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Hydrothermal Pre-Treatment Process of Phosphogypsum for Enhanced Rare Earths Recovery

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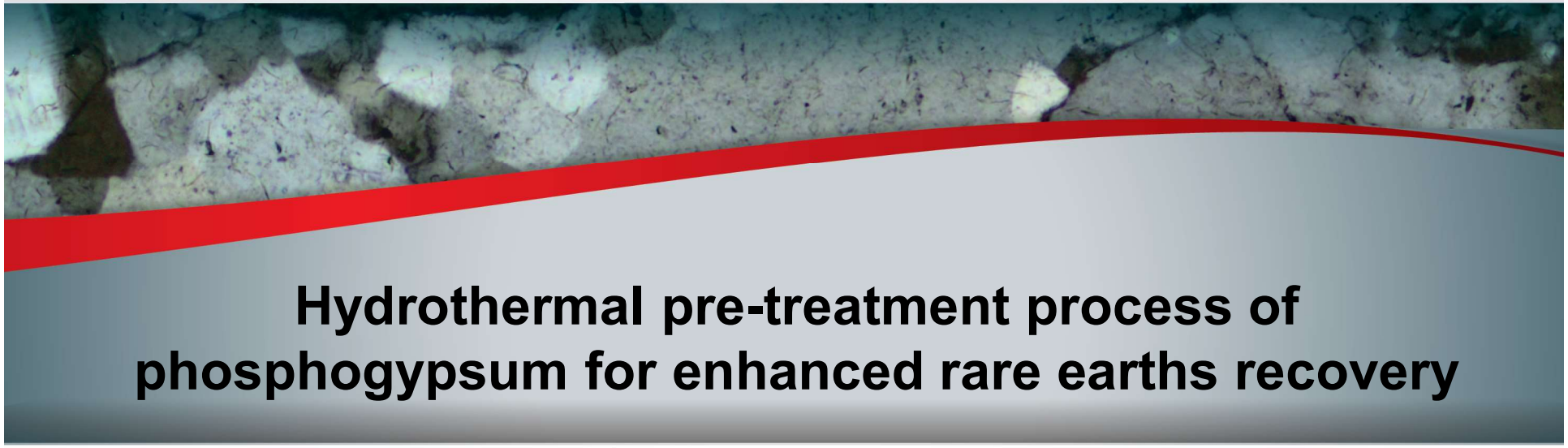

Hydrothermal pre-treatment process of phosphogypsum for enhanced rare earths recovery

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Phosphogypsum (PG) and Rare Earths

$$\text{Phosphate ore} + H_2SO_4 \rightarrow H_3PO_4 + CaSO_4.nH_2O$$

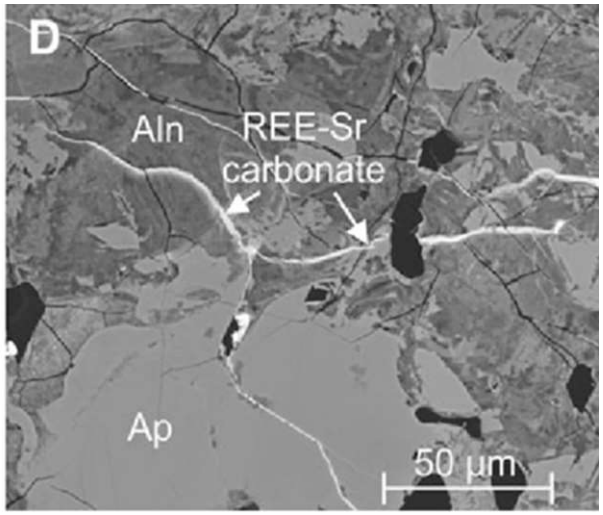
"Wet phosphoric acid process"

n = 2 : $CaSO_4.2H_2O$

n = ½ : $CaSO_4.½H_2O$

n = 0 : $CaSO_4$

- 70% to 90% of REEs originally in phosphate ore end-up in PG;



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Phosphogypsum (PG) as a source of REE

$$\text{Phosphate ore} + H_2SO_4 \rightarrow H_3PO_4 + CaSO_4.nH_2O$$

"Wet phosphoric acid process"

n = 2 : $CaSO_4.2H_2O$

n = ½ : $CaSO_4.½H_2O$

n = 0 : $CaSO_4$

- 70% to 90% of REEs originally in phosphate ore end-up in PG;
- Average REEs content in PG between 0.27 wt.% and 0.8 wt.%;
- PG considered a secondary resource for REEs

