Phosphogypsum as the main waste of P-fertilizers industry: environmental challenges and valorization opportunities

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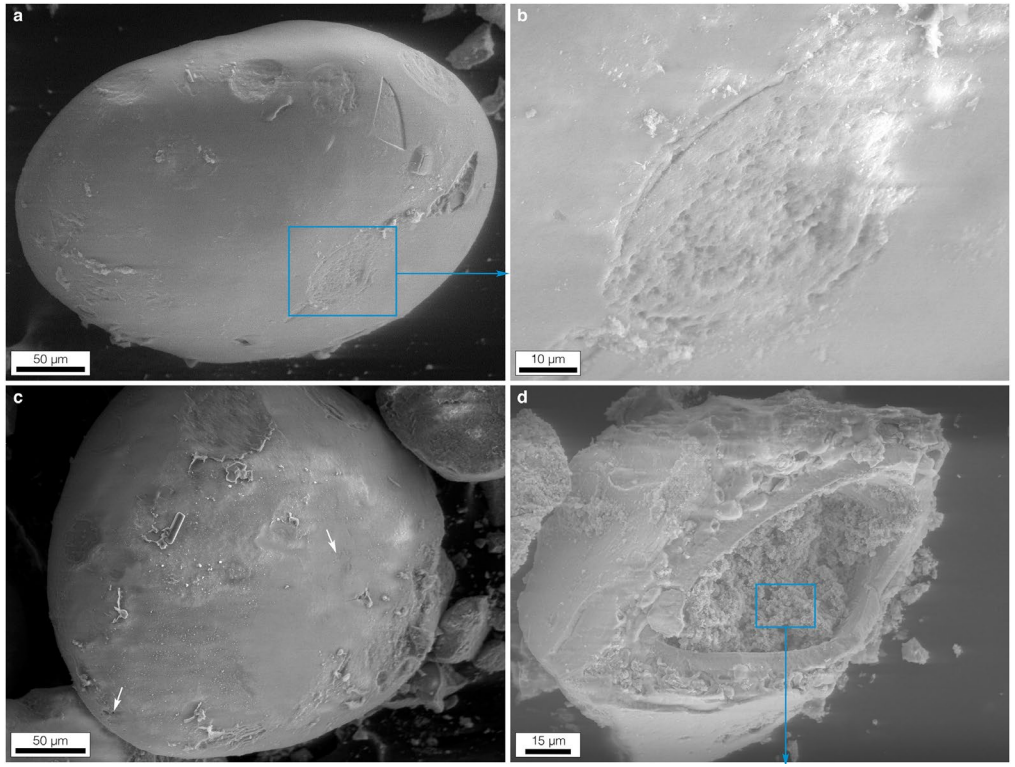
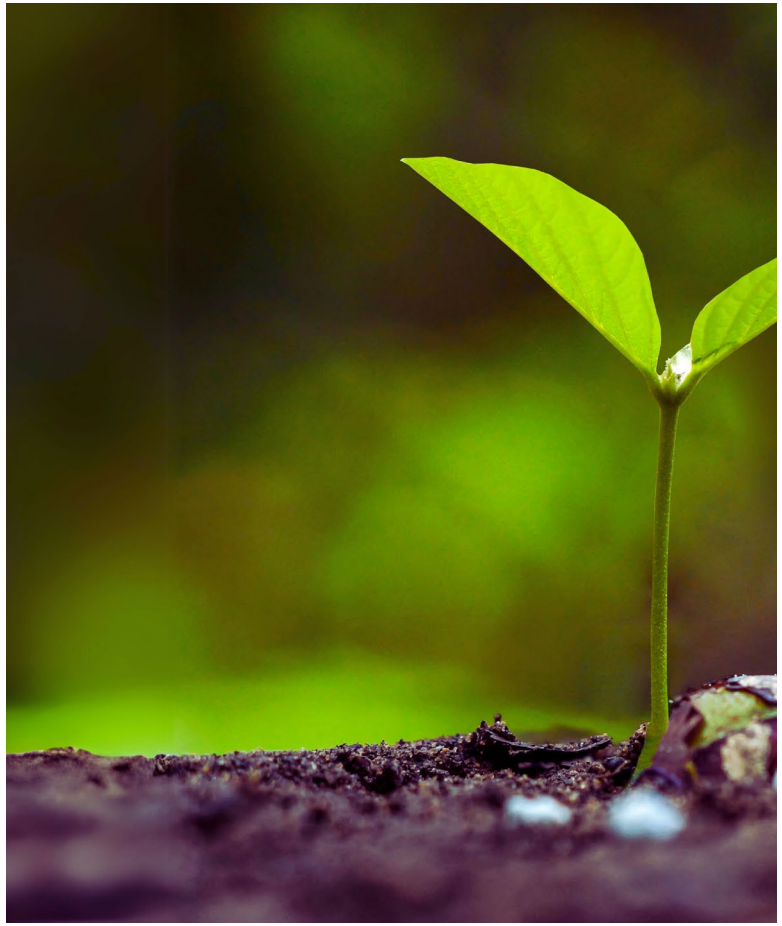
In collaboration with: **Fatima Akfas**

