Chromatographic Separation of Rare Earth Elements as Anionic Complexes by Ion Exchange

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Background / Phosphogypsum

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
mg/kg (ppm)	31.8	260.2	735.4	102.2	422.6	64.0	15.8	37.0	3.4	13.4

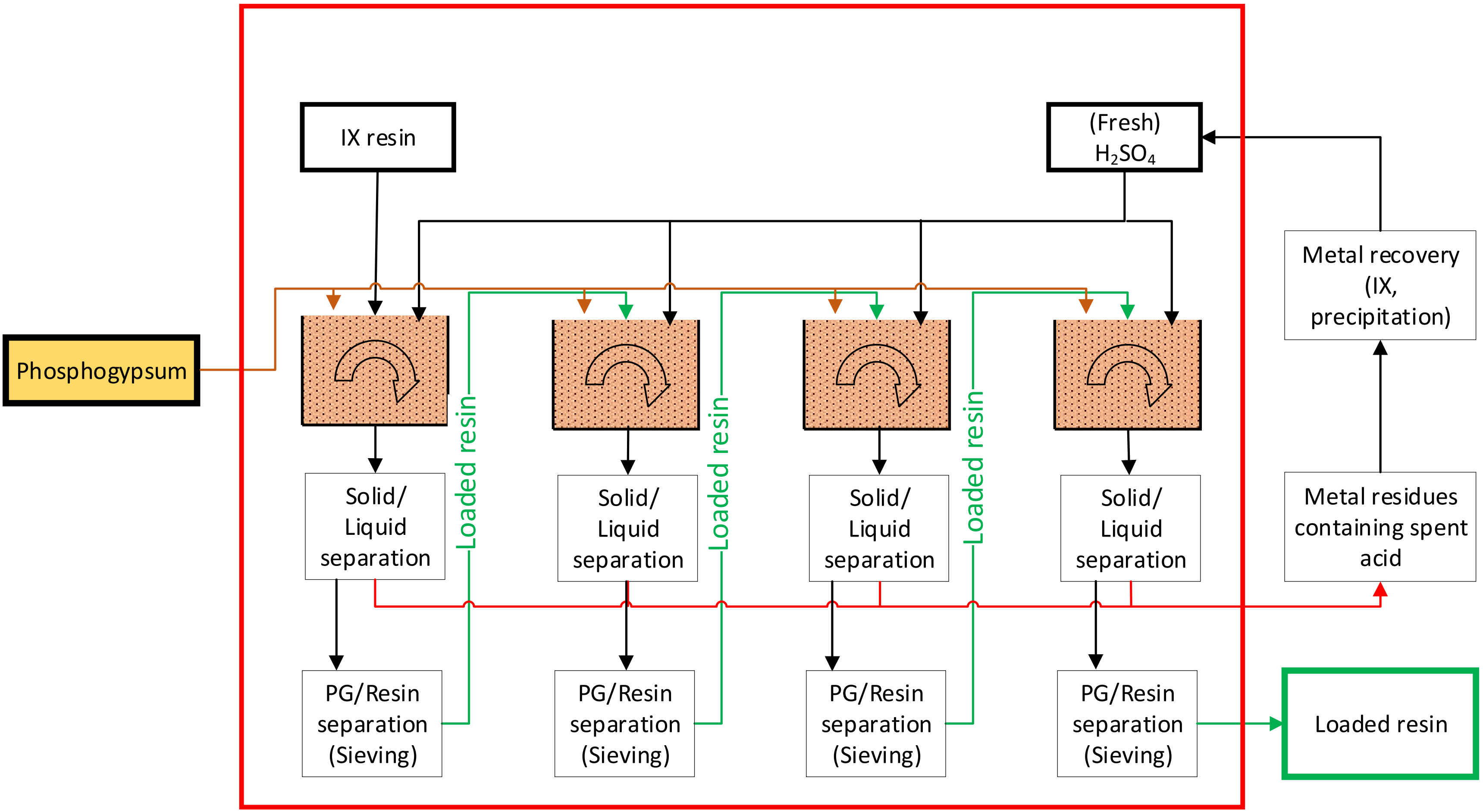
- Rare earth content 1.7 grams per kilogram of phosphogypsum (Siilinjärvi, Finland)
- La-Nd being most important REEs

Phosphogypsum pile at fertilizer plant in Siilinjärvi, Finland. Source: YLE

- Globally available in large amounts (global production 100-280 Mt per year), metal content varies depending on the source. Apatite naturally contains rare earths
  - Most light rare earths are sorbed to the gypsum waste
  - Majority of heavy rare earths end up in the phosphoric acid

