ELECTRO-ASSISTED EXTRACTION OF CRITICAL RAW MATERIALS FROM COAL ASH

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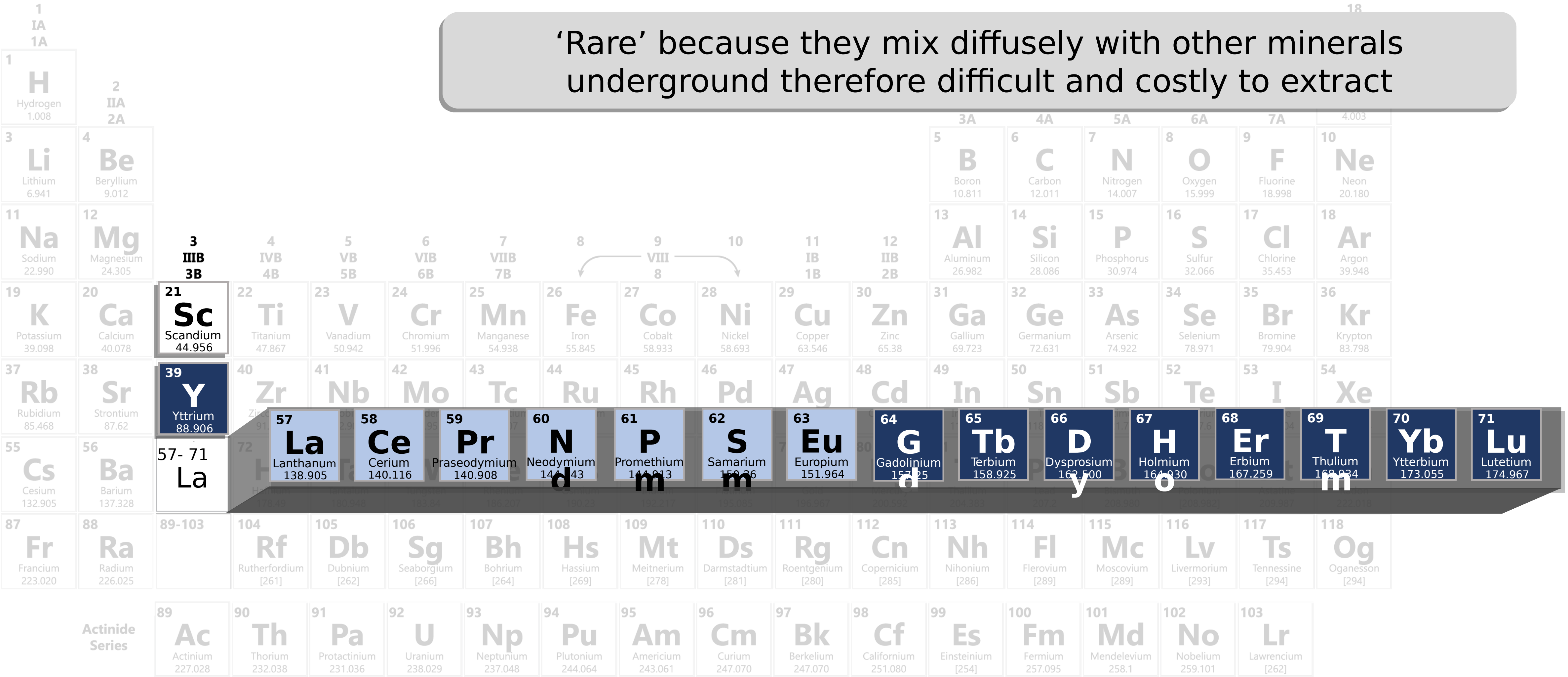
Rare Earth Elements (REEs)

‘Rare’ because they mix diffusely with other minerals underground therefore difficult and costly to extract