MIT Global Summit on Mine Tailings Innovation

1. Phosphate value chain and PG generation



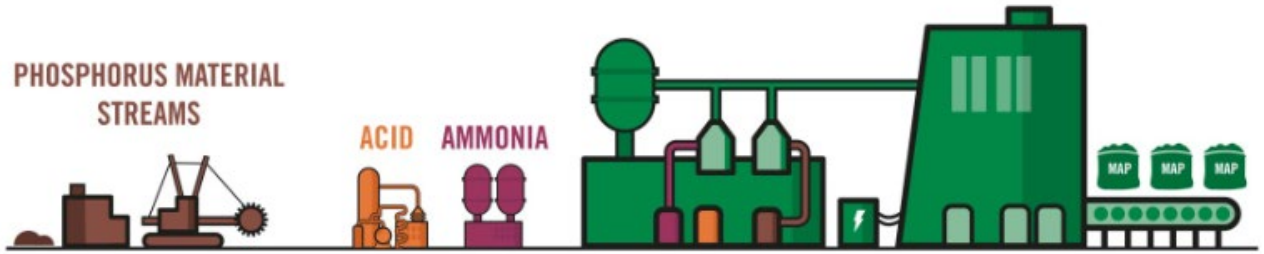


✓ It is about food security.
✓ Very stable mineral (apatite).

✓ Soluble fertilizers (NPK or others).

1. Phosphate value chain and PG generation

The wet process to produce phosphoric acid



The Mining Industry

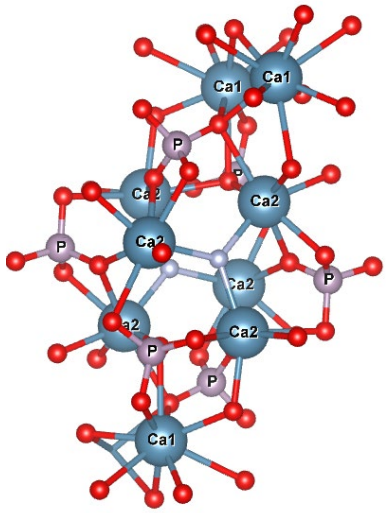
The Fertilizer Industry

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \xrightarrow{70\text{-}80°C} 3H_3PO_4 + HF + 5(CaSO_4.2H_2O)$$

1. Grinding and conditioning of the phosphate rock
2. Dissolution of the phosphate rock with H_2SO_4 (60 wt.%)
3. Filtration
4. Washing of PG by water

Phosphate ore

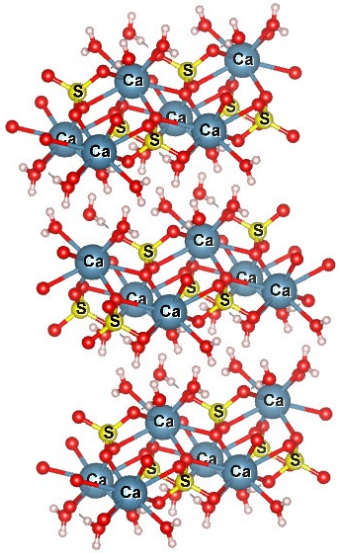
Subject to wide compositional variation and many substitutions in the crystal structure.