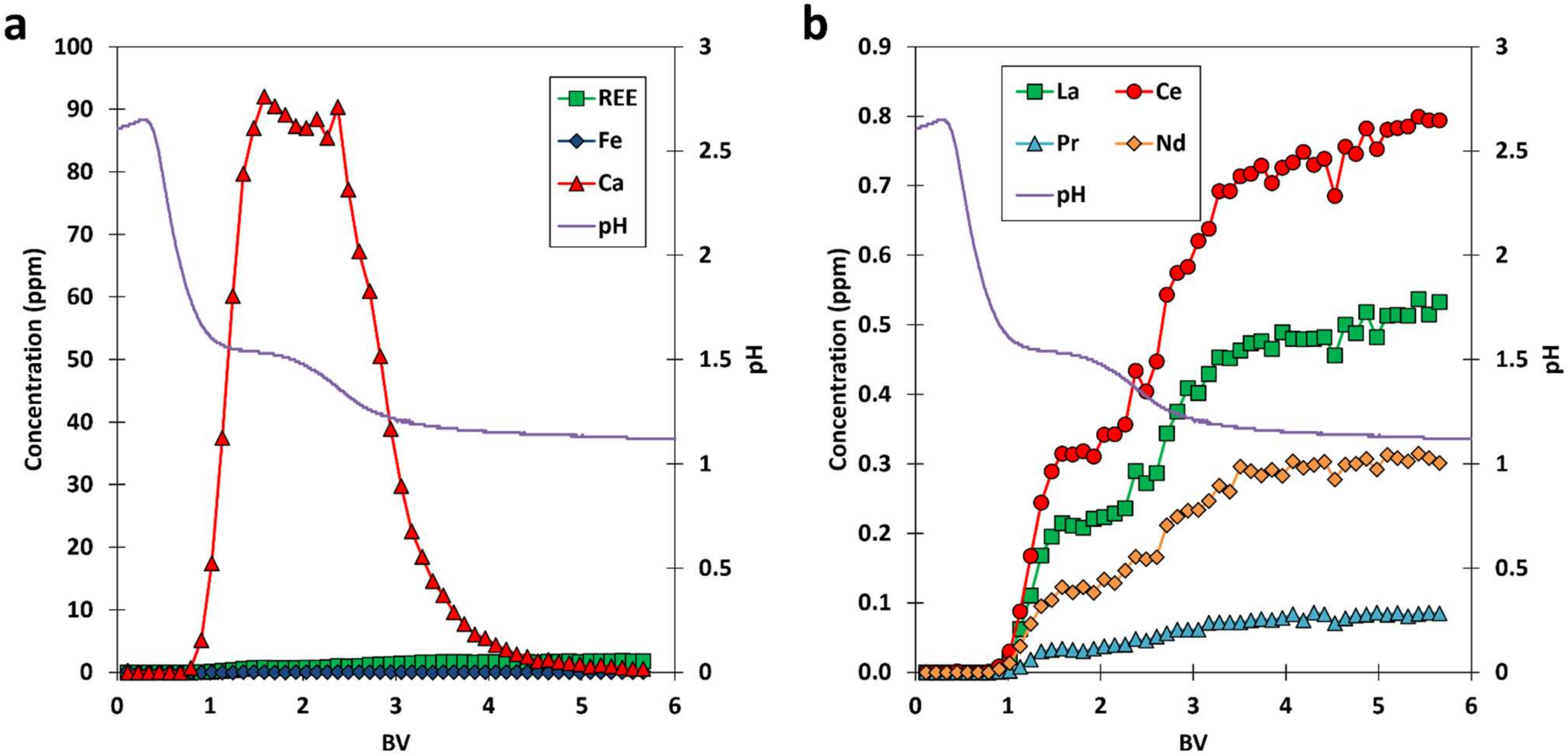
ALTA 2023

Resin-in-Leach (RIL)

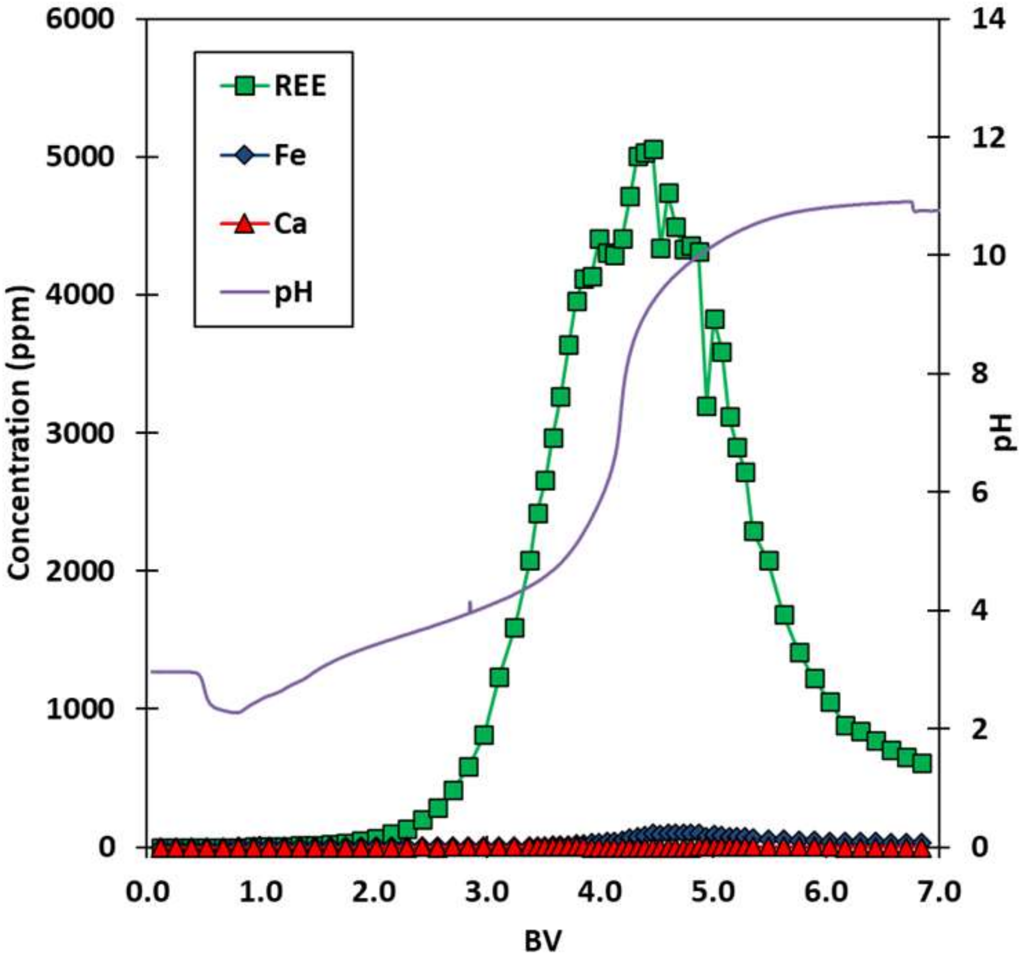


Ca	Fe	La	Ce	Pr	Nd
4.12	20.54	11.34	34.22	4.47	17.33

- REEs are extracted from phosphogypsum with multiple consecutive RIL steps.
- Resin remains the same. Loading increases every step.
- Fresh slurry (PG/acid mixture) is created for every cycle.

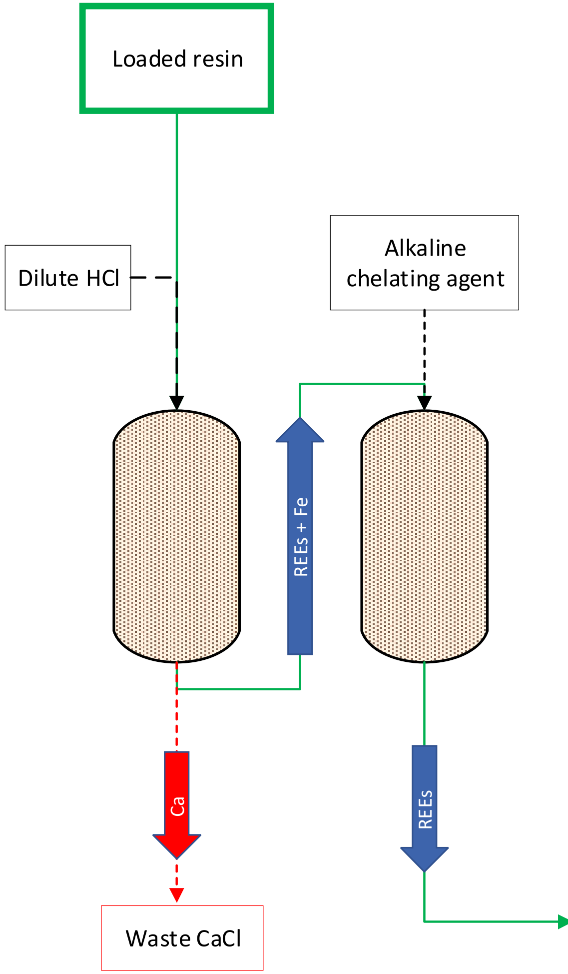


- Ca is washed from loaded resin with dilute HCl.
    - Fe is not affected by the dilute HCl
    - Minor REE leakage is observed which is insignificant.



