2)
- Scrubbing 7 stages (SX3)

Step 3: separation Dy-Ho-(Y) // Er
- Extraction 4 stages (SX4)
- Scrubbing 3 stages (SX5)

Step 4: Extraction Dy-Ho, Y (SX6)

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# Extraction of Dy, Ho, Y



- Retention time 6 min
- Presaturation necessary: batch contact of 2 M Cyanex 923 with 0.8 M NaCl in ethylene glycol +10 vol% water
- Emulsion problems occurred, yet ‘temporary’
- Complete extraction of REE
- Still metal impurities (300 ppm) in MP (Al, Ca, Mg, Mn, Ni)

LP phase flow: 1.20 L/h

MP phase flow: 1.20 L/h

| element | %E | Conc MP (ppm) | Conc LP (ppm) |
|---|---|---|---|
| Y | 100 | 0 | 881 |
| Dy | 100 | 0 | 32 |
| Ho | 100 | 0 | 9 |
| Er | 100 | 0 | 4 |
| Tm | - | 0 | 0 |
| Yb | - | 0 | 0 |
| Lu | - | 0 | 0 |

**MP:** 30 ppm Dy, 6 ppm Ho, 8 ppm Er, 766 ppm Y, 0.8 M NaCl, 10 vol% $H_2O$, EG
**LP:** 2 M Cyanex 923, petroleum ether

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# Stripping of REEs and calcination

- Stripping of LP (0.1 M Cyanex 923) phase loaded with Fe, Zn
  - Not studied in detail, precipitation stripping with oxalic acid, ammonia or NaOH
- Stripping of LP (1 M Cyanex 923) phases loaded with Tm, Yb, Lu
  - Stripping with aqueous oxalic acid solution: MP:LP = 1:1 and 2x stoichiometric amount
  - After calcination (900 °C, 1.5 h): REO purity 99.8%
- Stripping of LP (1 M Cyanex 923) phases loaded with REE, transition metals
  - Stripping with aqueous oxalic acid solution: MP:LP = 1:1 and 2x stoichiometric amount
  - After calcination (900 °C, 1.5 h): $Er_2O_3$ purity 8%; enrichment factor = 2
- Stripping of LP (2 M Cyanex 923, presaturated) phases loaded with REE, transition metals
  - Stripping with aqueous oxalic acid solution: MP:LP = 1:1 and 2x stoichiometric amount
  - After calcination (900 °C, 1.5 h): REO purity 98.7%

  No volume change observed during stripping – traces of ethylene glycol in aqueous solution

# Conclusions



- Non-aqueous extraction system has been developed:
  - MP: 10 g $L^{-1}$ HREE, NaCl, 10 vol% water, ethylene glycol
  - LP: 0.1 – 2 M Cyanex 923 in petroleum ether
- Successful separation of HREEs into 2 groups:
  - Only 16 stages needed in total (compared to 70 in conventional process)
  - Purity Tm-Yb-Lu: 99.8% / Purity Dy-Ho-(Y)-Er: 98.7%
- Purification of Er is challenging due to scrubbing limitations
- Non-aqueous process feasible on mixer-settlers; adjusted design would reduce emulsion band thickness
- Future challenges:
  - Taking into account the removal of all impurities
  - Reusing the MP phase after extraction: how to maintain the water content, while adding HCl
  - Optimizing and improving separation into pure, single-element REE products
  - Costs of pilot process exceed the revenue:
    optimization of throughput (e.g. REE concentration increase) and chemicals consumption

# Paper reference

Solvometallurgy & rare earths

H2020 NEMO

Equipment & Materials

Mixer-settler pilot

**Conclusions**

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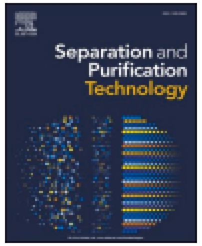


Check for updates

## Separation of heavy rare-earth elements by non-aqueous solvent extraction: Flowsheet development and mixer-settler tests

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B. Dewulf, S. Riaño and K. Binnemans, Separation of heavy rare-earth elements by non-aqueous solvent extraction: flowsheet development and mixer-settler tests, *Separation and Purification Technology*, **2022**, *290*, 120882. DOI: 10.1016/j.seppur.2022.120882.

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