Dissolution – precipitation reaction

H_2SO_4 at 70-80°C

O **P** **S** **Ca**

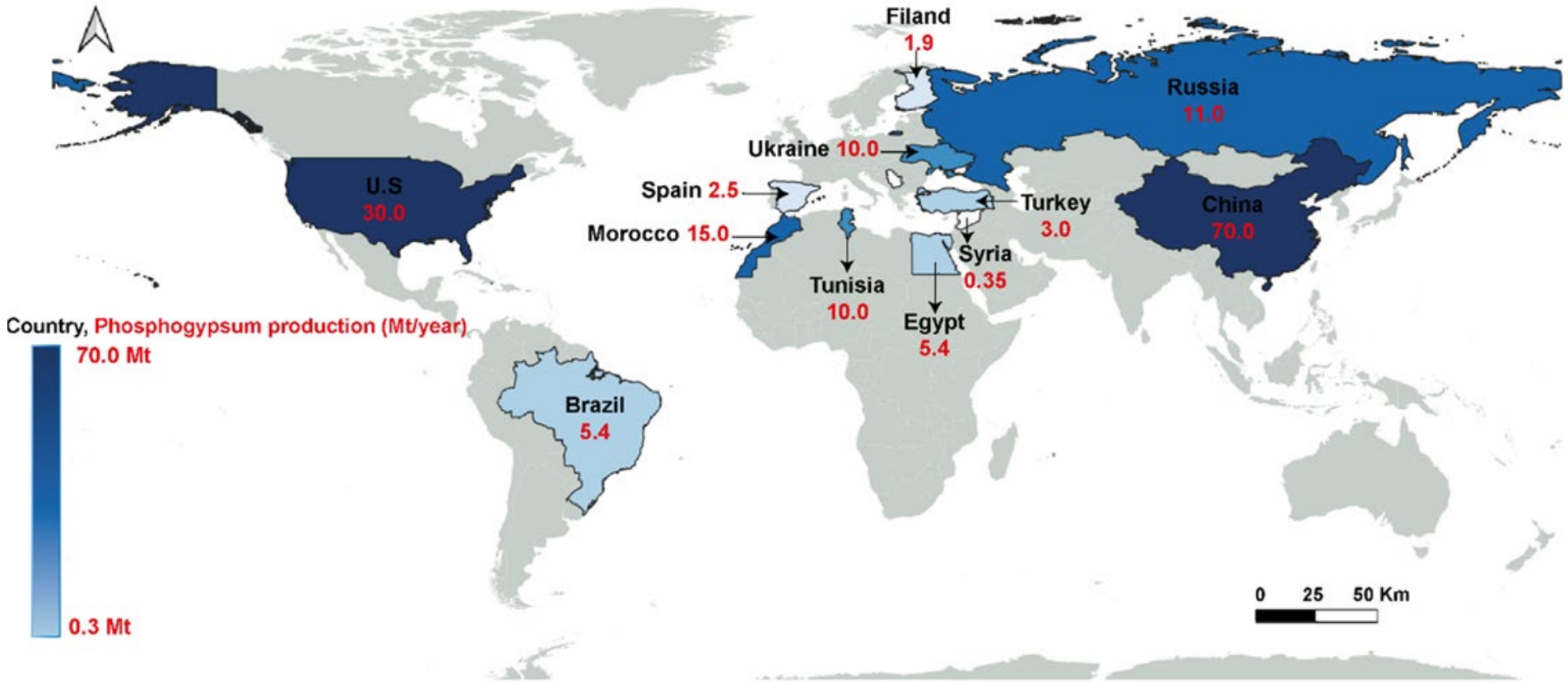


- The **major elemental composition** of PG **varies depending** on the type of **wet phosphoric acid process** used.
- The **minor element** composition may vary greatly following **the source of the phosphate rock.**
- **These elements** undergo processes like **precipitation into a mineral phase**, **co-precipitation**, **entrapment in pores, adsorption, absorption onto organic or inorganic surfaces**.