- In the beginning of the graph, the heavier REEs (HREE) are more concentrated than La-Nd.
- It can be used to collect HREE fraction
  - Low concentration of 0.22 g/L
  - Sm-Lu 36.7% out of all REE
  - As comparison Sm-Lu make 6.9% of REEs in main fraction (3.1-6.0 BV).
- Fe is not effectively recovered from the resin with alkaline MGDA
  - Alkalinity causes $Fe(OH)_3$ precipitation on the resin surface → Regeneration issues

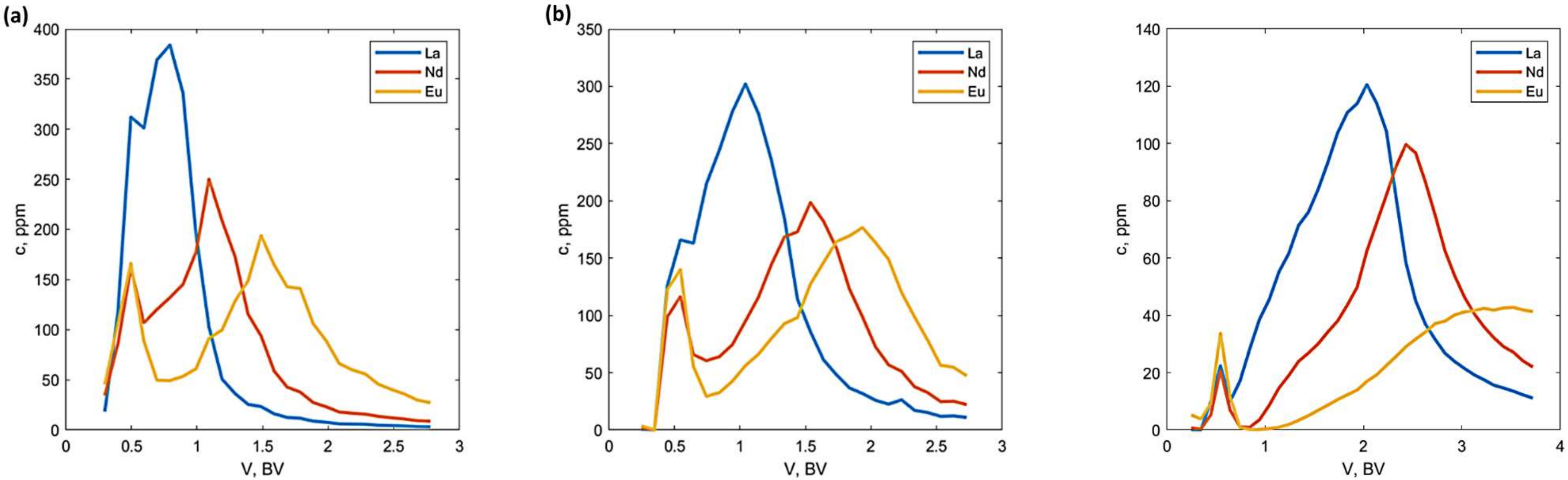
REE recovery



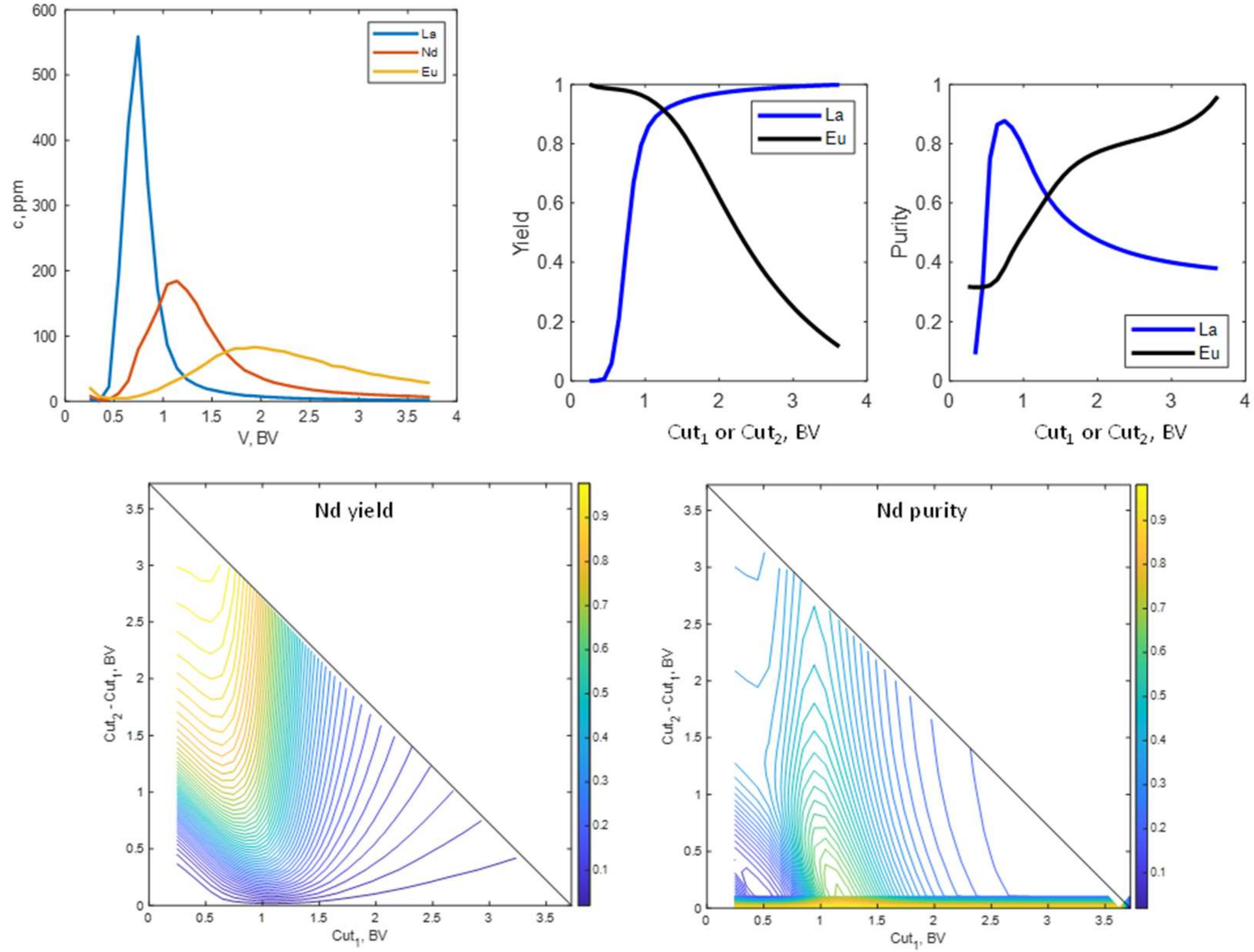
- Alkaline MGDA is used to recover REEs
- 3.2 g/L (REE) with purity of 98.27%