REEs applications

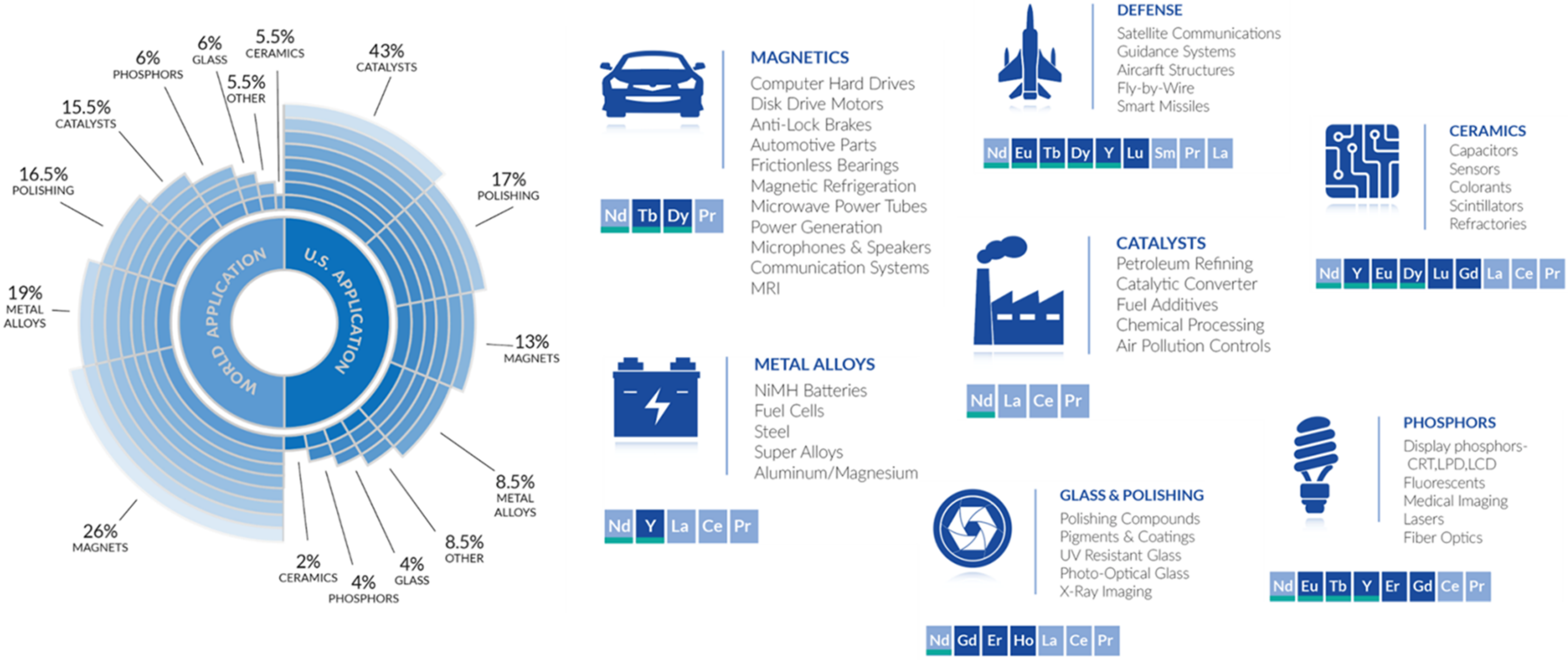


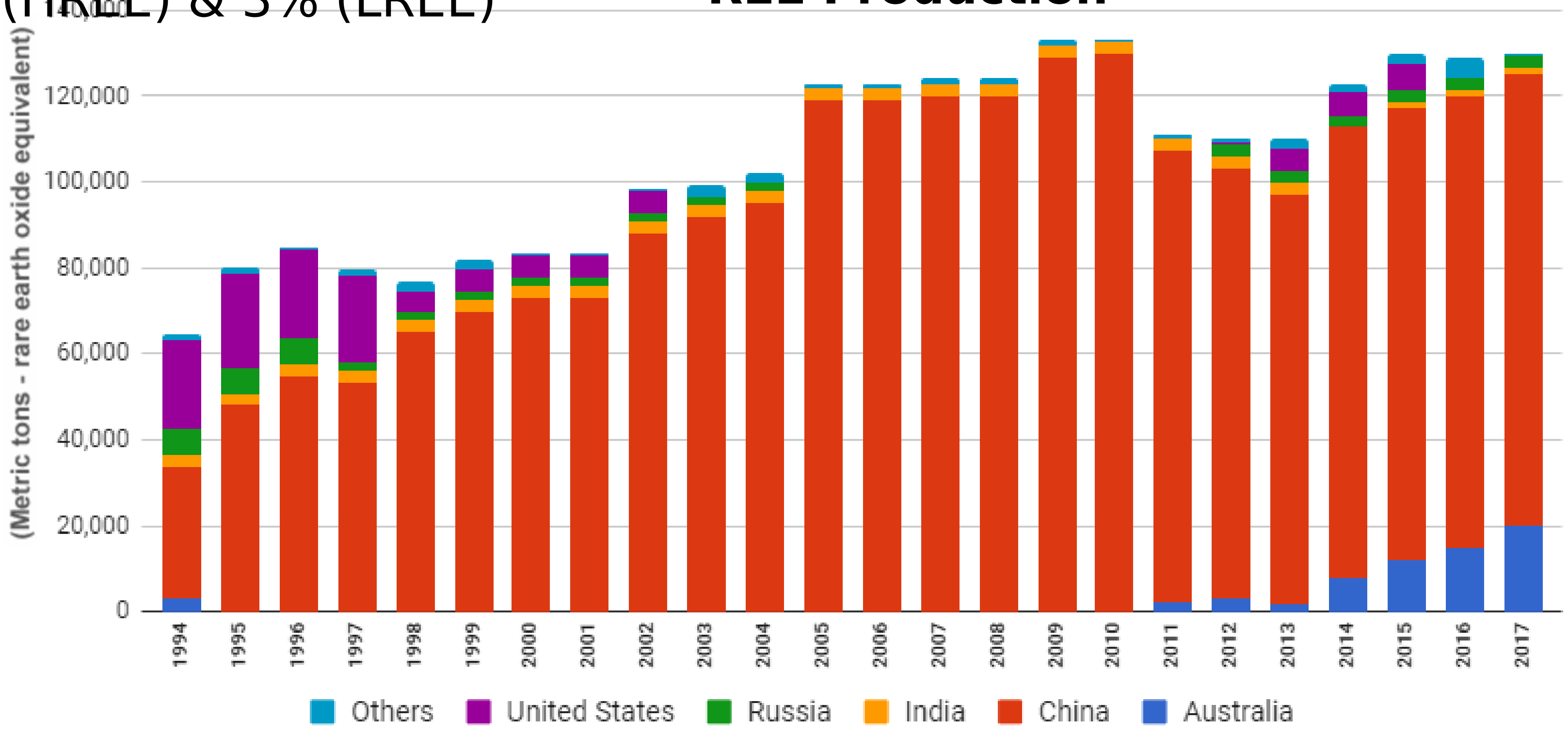
Chart by netl.doe.gov

Problem

EU overview

- EU is almost entirely dependent upon imports from China
- The 2011 REE-price crisis pointed to the need to reduce the dependence on China's imports[1]
- Substitution Index**: 0.96 (HREE) & 0.90 (LREE)[1]
- End of life recycling rate: 8% (HREE) & 3% (LREE)

REE Production



** 0 - 1: 1 means non-substitutable

1 EU, 2017

Source: Geology.com using data from the

Geopolitical strategy

UNITED STATES OF AMERICA

Final List of 35 Minerals deemed critical to U.S. National Security and Economy

2018 May (Dep. of Interior)

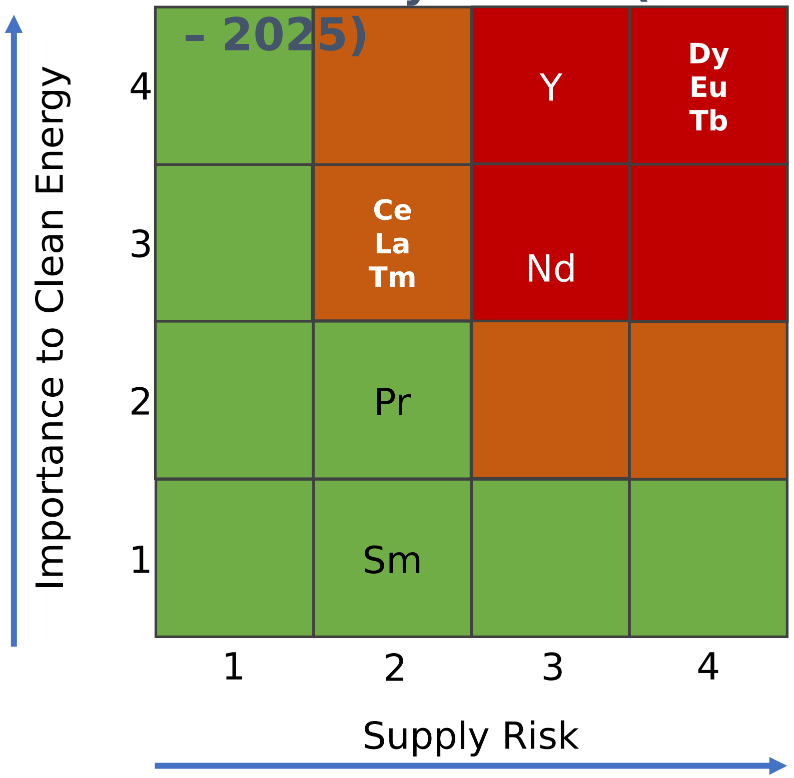
European Union

List of Critical Raw Materials for the EU – 27 CRMs

2017 September (European Commission)

- 2011 *Critical Materials Strategy* - by the U.S. Department of Energy - includes criticality assessments:
  - Supply challenges for 5 REE may affect clean energy technology deployment in the years ahead.

Criticality matrix (2015 – 2025)



(Based on the US Dept. of Energy, 2011)

Aim

Recovery of REEs from a **secondary resource** (e.g. coal by-product) through electro-based technologies

Efficient & environmentally-friendly separation and processing technology

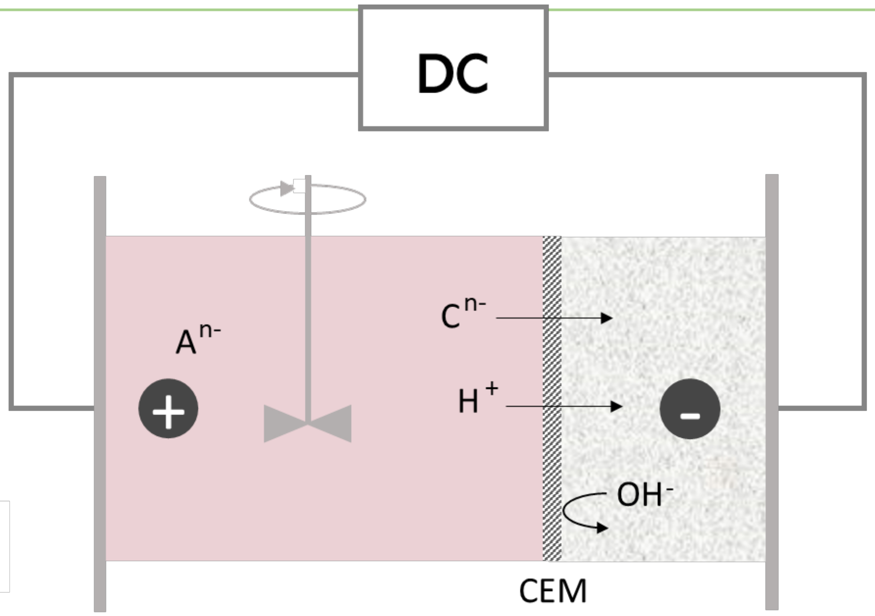
In progress:

- Assessment and analysis of the feasibility of **electrodialytic recover of REEs from anthracite ash**
- **Proof of concept**

Electrodialytic Process

Recover of REEs from fine anthracite coal ash under the influence of an applied low level direct current