(Akfas et al., 2024), (Akfas et al., 2023), (El Zrelli et al., 2019), (Rutherford et al., 1994)

2. Environmental challenges of PG management

Environmental issues related to phosphogypsum storage



- ✓ Huge environmental footprint
- ✓ +11 billion t of PG to be generated by 2050
- ✓ World most significant waste

(Caruso et al., 2016), (Maest et al., 2005), (Gaudry et al., 2006), (Tayibi et al., 2009)

2. Environmental challenges of PG management

PG management strategies

Dumped in Seawater

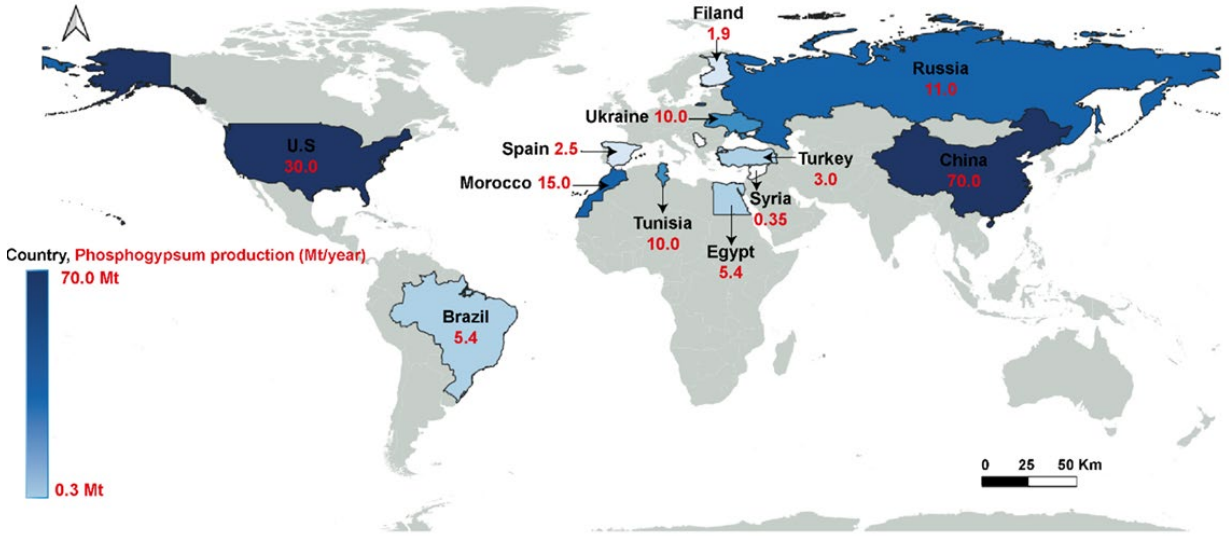
Restricting through global environmental policies: the UN Sustainable Development Goals, the Paris Agreement on Climate Action, the International Maritime Organization's London Convention, and the broader dedication to advance a green circular economy.

Surface storage

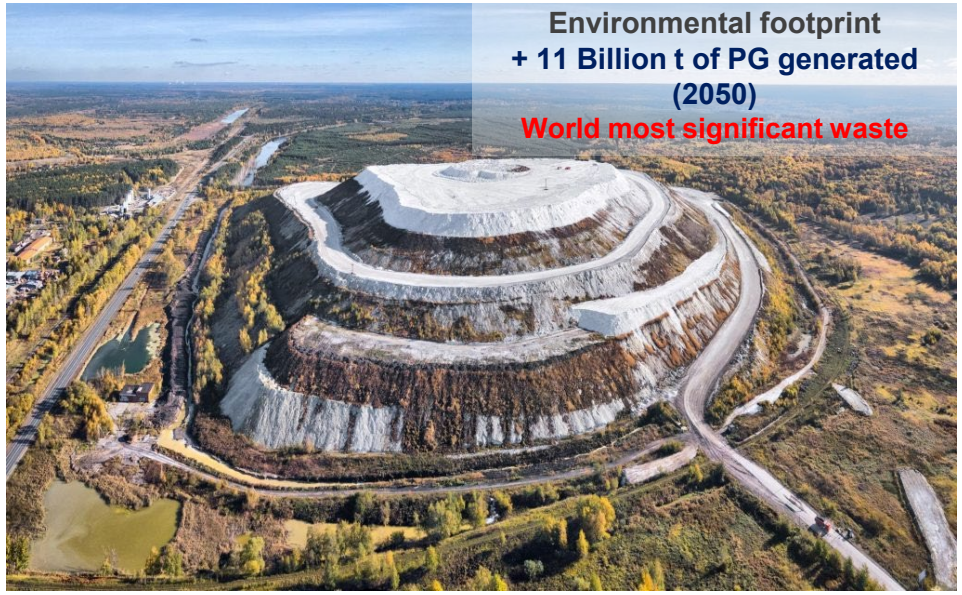
(Akfas et al., 2024), (Cánovas et al., 2018), (El Zrelli et al., 2018) ,(Guerrero et al., 2021), (Santos et al., 2006)

2. Environmental challenges of PG management

Environmental issues related to phosphogypsum storage



Repartition map of the annual volume of phosphogypsum generated around the world.