Element	(BV = 3.1–6.0); %	Element	(BV = 3.1–6.0); %
Ca	0.09	Eu	0.80
Sc	0.01	Gd	1.83
Fe	1.65	Tb	0.15
Sr	0.00	Dy	0.57
Y	1.79	Ho	0.07
La	15.19	Er	0.12
Ce	45.02	Tm	> 0.01
Pr	5.93	Yb	0.04
Nd	23.46	Lu	> 0.01
Sm	3.28		

- Chromatographic separation process was investigated first with synthetic MGDA-REE mixture.
  - Three REEs were selected: La, Nd, Eu
- Aim was to find suitable resin, mobile phase etc. other optimal conditions for separation.
- IRA-410 was chosen as separation material
  - Other resins were investigated but IRA-410 (type II SBA with 6% DVB)
- Dilute HCl is used as mobile phase
- Separation relies on stability differences between MGDA-REE complexes.
  - Dilute acid weakens (protonates) the weakest REE-MGDA complex first.
    - Order of elution is thus La, Nd, Eu.
  - Findings from the synthetic research were used with authentic material.

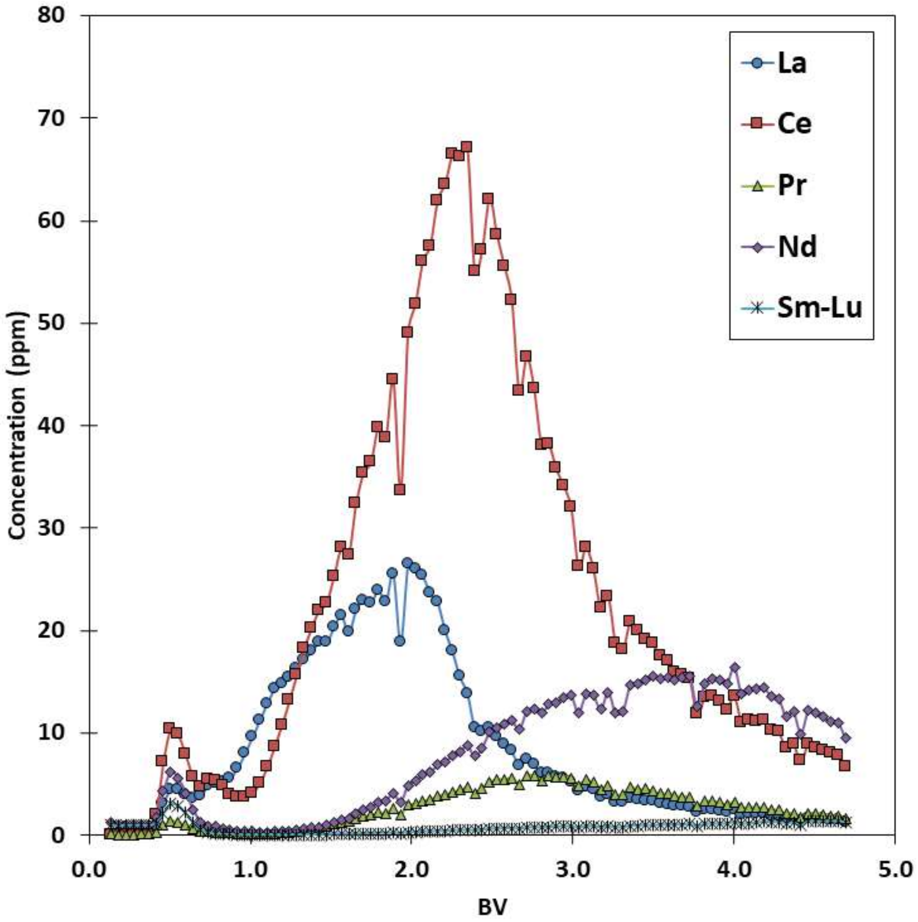


• Few examples with the synthetic feed