Anode (eq.)
$2H_2O - 4e^- \rightarrow O_2 + 4H^+$

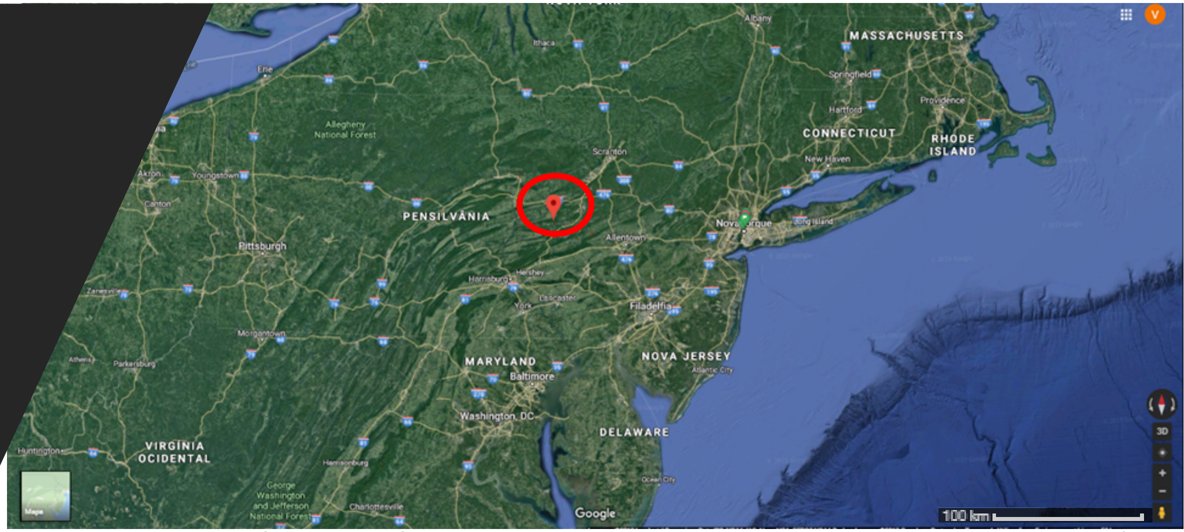


Cathode (eq.)
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Matrix compartment: anode

Anthracite origin

- Blaschak Coal Corporation, Centralia, PA, USA
- Northern Pennsylvania
  - Lat. 40.8° N, Long. 76.36° W
- **Mammoth Vein**



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Methodology

Processing

Cut
Crush
Grinding
Ashing

Characterization

ICP
EDX
SEM-EDS

REE recover

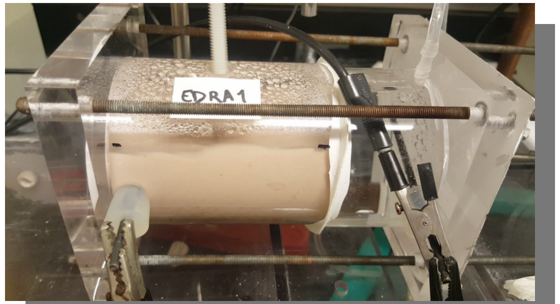
pH desorption test
ED experiments

Extraction/Analysis

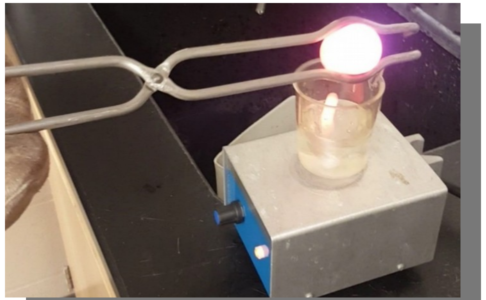
Fluxing
ICP

Anthracite

Anthracite ash ASTM (D3174-12)