A substantial amount of storage space needed for an extended period

The residual acidity

The presence of various trace elements

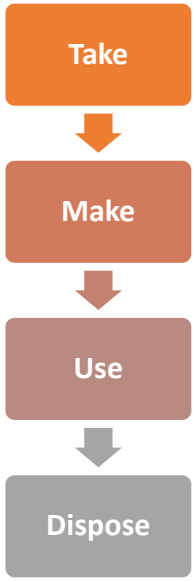
The presence of radioactive elements

(Caruso et al., 2016), (Maest et al., 2005), (Gaudry et al., 2006), (Tayibi et al., 2009)

2. Environmental challenges of PG management

Phosphogypsum management strategy

Least favored option



Linear economy

Most favored option

Circular economy

The Triple Bottom Line (TBL) framework assesses the success of a business by balancing **financial, social, and environmental performance.**

Consideration for selecting the right valorization strategy

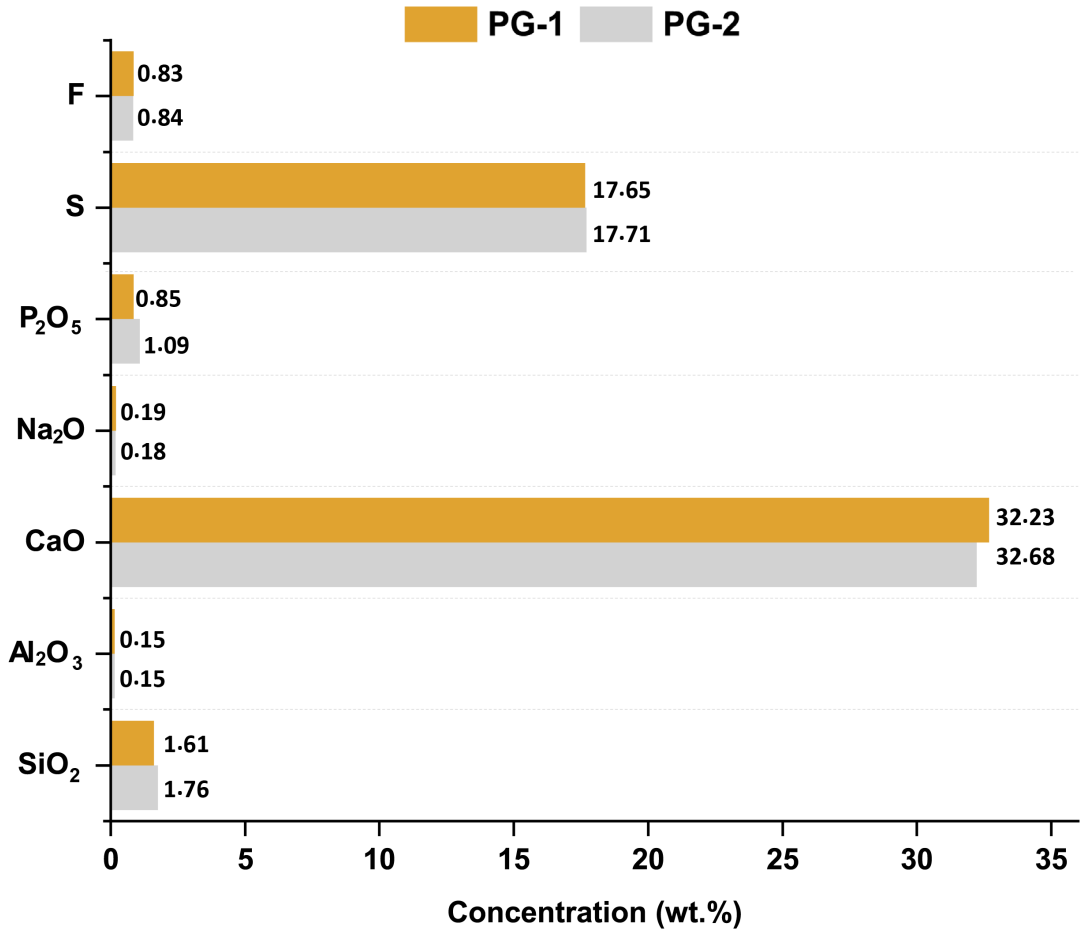
- ❑ **The economic viability and scalability of the valorization strategy;**
- ❑ **The large-scale consumption of phosphogypsum;**
- ❑ **The environmental impact associated with the developed process;**
- ❑ **The radioactive composition of the phosphogypsum;**