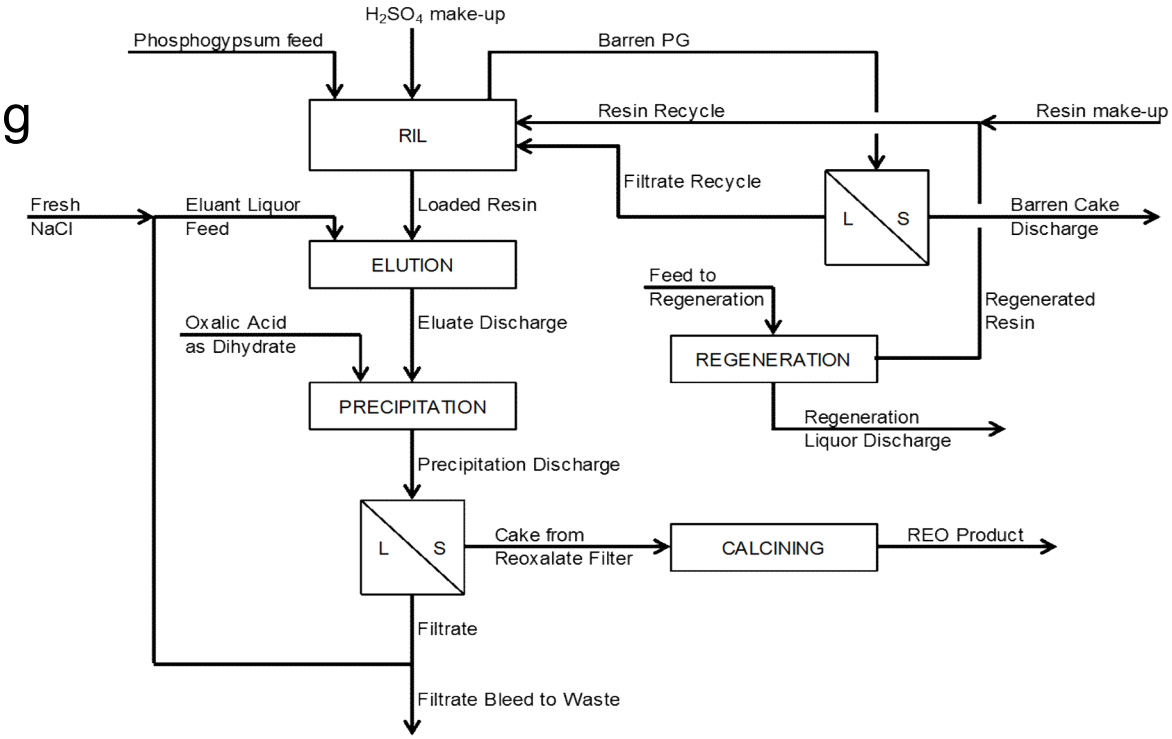
	Worldwide	In South Africa
PG dumps, t	>7 billion	>70 million
Current growth rate, t/a	150-200 million	13,000-20,000

Methods for REE recovery from PG

- Chemical conversion to $CaCO_3$, $REECO_3$, $(NH_4)_2SO_4$

- Bio-technologies
  - ✓ Bio-enhanced leaching
  - ✓ Sulphate reduction

- Leaching
  - ✓ HNO_3
  - ✓ HCl
  - ✓ H_2SO_4



- ***Resin-in-Leach*** process developed and piloted at Mintek (2011-2012): @ a price of >$21/kg for mixed REE oxide @ an overall recovery of 15% economics may already be favourable; **BUT** implementation requires significant financial investment