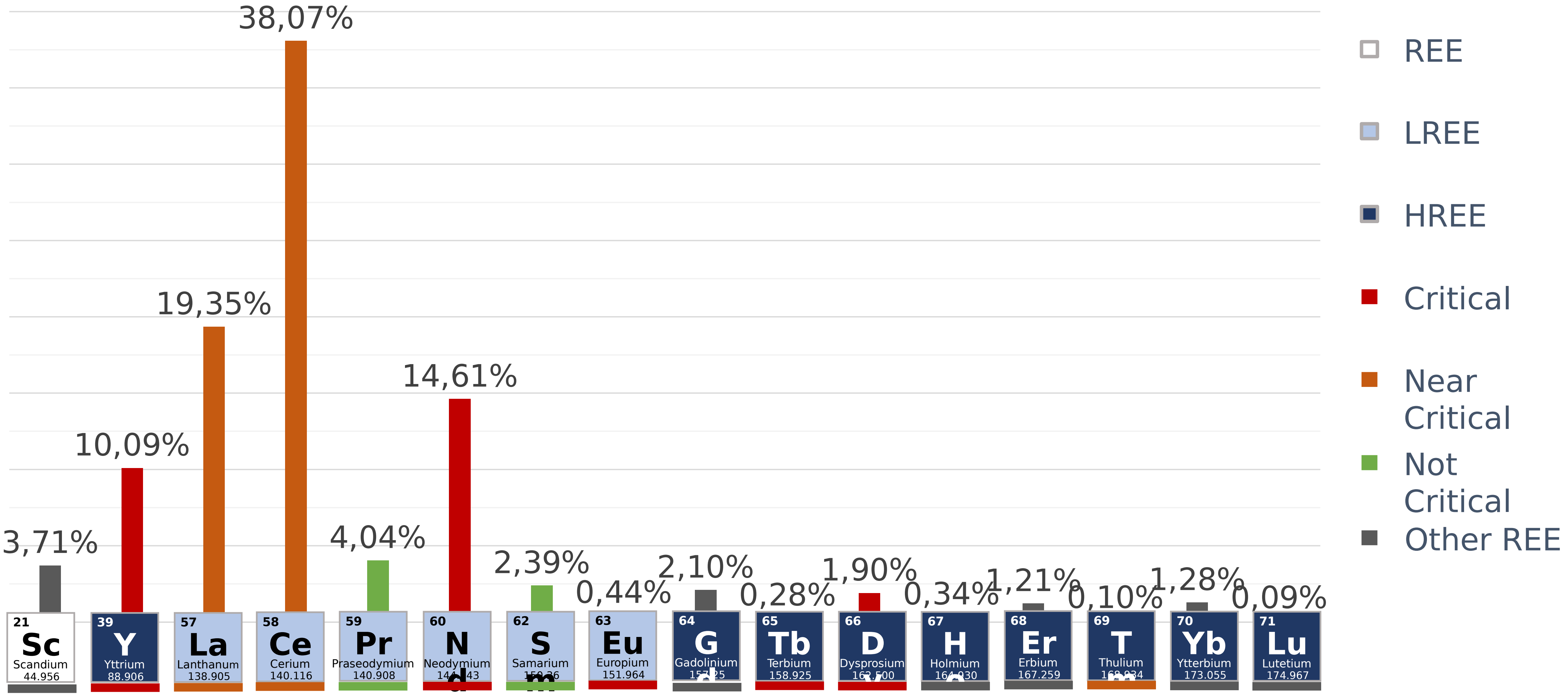
Electrodialytic cell



Fluxing

Characterization

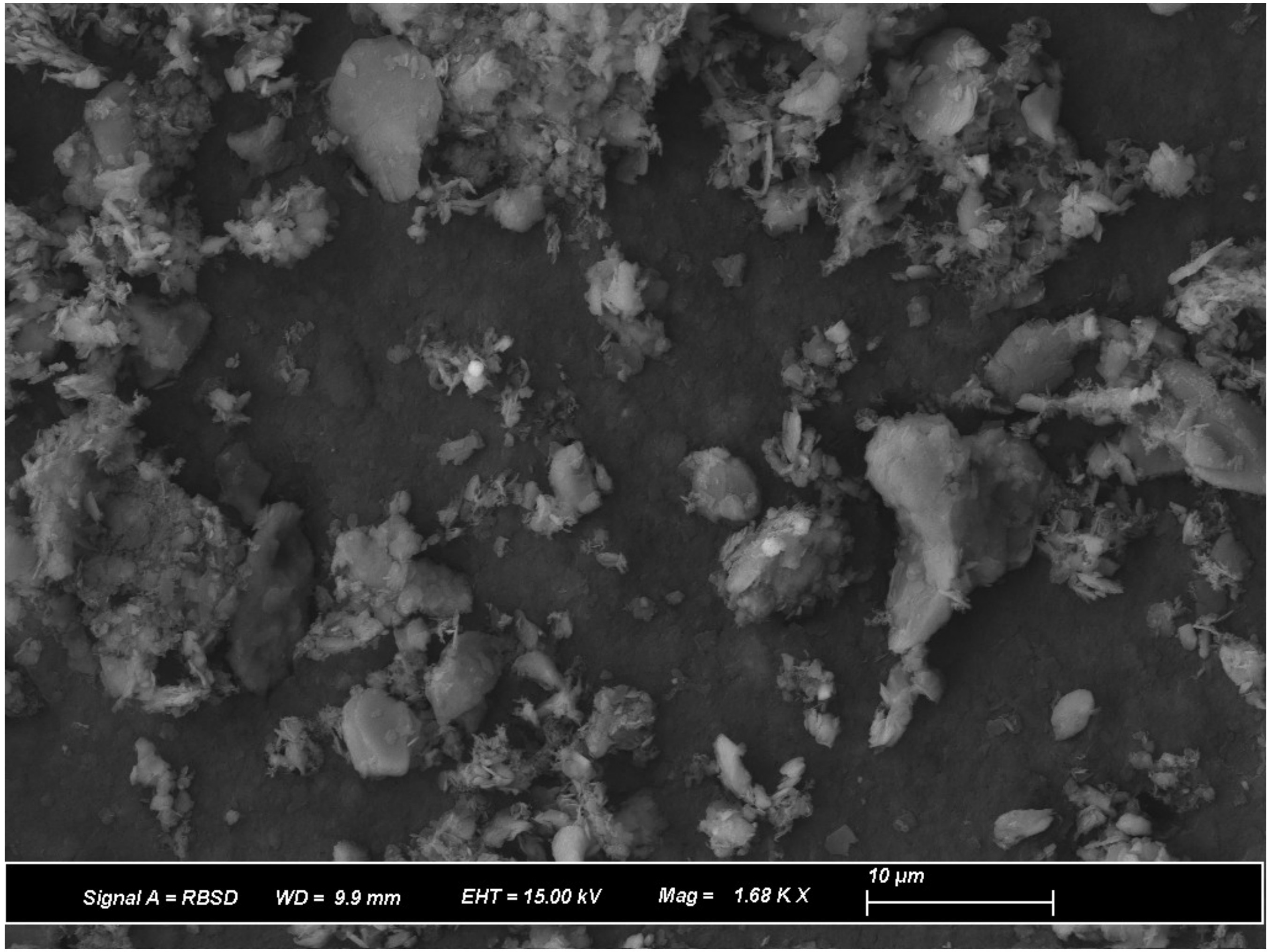
Relative REE content in anthracite ash



Characterization

Particle morphology of anthracite ash

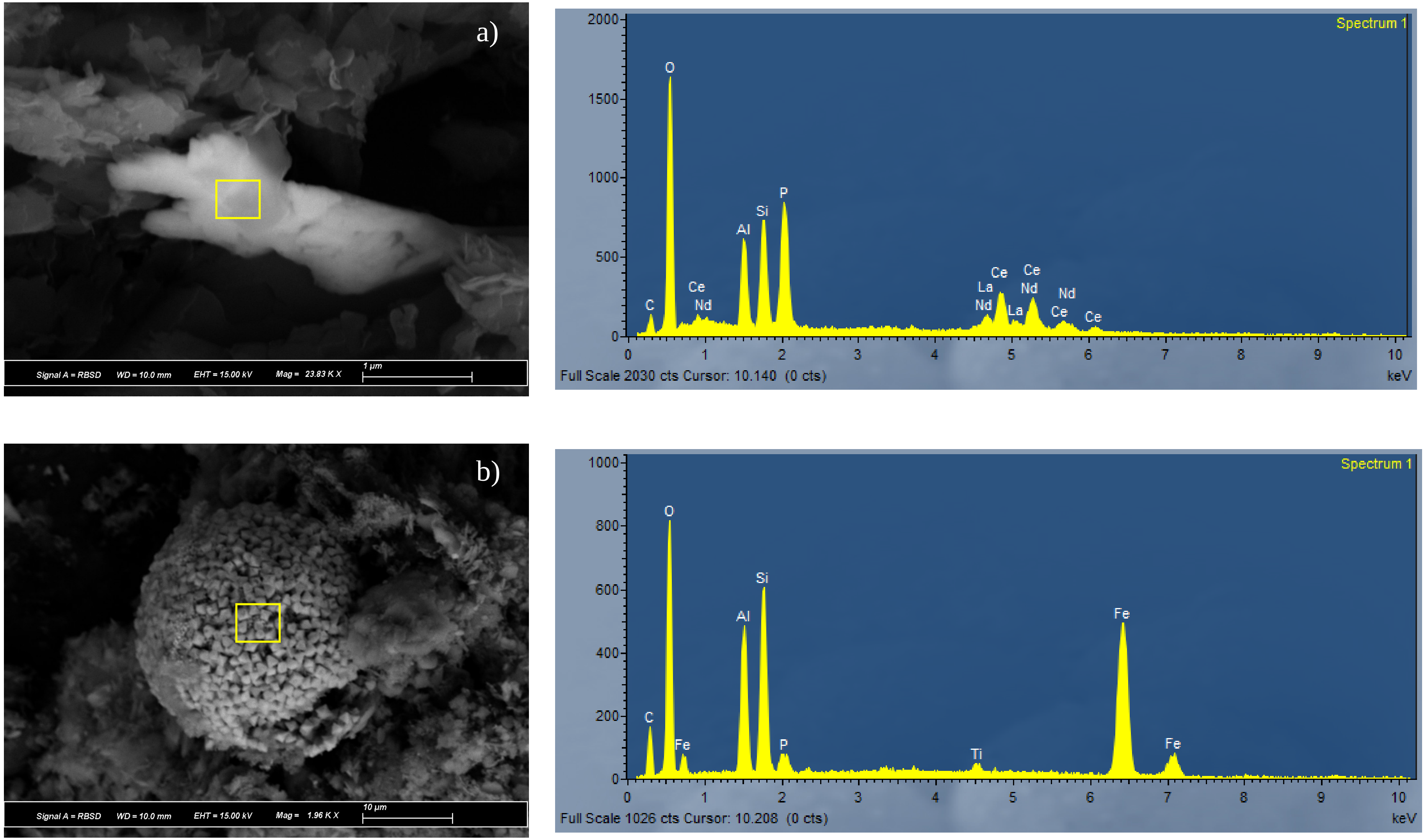
- Disperse
- Angular
- Size range: 1 to 10 um



SEM microphotograph of anthracite ash

Characterization

Particle morphology of anthracite ash



Trace elements

- Carbon
- Oxygen
- Aluminum
- Silicone
- Phosphorus
- Titanium
- Iron

REEs

- Lanthanum
- Neodymium
- Cerium

SEM microphotographs and respective EDS spectra of a) REE particle; b) agglutination of minerals