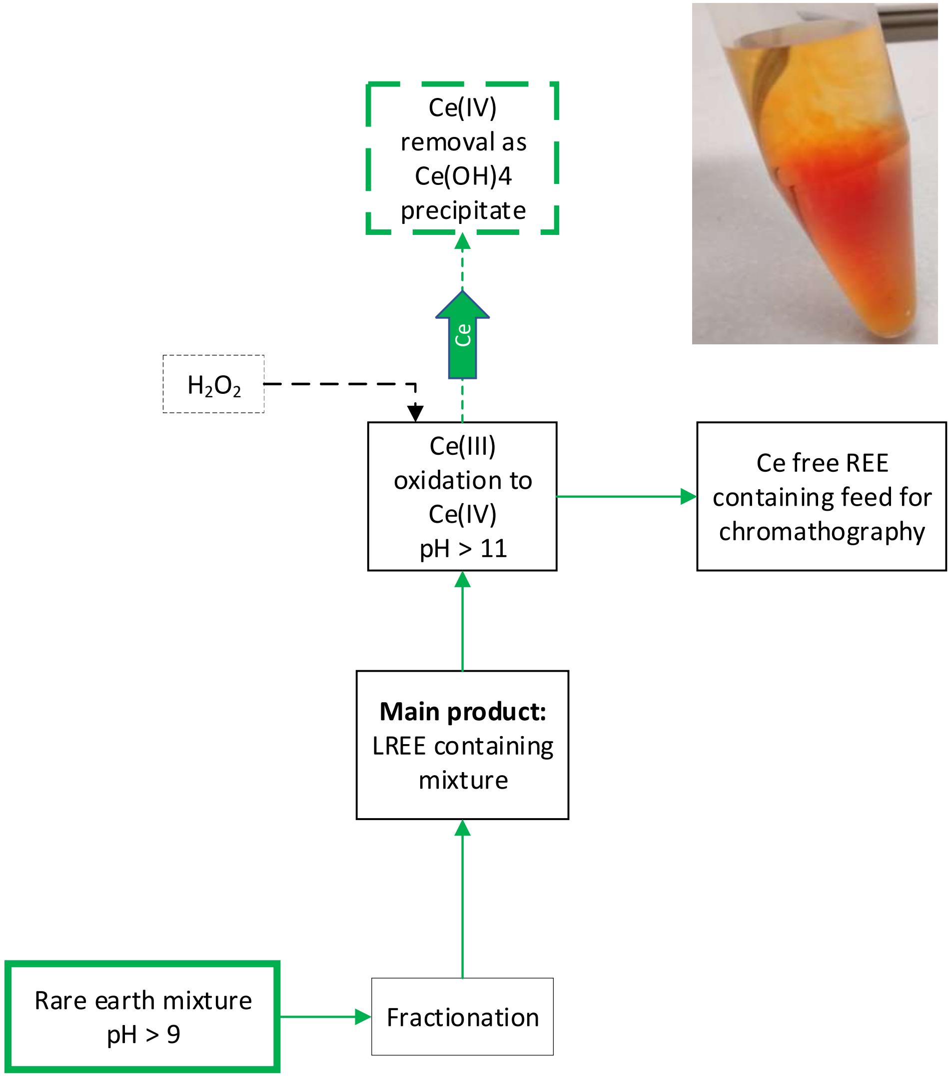


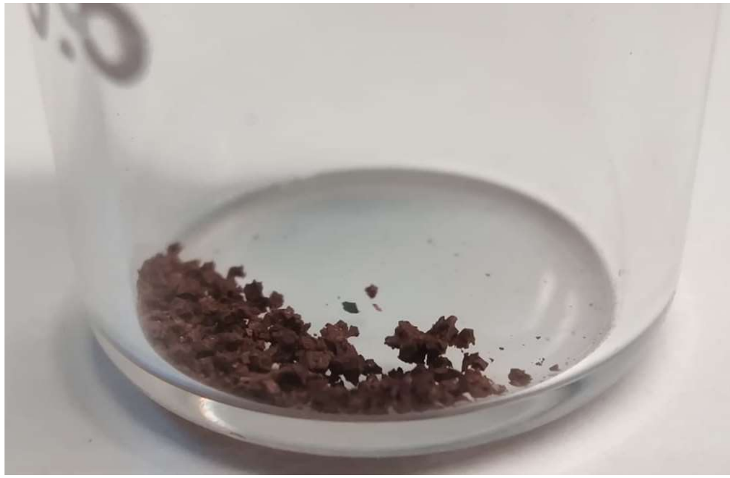
- With suitable conditions, the significant difference between REE-MGDA complexes can be achieved.
- From good separation, product fractions can be collected.

Chromatographic separation – Real feed

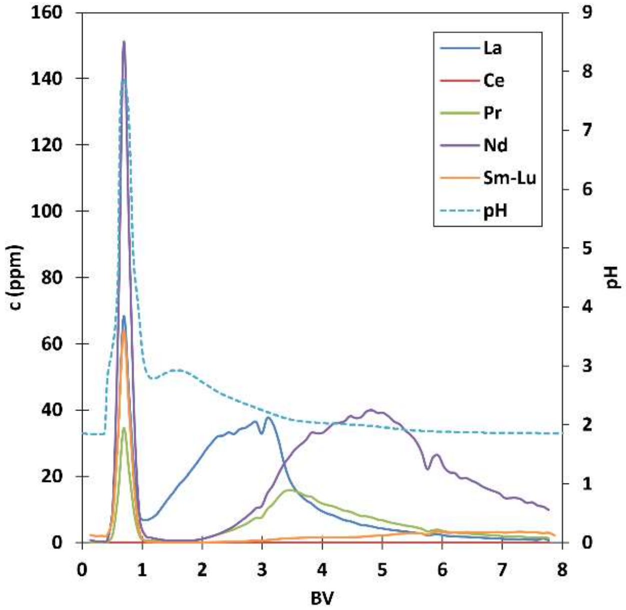


- One of the first experiments with authentic REE-MGDA product
- Systems follows same principles that were discovered with synthetic feed.
  - Trace impurities (mainly Ca and Fe) do not affect the separation.
- Ce excess affects the separation
- Without Ce the separation could be decent
- → Ce needs to be removed from the feed solution

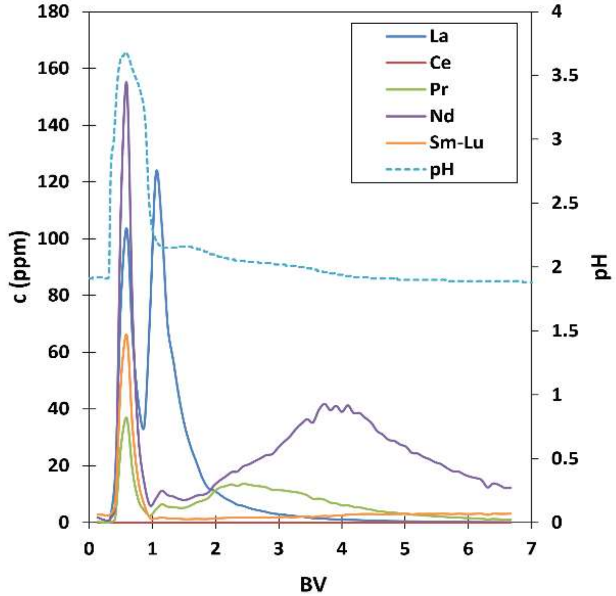




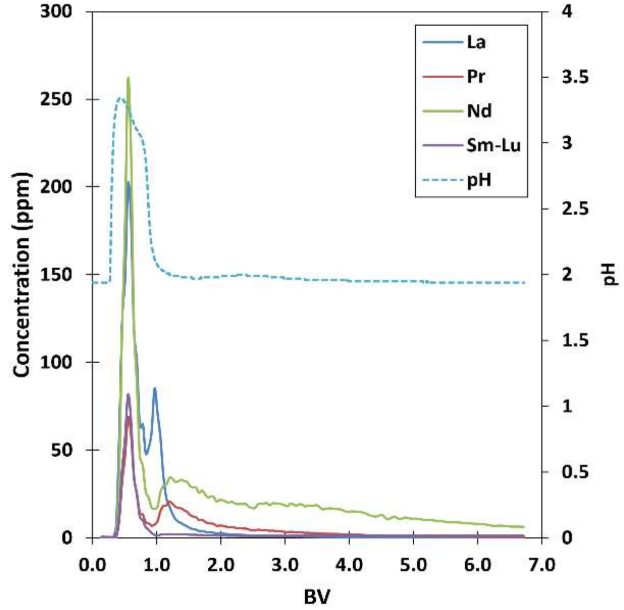
- Ce content 85,68%
- Other metals:
  - La: 8,53%
  - Fe: 2,66%
  - Pr: 0,91%
  - Nd: 1,37%
- Fe+Ce+La+Pr+Nd: 99,14%
- Better purities for Ce fraction are achieved ~93%