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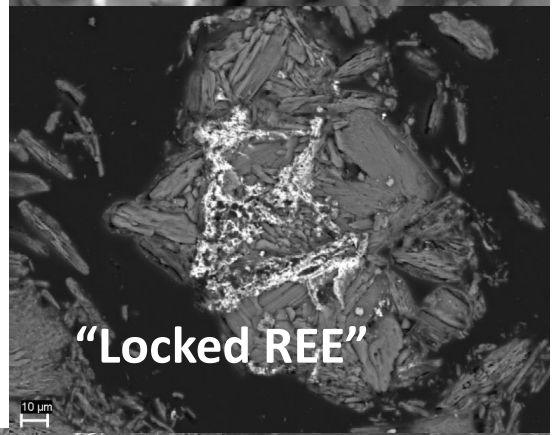
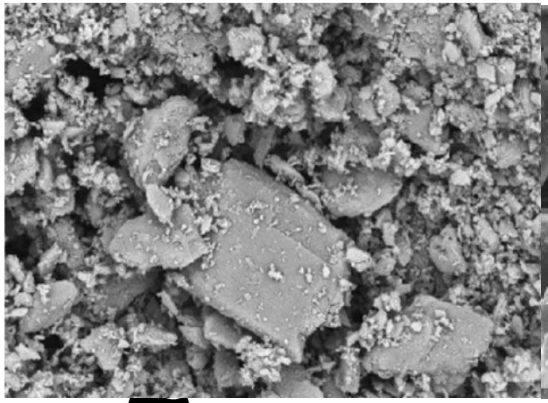
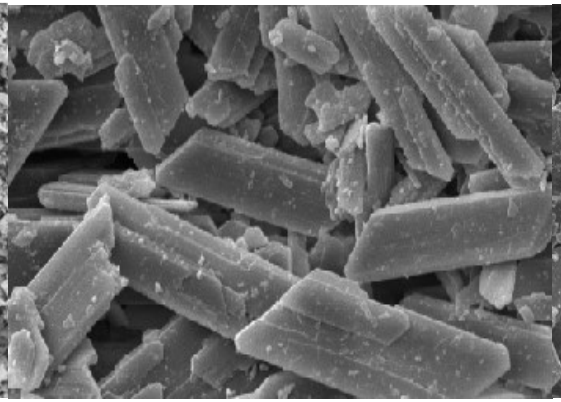
Non-destructive methods most attractive BUT…

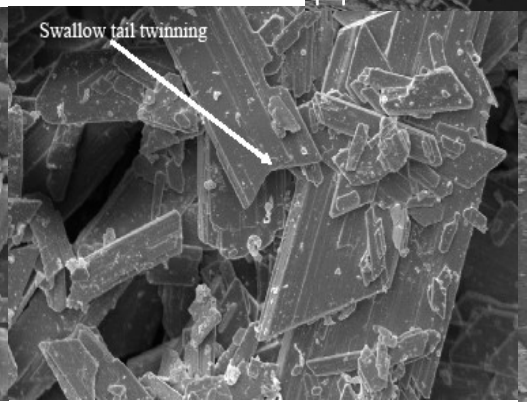
REE recovery varies from 5 to 80 % depending on:

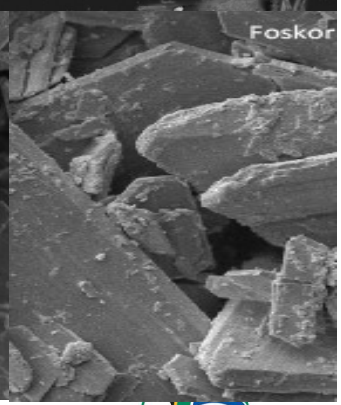
- Origin of the raw material (apatite);
- Specifics of the wet-phosphoric process;
- Age of the sample and conditions of storage











Recovery of REE from PG: problem statement

The Problem

- PG is highly variable
- Low and variable REEs recovery

Research Question

How can REEs associated with PG be “unlocked” and lead to increased recovery?

Upfront limitations:

- minimum use of reagents & generation of as little waste as possible
- conversion of PG into a saleable product

Approach followed…

- Construction industry uses “dry” and “wet” methods for natural gypsum conversion into hemihydrate
- Apply two approaches to modify gypsum and then
- Recover REEs from the *modified* PG, and for comparison, from the *as received* (unmodified) PG
- If found to be successful => confirm efficiency on various samples

Sources of PG:

- ✓ *Rustenburg (initial testwork)*
- ✓ Richards Bay
- ✓ Phalaborwa

PG modification and REE extraction

Phosphogypsum
"as received"

"Dry" conversion:

calcining @ 100°C for 24 hrs

"Wet" conversion:

autoclaving @ 120°C for 5 hrs
(10% m/m solids)

REE recovery:

20 % (m/m) solids,
ambient temperature,
100 g/L H_2SO_4,
24 hrs residence time

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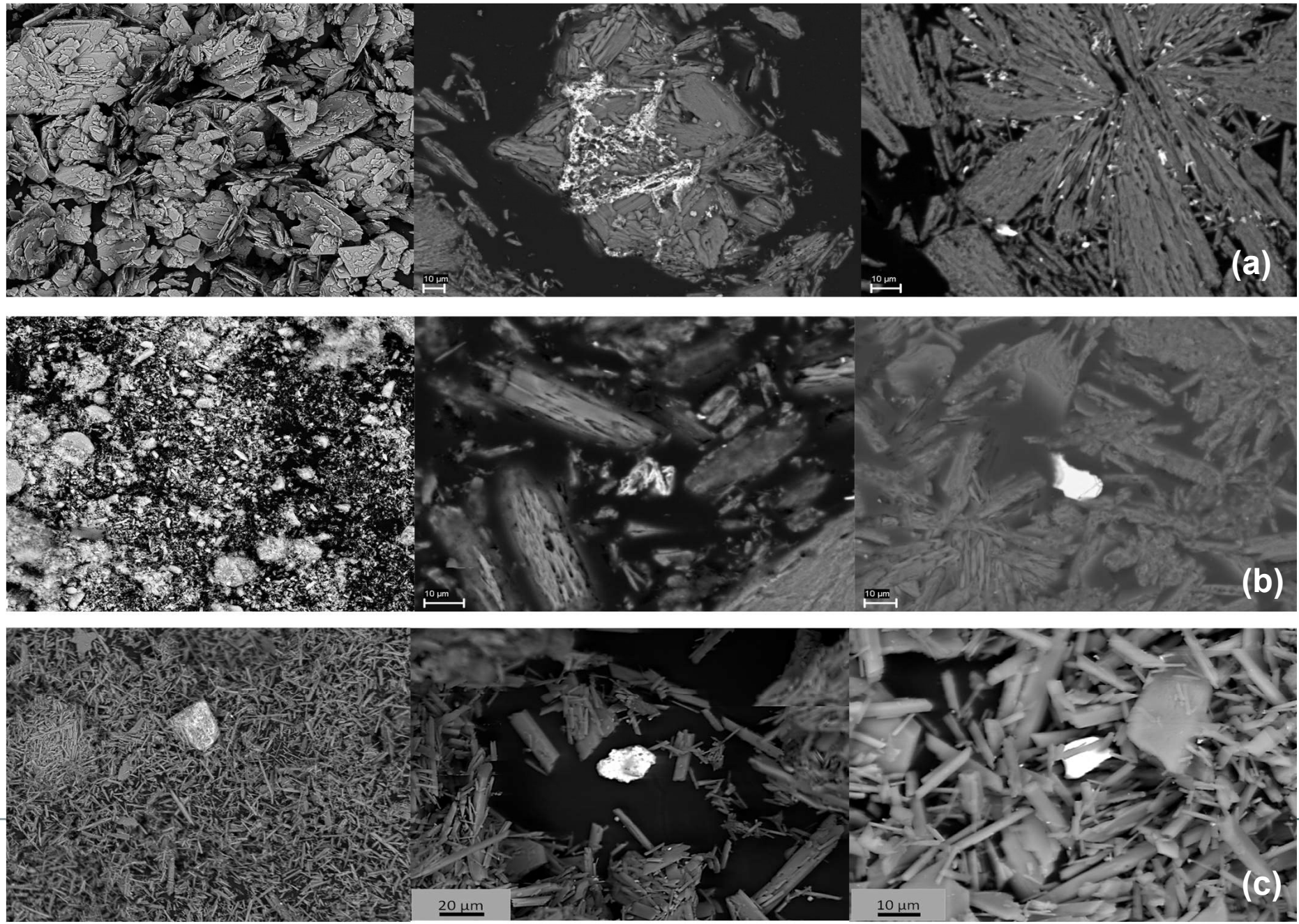