pH desorption from anthracite ash

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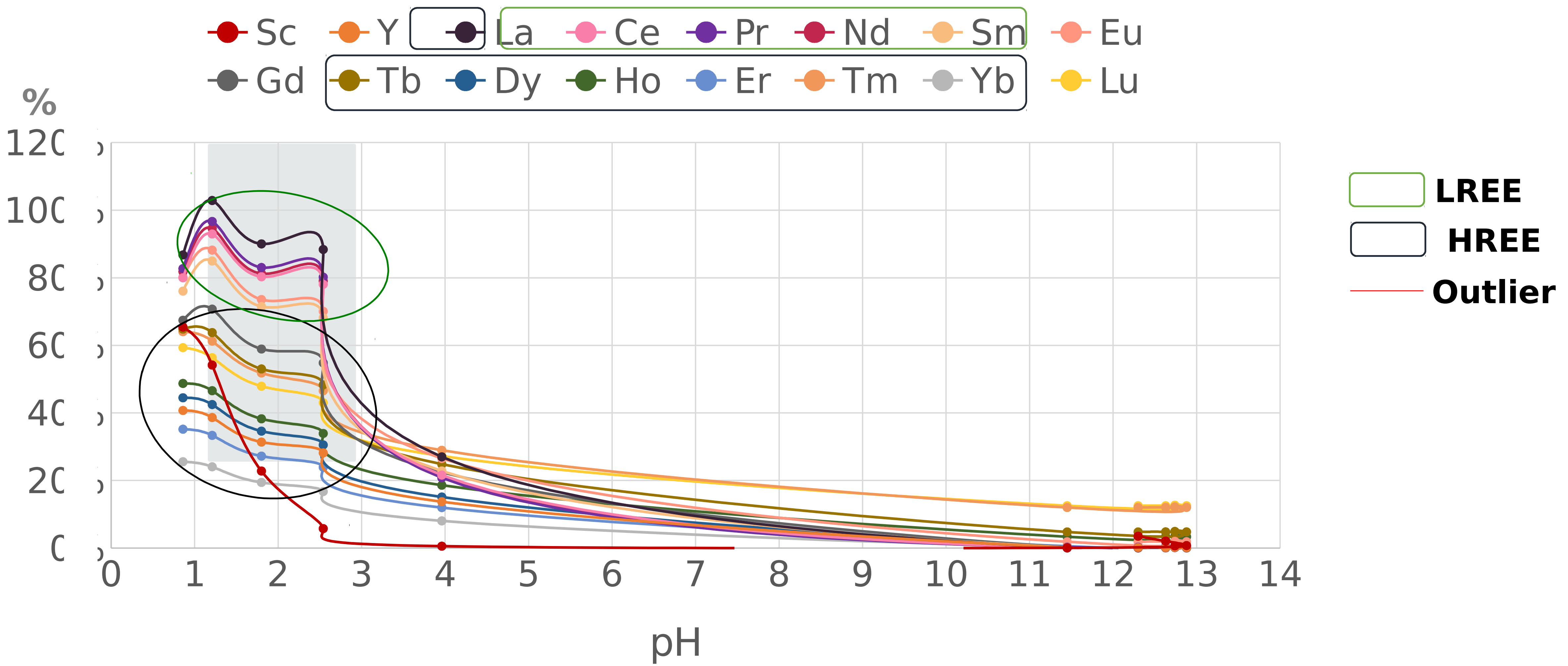
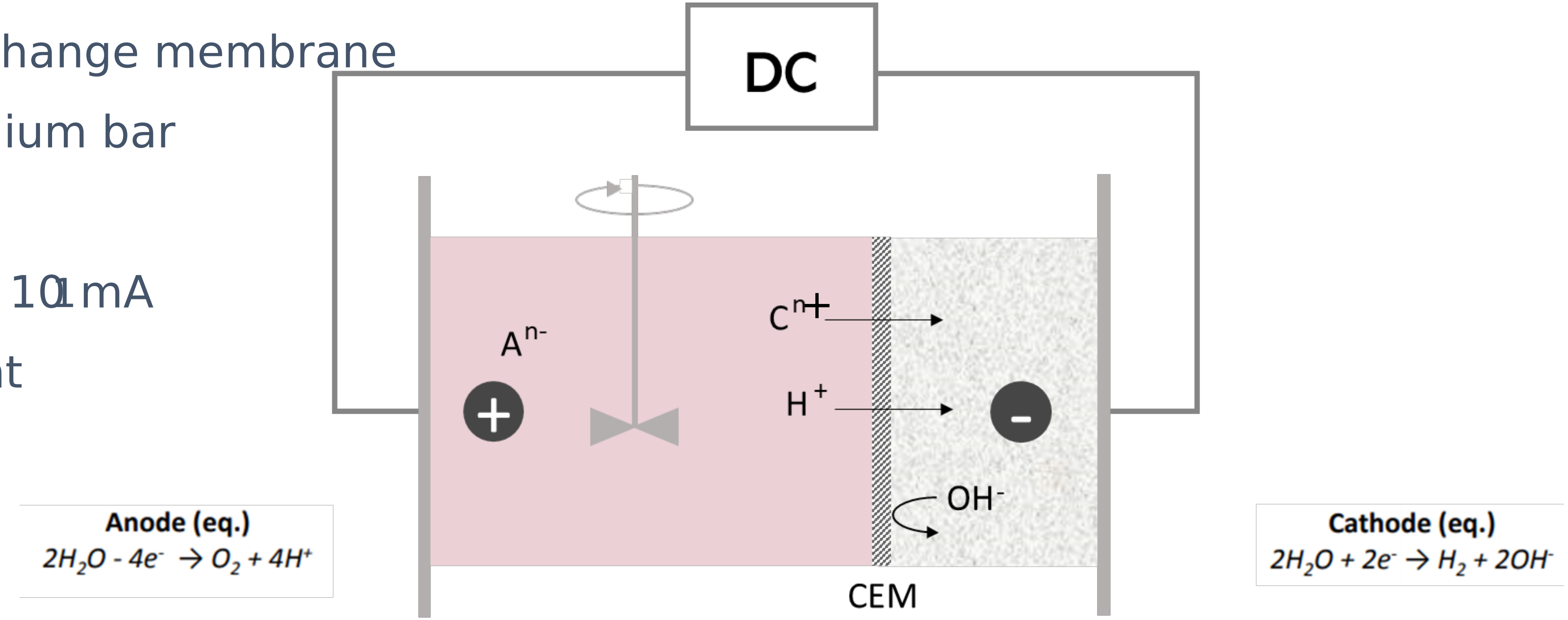


ED experiments

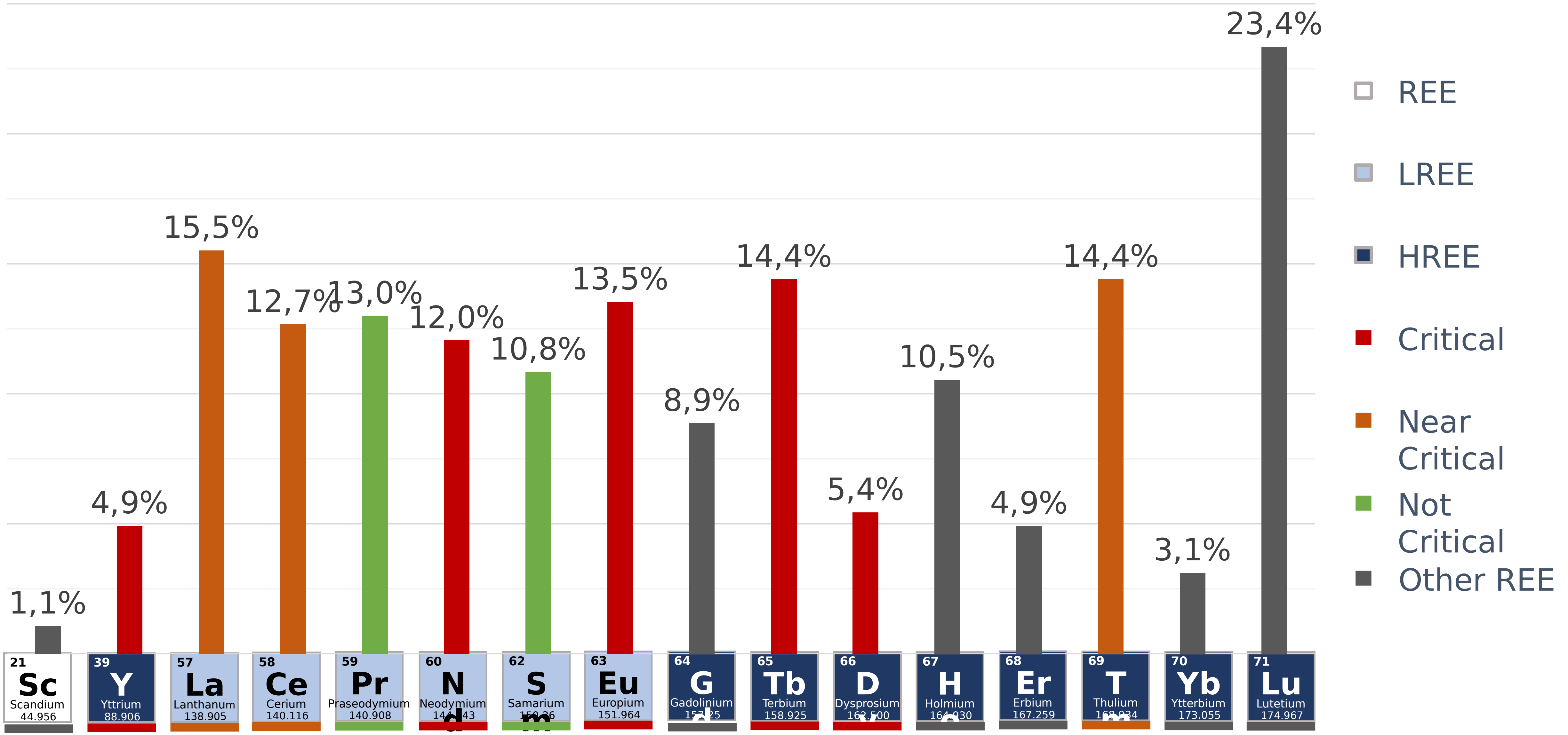
- 2C-ED cell
- L/S = 15
- CEM = cation exchange membrane
- MMO coated titanium bar
- Time: 3 days
- Current intensity: 10 mA
- pH: no adjustment



Ferreira et al. 2019, *Water Air & Soil Pollution*, 230(4): 78-88.