pH ~ 9



pH ~ 6

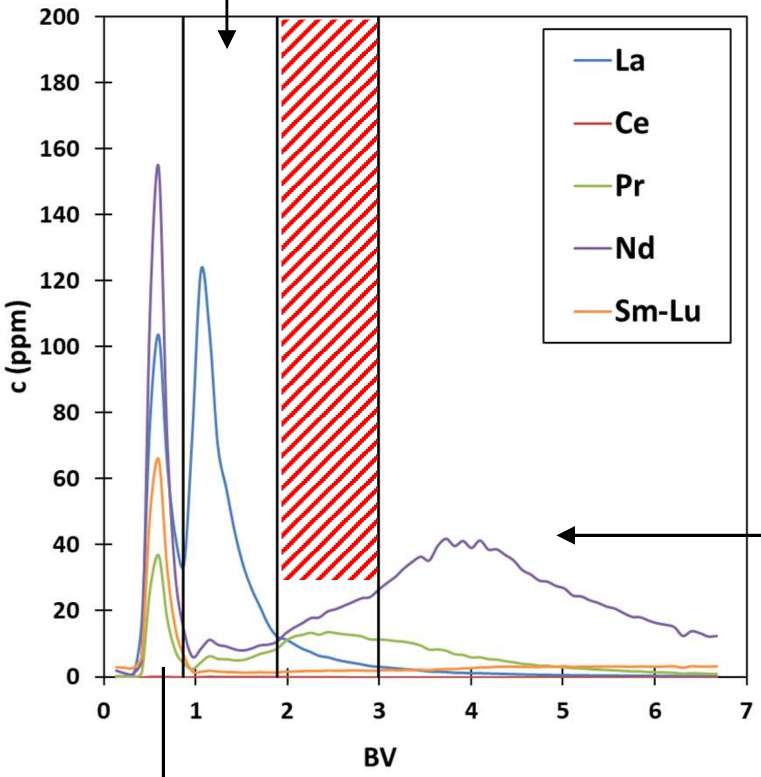


pH ~ 3

- Equal feed size
- Equal flow rate
- Same mobile phase
- Different feed pH

Chromatograms

La fraction; *Pu%*: 74.39% *Y%*: 54.01%

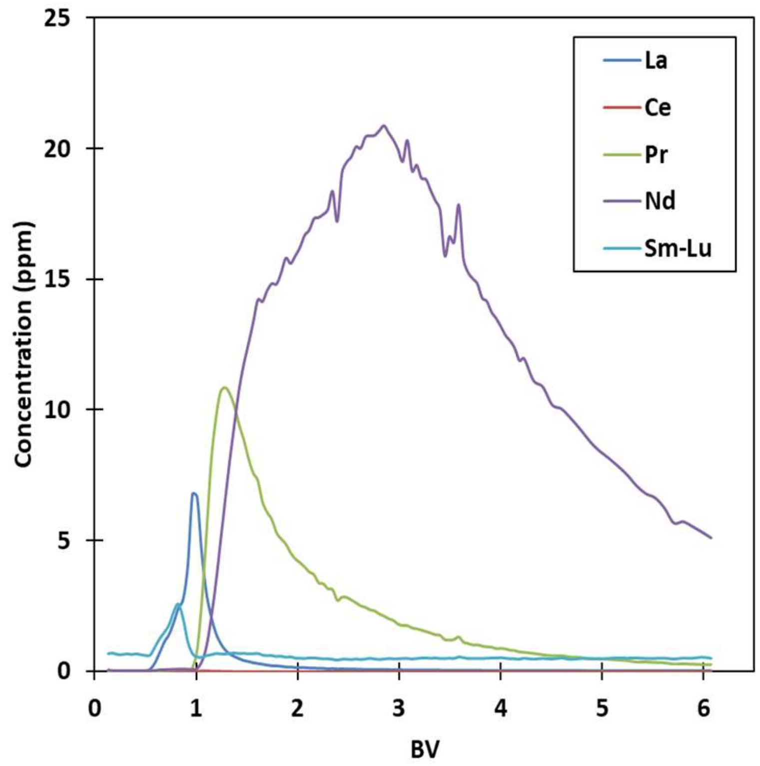


“Front peak” can be recycled

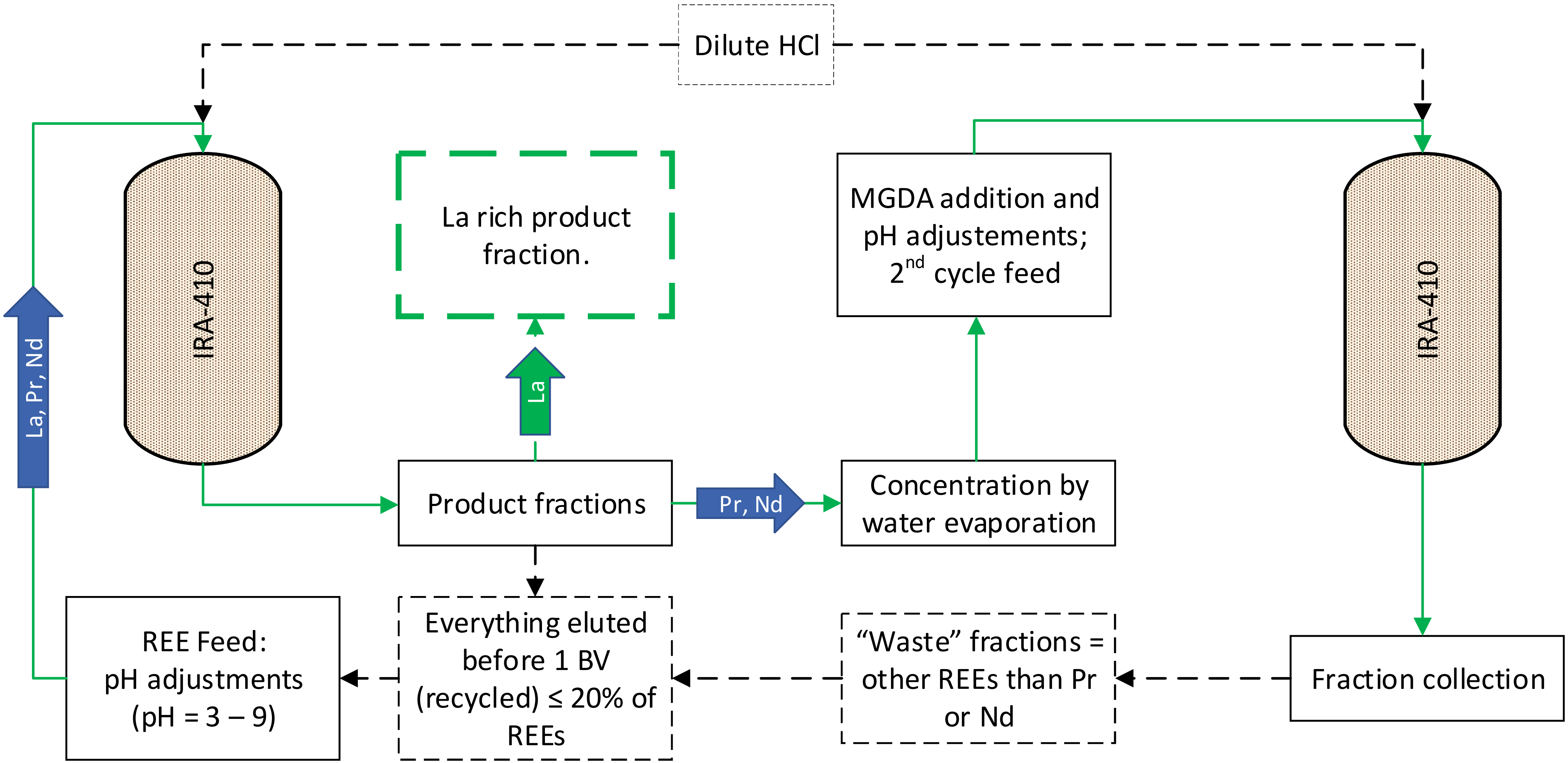
Pr+Nd fraction

Condensation

MGDA addition etc.



Pr+Nd product fraction (collected starting from 1.20 BV. Pr yield 91.3% and purity 14.3%. Nd yield 86.9% and purity 81.2%

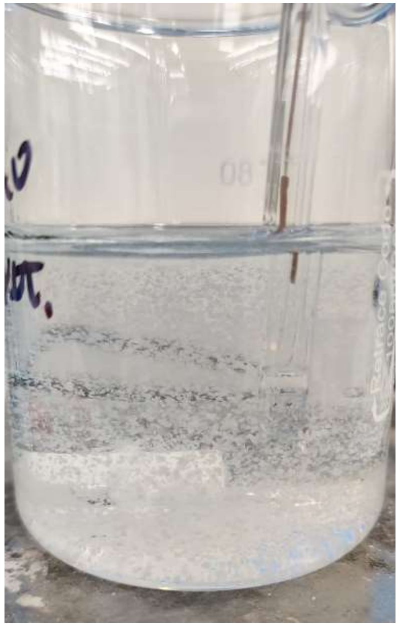


Dilute HCl