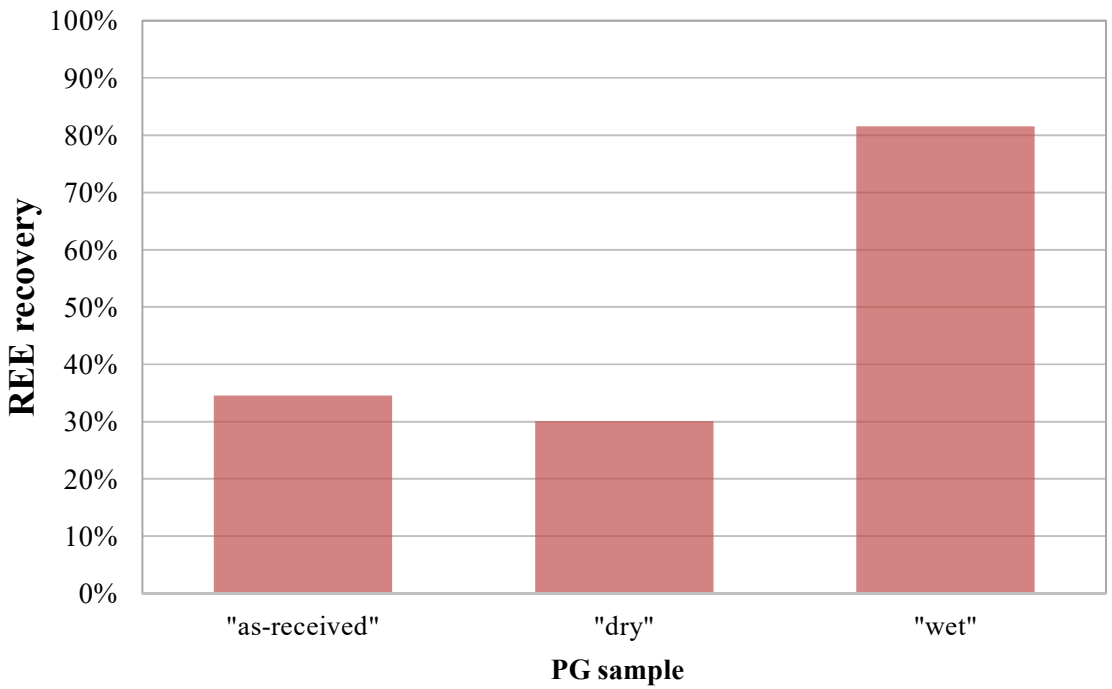
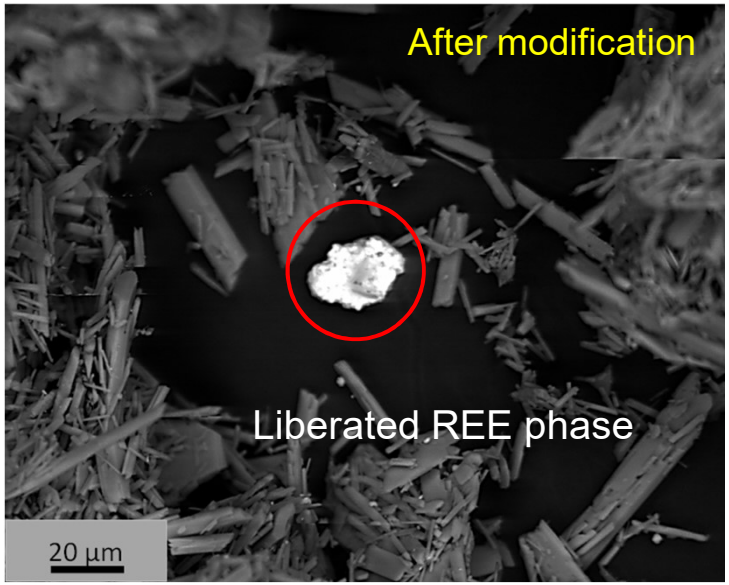
SEM: (a) PG “as is”, (b) after “dry” and (c) “wet”