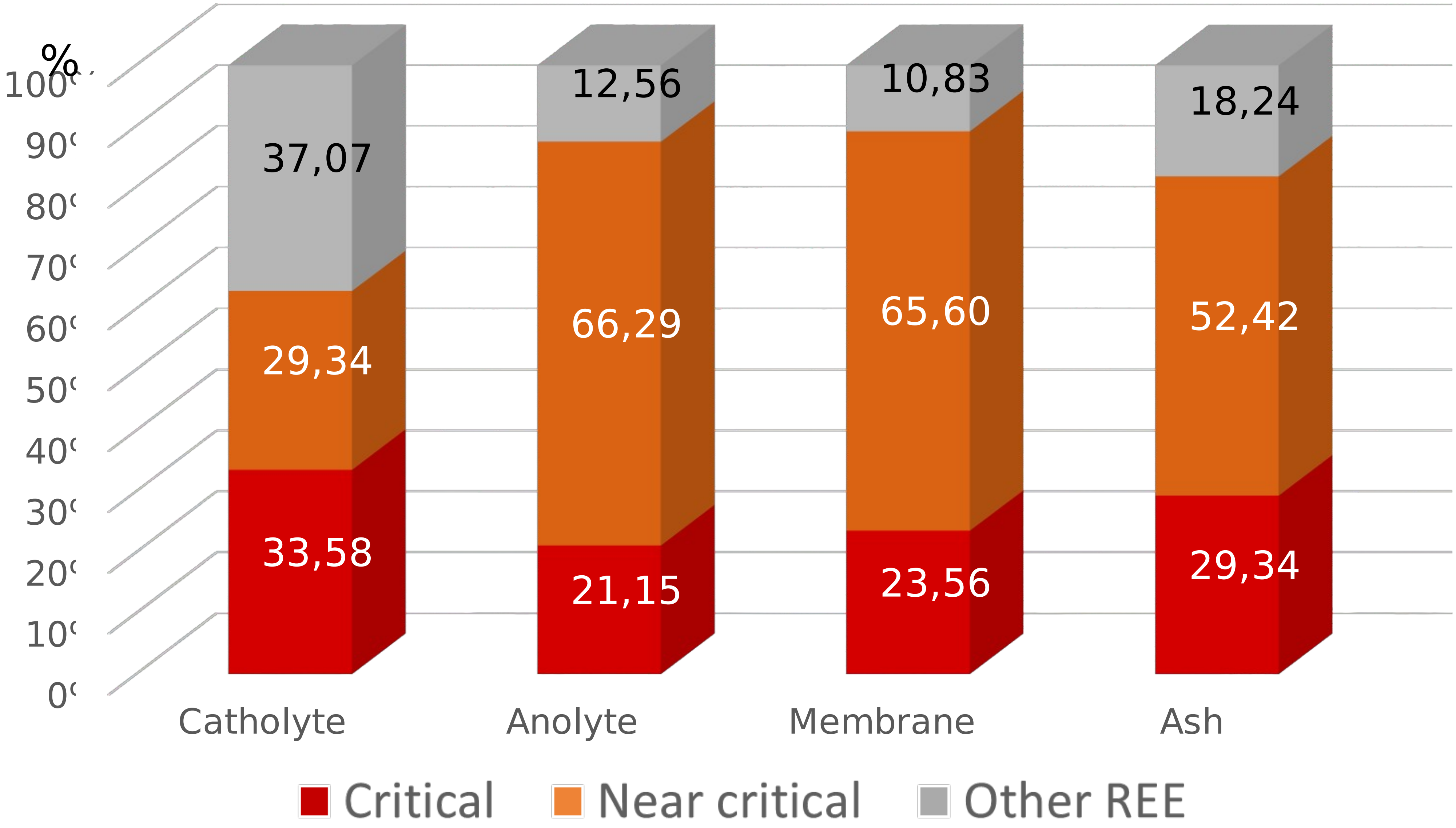
Results

Desorped REEs after ED



Results

REEs criticality analysis of relative content after ED



Conclusions

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ED process is a promising extraction technique for rare earth elements recover from coal ash

- REE desorption improved with the ED process
- LREE show higher desorption rates
- HREE show promising capabilities of passing through the CEM

Critical REEs	Relative % of REEs desorped by ED
Tb	14.4
Eu	13.5
Nd	12.0
Dy	5.4
Y	4.9

References

- Blaschak Coal Corporation, 2019. Representative analysis Lattimer mammoth vein. Accessed in June 2019 http://www.blaschakcoal.com/wp-content/uploads/Lattimer-Mammoth-Vein-Rep-Analysis.pdf
- European Commission, 2017. (COM(2017) 490) ‘on the 2017 list of Critical Raw Materials for the EU’ 2017.
- Ferreira, A.R.; Couto, N.; Ribeiro, A.B.; Ottosen, L.M. 2019. Electrodialytic arsenic removal from bulk and pre-treated soil. 2019, Electrodialytic arsenic removal from bulk and pre-treated soil. *Water Air & Soil Pollution,* **230**(4):78-88.
- NETL - National Energy Technology Laboratory. REE Program. Accessed in June 2019, https://netl.doe.gov/coal/rare-earth-elements/program-overview/background
- REE - Rare Earth Elements and their Uses. Accessed in June 2019, https://geology.com/articles/rare-earth-elements/
- US DoE, 2011. Critical Materials Strategy report. US Department of Energy

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This work has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 778045, and from FCT/MEC through grant UID/AMB/04085/2019 to the Research unit CENSE – Center for Environmental and Sustainability Research. N. Couto also acknowledges FCT Investigator Contract CEECIND/04210/2017.

pH desorption

LREE

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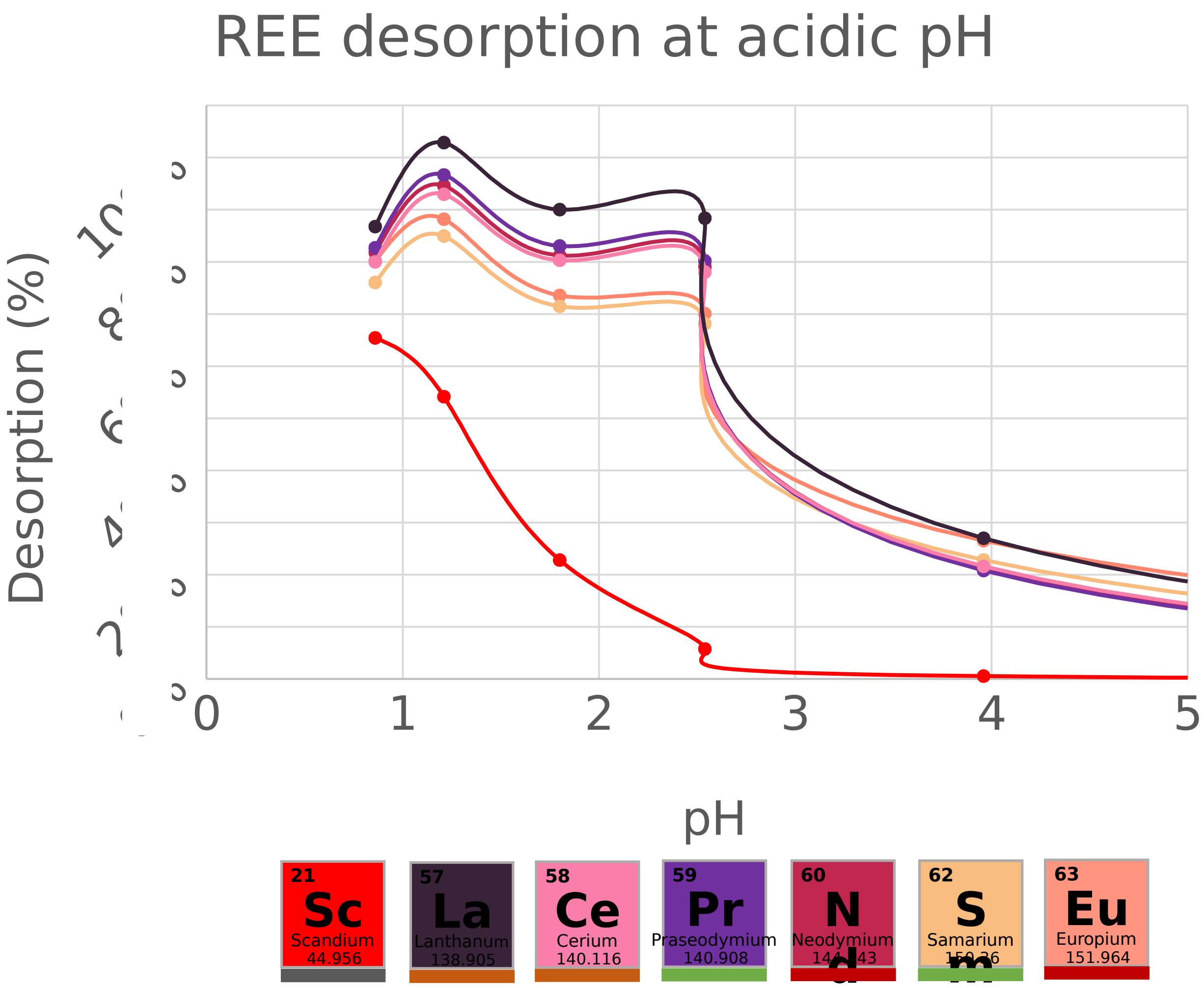