IRA-410
La rich product fraction.
MGDA addition and pH adjustements; 2nd cycle feed
IRA-410
La, Pr, Nd
La
Product fractions
Pr, Nd
Concentration by water evaporation
REE Feed: pH adjustments (pH = 3 – 9)
Everything eluted before 1 BV (recycled) ≤ 20% of REEs
"Waste" fractions = other REEs than Pr or Nd
Fraction collection

Oxalate precipitation

Synthetic Nd-MGDA +
K-oxalate

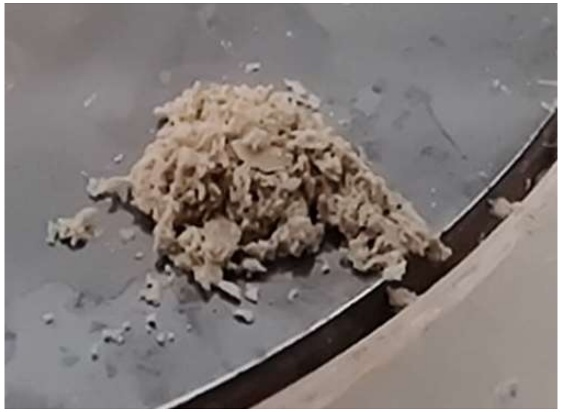
+ HCl,
pH < 8



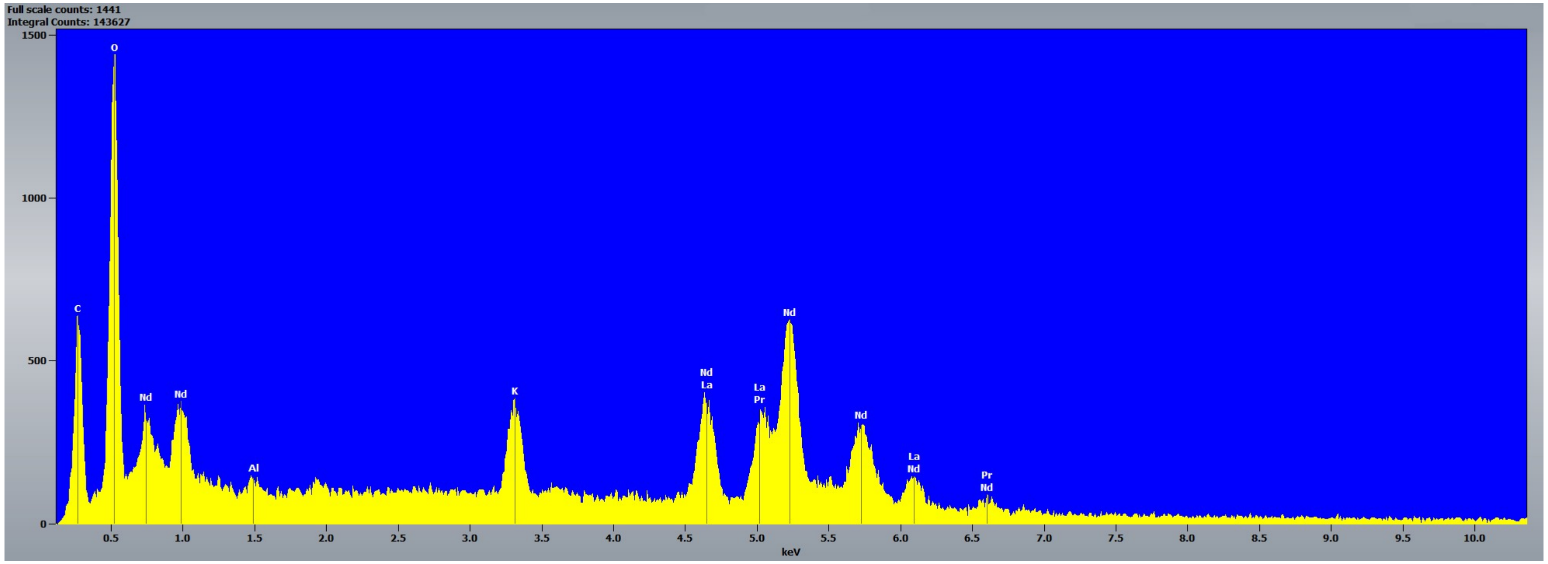
K-MGDA-REE precipitated from the process product. Mainly Pr-Nd oxalate.