REE leaching from PG “as is” and after conversion





Wet/hydrothermal way of PG modification =>

- distinct change of crystals structure,
- liberation of REE phases and
- noticeable increase in recovery of REE in subsequent leach

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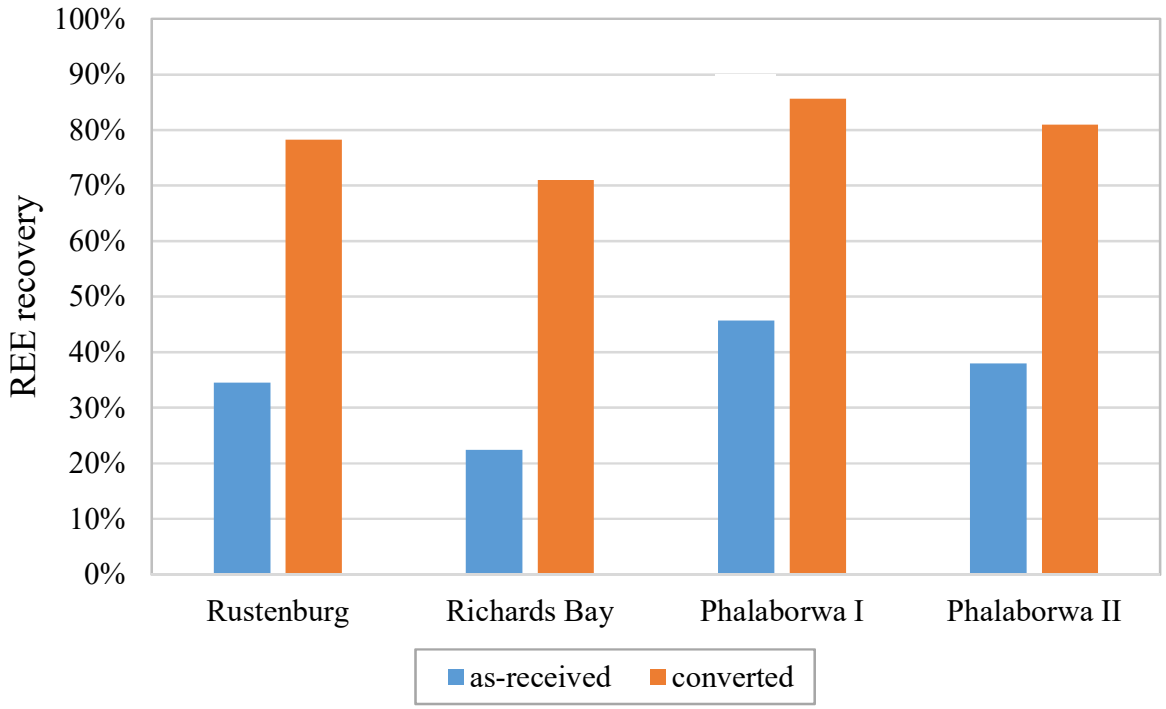
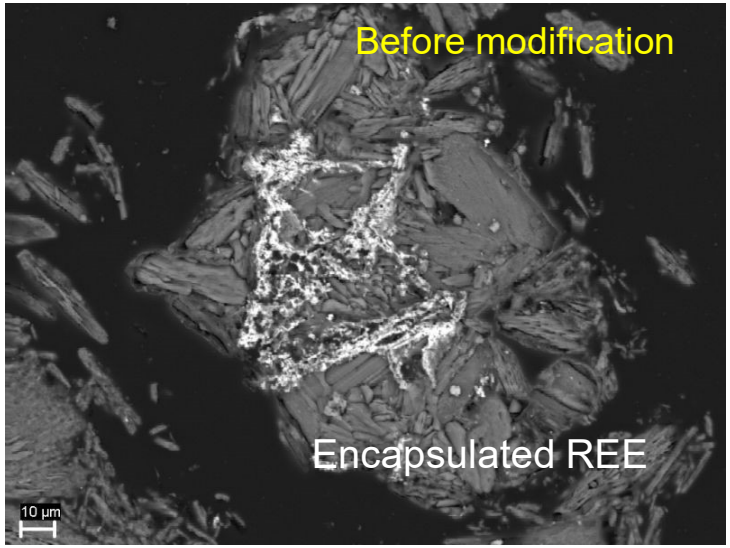
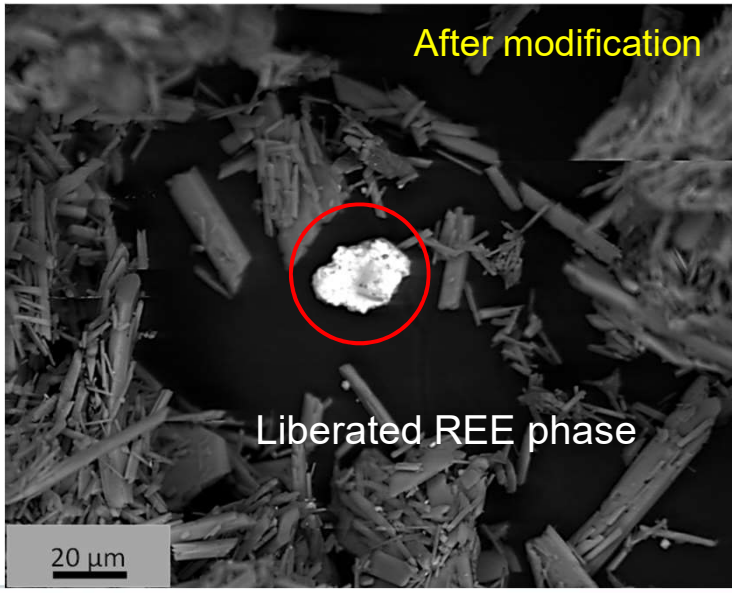
Recovery of REE from variability samples