LREE

- Stable complexes are the first to desorp
- Higher desorption rates compared to HREE

Tendency

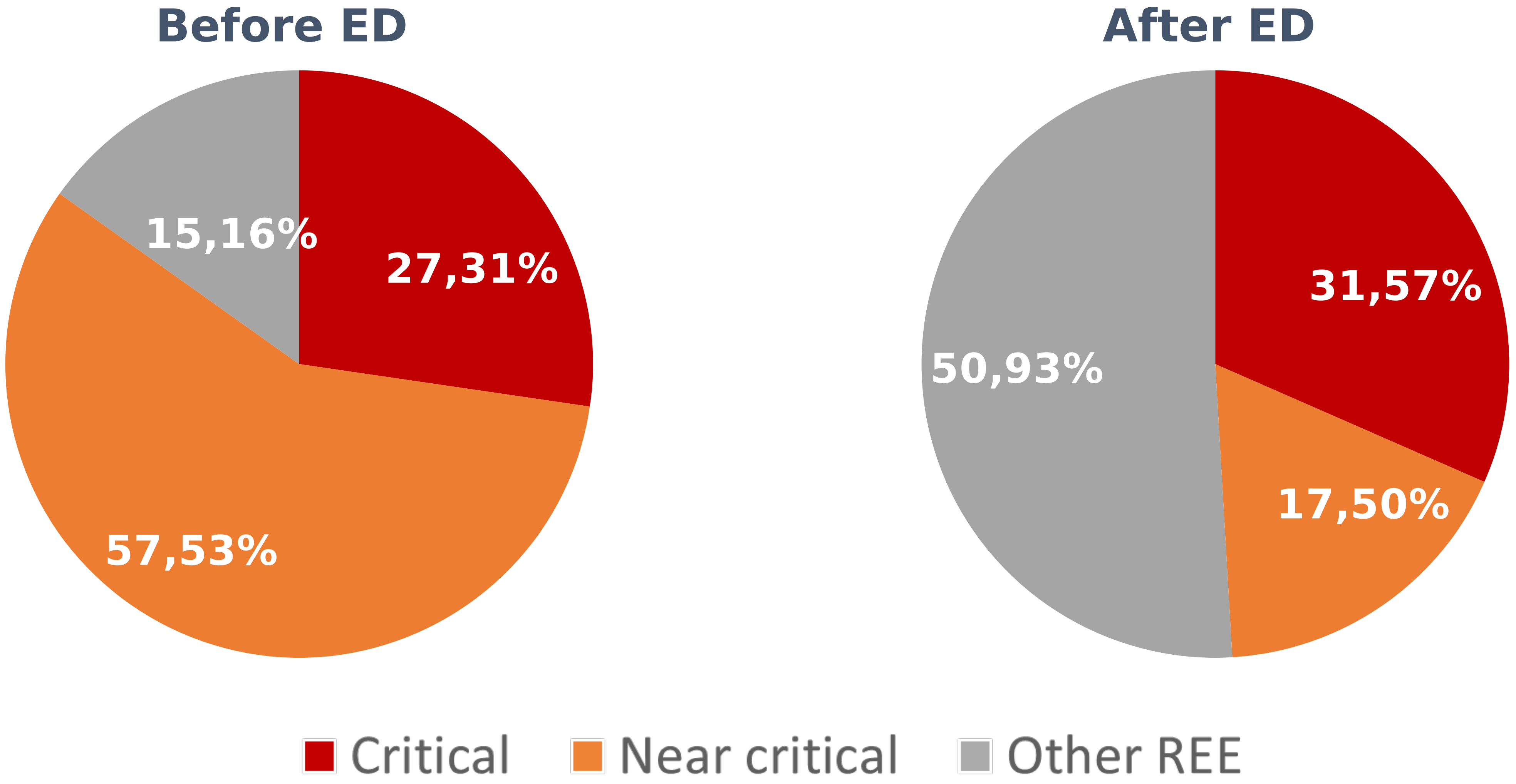
- Desorption starts from lower to higher atomic number (i.e. inversely related with ionic radius)