- Precipitation experiment with synthetic materials.
  - Precipitation does not occur if the pH > 9.
  - Decrease in pH (< 8) allows the precipitates to form.
  - Same applies to the authentic material.

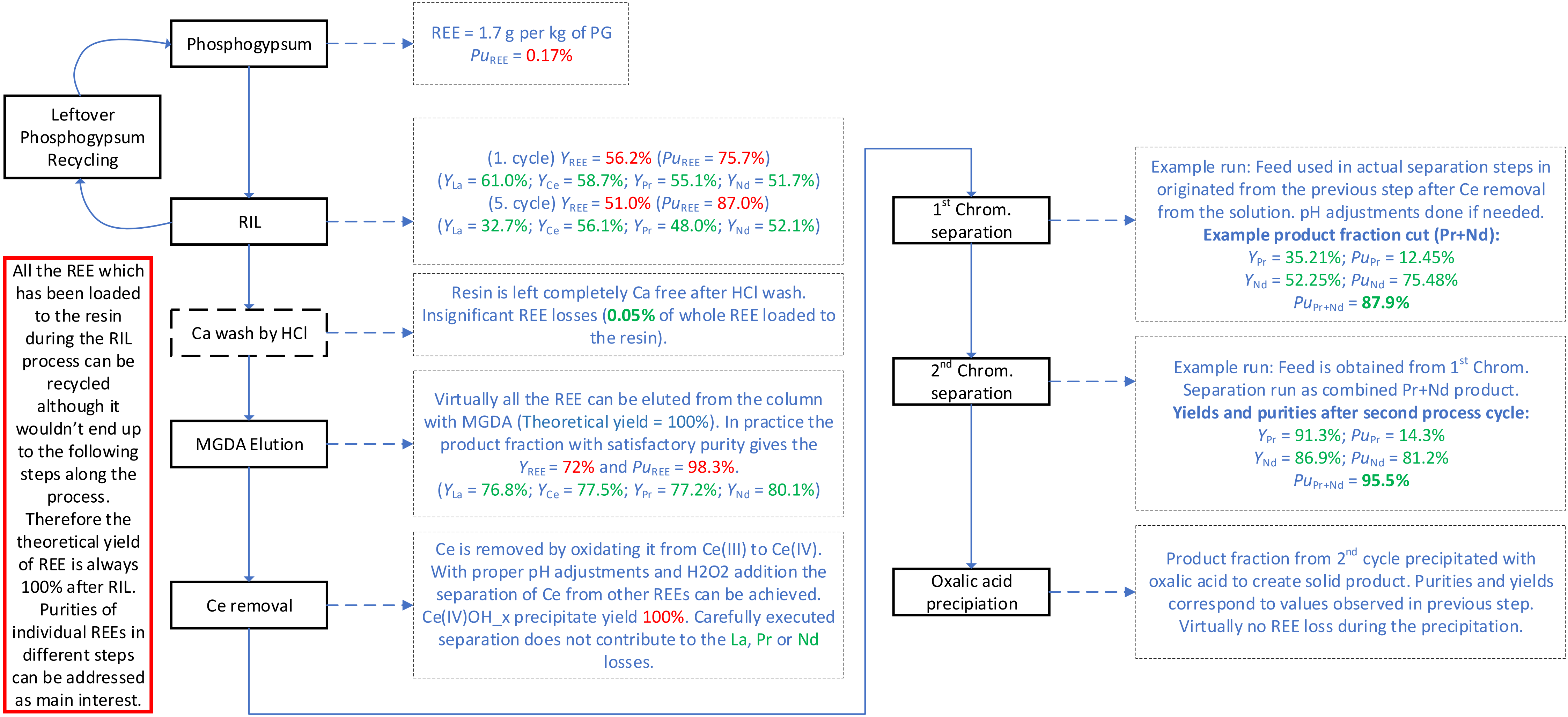
No chemical modification needed after separation



Element	%
Pr	13.36
Nd	82.74
Ca, Sc, Fe, Sr	0.07
Other REEs	3.84



Element	w-%
C	6.8
O	9.1
K	4.5
La	18.4
Pr	12.0
Nd	48.8


Phosphogypsum
REE = 1.7 g per kg of PG
Pu_{REE} = 0.17%
Leftover Phosphogypsum Recycling
RIL
(1. cycle) Y_{REE} = 56.2% (Pu_{REE} = 75.7%)
(Y_{La} = 61.0%; Y_{Ce} = 58.7%; Y_{Pr} = 55.1%; Y_{Nd} = 51.7%)
(5. cycle) Y_{REE} = 51.0% (Pu_{REE} = 87.0%)
(Y_{La} = 32.7%; Y_{Ce} = 56.1%; Y_{Pr} = 48.0%; Y_{Nd} = 52.1%)
All the REE which has been loaded to the resin during the RIL process can be recycled although it wouldn't end up to the following steps along the process. Therefore the theoretical yield of REE is always 100% after RIL. Purities of individual REEs in different steps can be addressed as main interest.
Ca wash by HCl
Resin is left completely Ca free after HCl wash. Insignificant REE losses (0.05% of whole REE loaded to the resin).
MGDA Elution
Virtually all the REE can be eluted from the column with MGDA (Theoretical yield = 100%). In practice the product fraction with satisfactory purity gives the Y_{REE} = 72% and Pu_{REE} = 98.3%.
(Y_{La} = 76.8%; Y_{Ce} = 77.5%; Y_{Pr} = 77.2%; Y_{Nd} = 80.1%)
Ce removal
Ce is removed by oxidating it from Ce(III) to Ce(IV). With proper pH adjustments and H2O2 addition the separation of Ce from other REEs can be achieved. Ce(IV)OH_x precipitate yield 100%. Carefully executed separation does not contribute to the La, Pr or Nd losses.
1st Chrom. separation
Example run: Feed used in actual separation steps in originated from the previous step after Ce removal from the solution. pH adjustments done if needed.
Example product fraction cut (Pr+Nd):
Y_{Pr} = 35.21%; Pu_{Pr} = 12.45%
Y_{Nd} = 52.25%; Pu_{Nd} = 75.48%
Pu_{Pr+Nd} = **87.9%**
2nd Chrom. separation
Example run: Feed is obtained from 1st Chrom. Separation run as combined Pr+Nd product.
Yields and purities after second process cycle:
Y_{Pr} = 91.3%; Pu_{Pr} = 14.3%
Y_{Nd} = 86.9%; Pu_{Nd} = 81.2%
Pu_{Pr+Nd} = **95.5%**
Oxalic acid precipitation
Product fraction from 2nd cycle precipitated with oxalic acid to create solid product. Purities and yields correspond to values observed in previous step. Virtually no REE loss during the precipitation.

Group

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- Prof. Tuomo Sainio

Thank you for your attention!
Questions?