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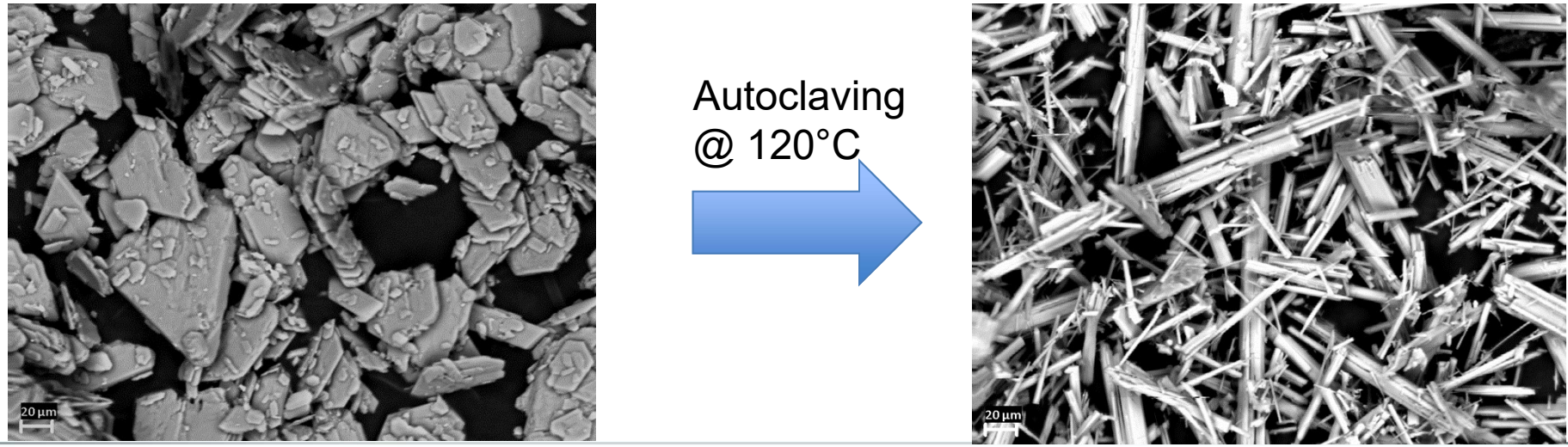
To address economics of REE recovery

Parameters/options to be optimized/tested:

- Temperature
- Solids content
- Residence time
- Slow cooling/flash cooling
- Subsequent REE phases upgrade via magnetic separation or flotation
- Hydrothermal treatment of PG => α-hemihydrate – better product for construction industry



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Hydrothermal conversion and construction industry

Giulini process (2 plants in Western Germany & 1 in Ireland):

- Feed - PG;
- Operating temperature - 120°C;
- Residence time – 1.5-2 hrs;
- pH 1-3
- Seeding
- Additives to control size and shape of α-hemihydrate (sulfite waste liquor or surface active substances)
- Filtration, drying and grounding

Material and process requirements per ton of α-hemihydrate				
Steam LP (tons)	Hot water (90°C) m^3	Electric power (KWh)	Process water (m^3)	Extent of conversion (%)
0.4-0.6	0.5	25+ (10 for drying)	2	70

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Hydrothermal conversion and construction industry

Imperial Chemical Industries, Inc. (ICI) α-hemihydrate process (semi-industrial process):

- Operating temperature - 150°C;
- 50 %(m/m) solids;
- Residence time – 3 minutes;
- 2 autoclaves;
- Crystal modifiers;
- Centrifuge for crystals separation at 100°C

Material and process requirements per ton of α-hemihydrate

PG (tons)	HP Steam (tons)	Electric power (KWh)	Water (tons)	Effluent (tons)	Extent of conversion (%)
1.22	0.35	45	1.5	1.7	70-80