Scandium

- Different electronic and magnetic properties

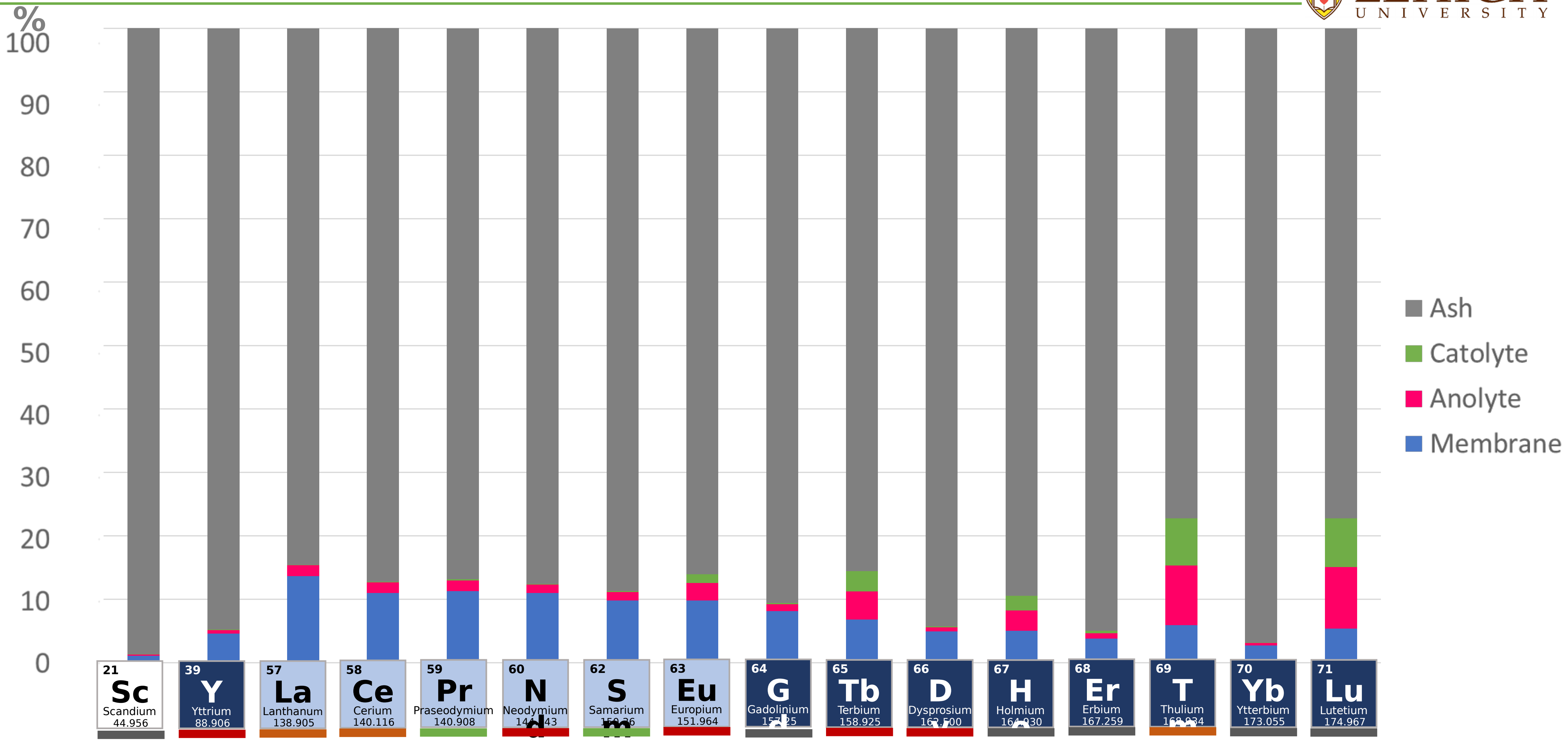
Results

Relative distribution of REEs in the ash



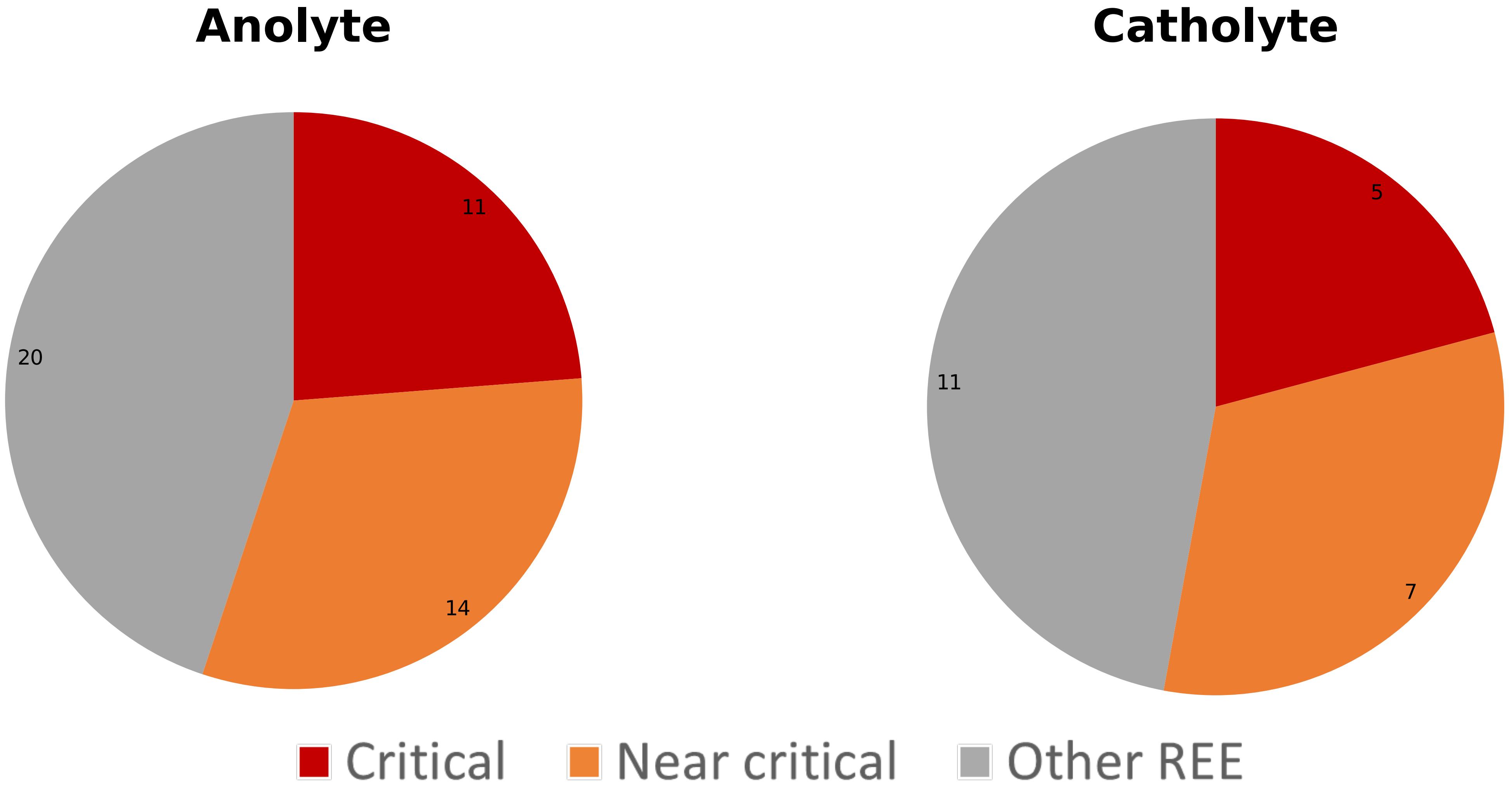
Results

REE distribution within the cell



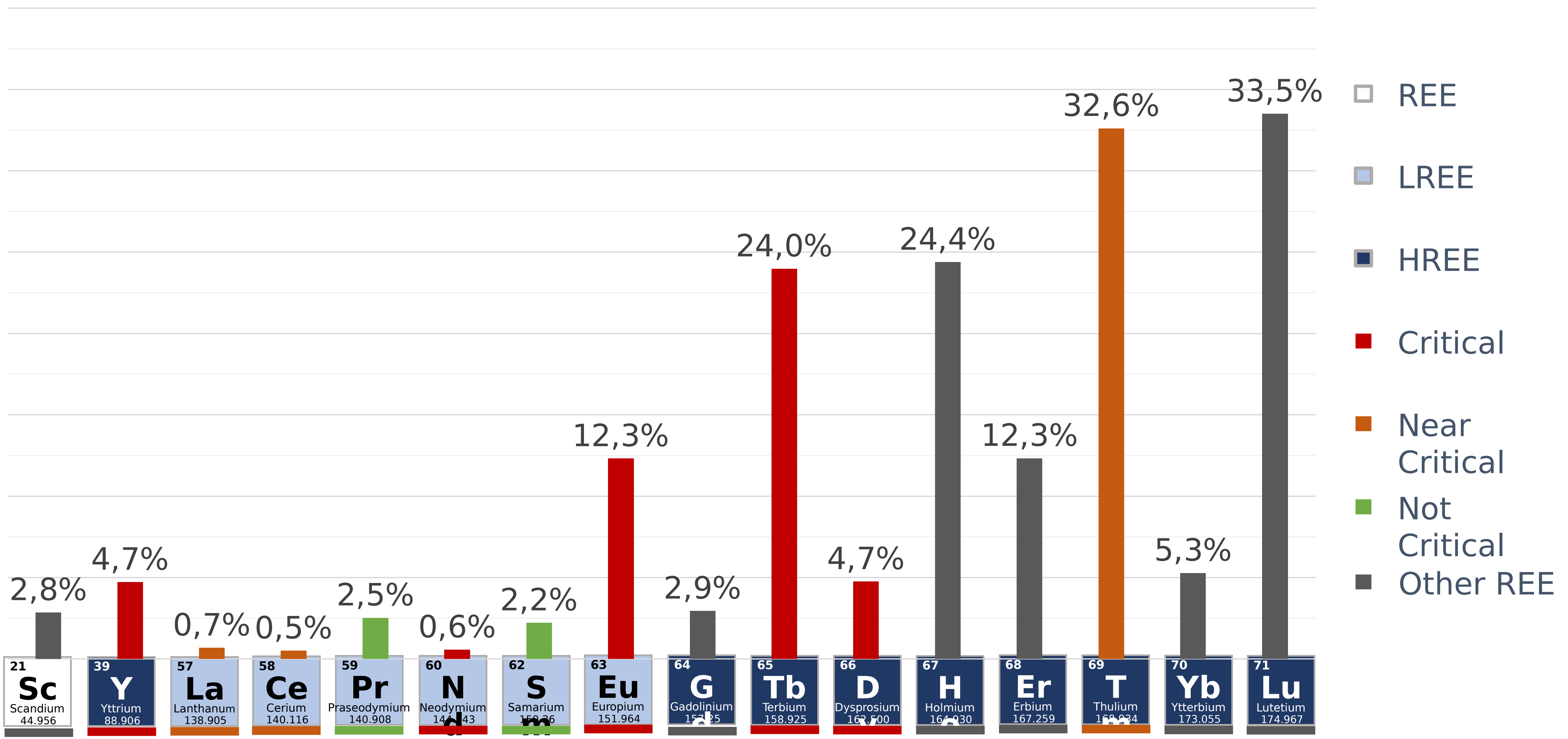
Results

Relative distribution of REEs in the liquid phase after ED



Results

REE in the catholyte after ED



Future Work

Experiment duration

- 7 days

✓ Higher desorption rates

pH adjustment

- In the catholyte (pH ~2)

✓ Prevention of ion element precipitation

✓ Prevention of the formation of aggregated elements around the electrodes and the membrane

✓ Prevent membrane obstruction

Increase current intensity

- 50 mA

✓ Higher desorption rate

✓ Higher migration speed of the REE from the anolyte to the catholyte