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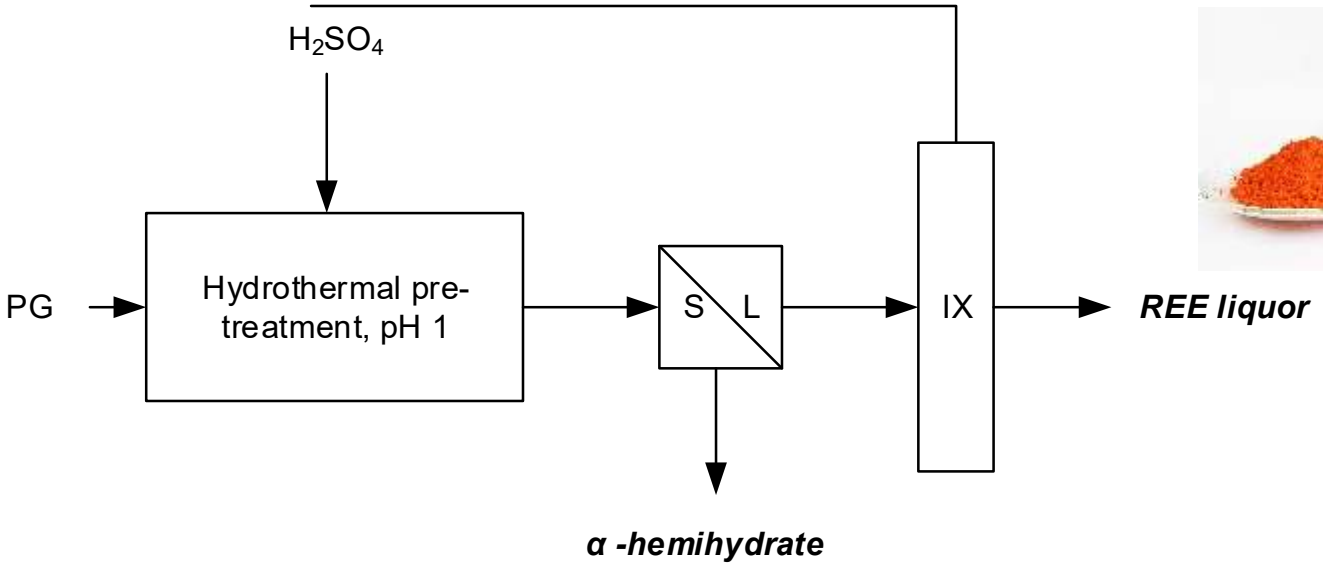
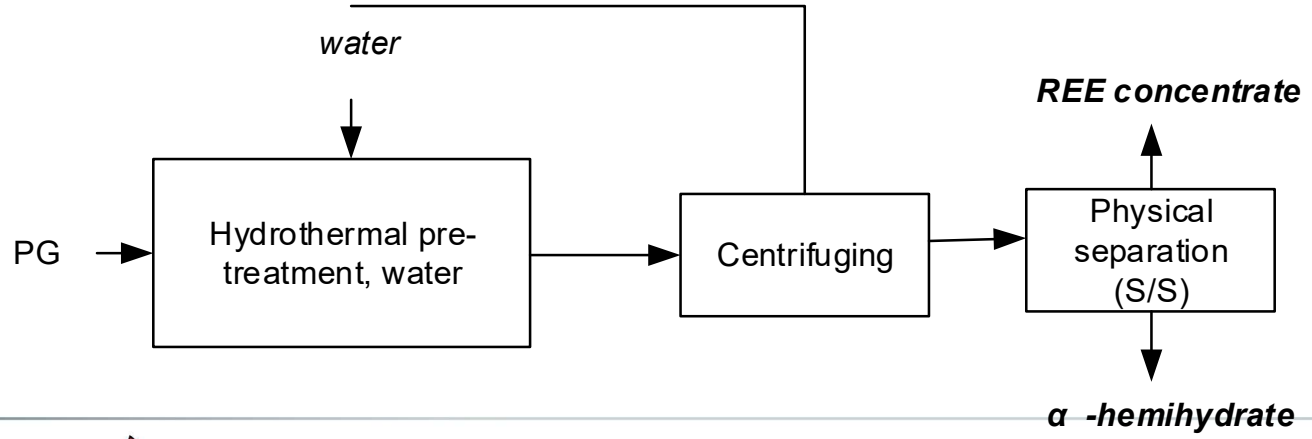
Flowsheets under consideration





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Conclusions

- During formation of phosphogypsum REE are partially locked in the gypsum structure => high REE recoveries require either complete dissolution of gypsum matrix or its recrystallization
- Hydrothermal modification process used in construction industry to produce α-hemihydrate releases up to 80% of REE associated with PG
- Further optimization testwork and evaluation of economics of the optimum flowsheet is required to confirm viability of simultaneous recovery of REE and production of high quality alpha-hemihydrate for construction industry

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Full paper to be presented…

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Part of Hydrometallurgy 2018--a symposium of the Extraction 2018 global extractive metallurgy conference

Title of paper: Hydrothermal modification of phosphogypsum to improve subsequent recovery of rare earth elements

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