  - ➢ **Atomic Energy Regulatory Board (AERB),**
  - ➢ **State Pollution Control Board (SPCBs),**
  - ➢ **The International Fertilizer Association (IFA),**
  - ➢ **IAEA Safety Standards,**

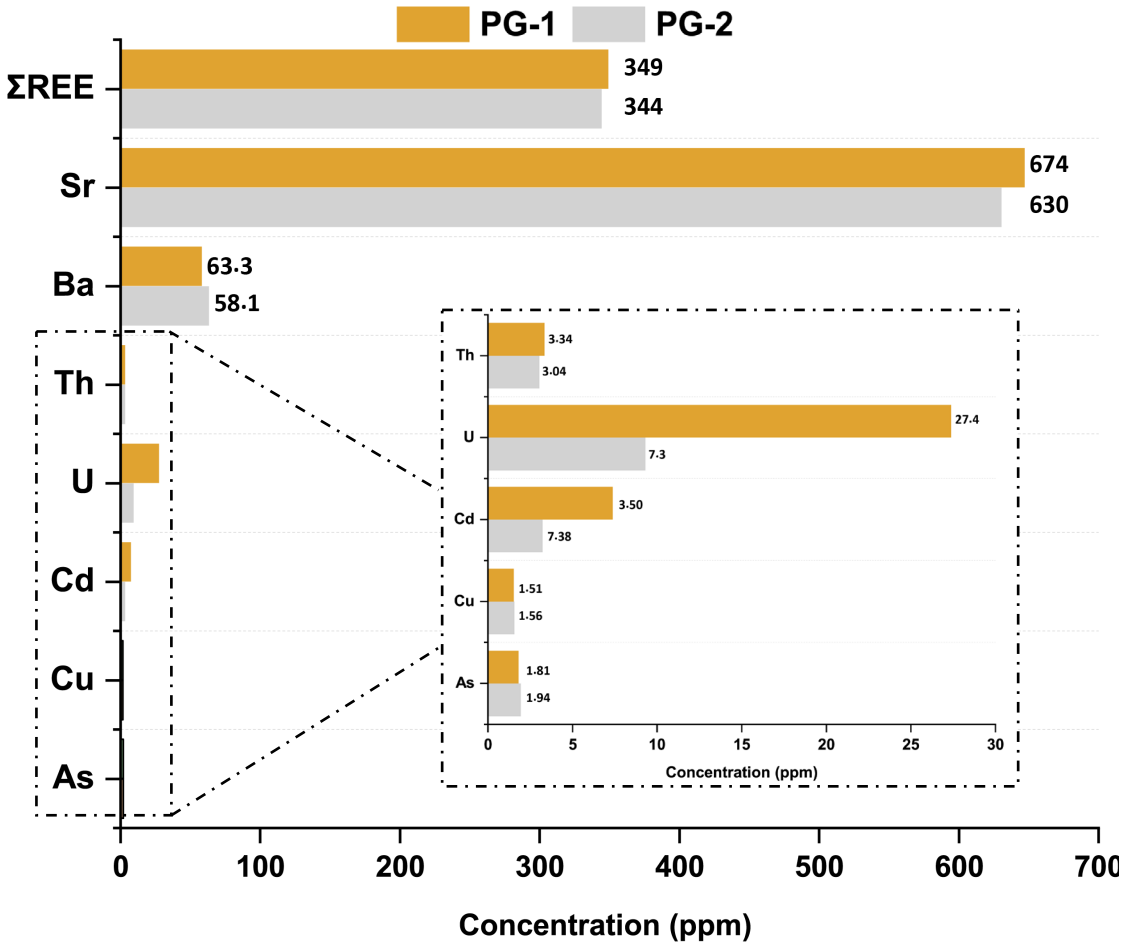
(Akfas et al., 2024), (Burton, 1987), (Contreras et al., 2015), (Lachehab et al., 2020)

3. Integral characterization of phosphogypsum

Chemical composition of phosphogypsum



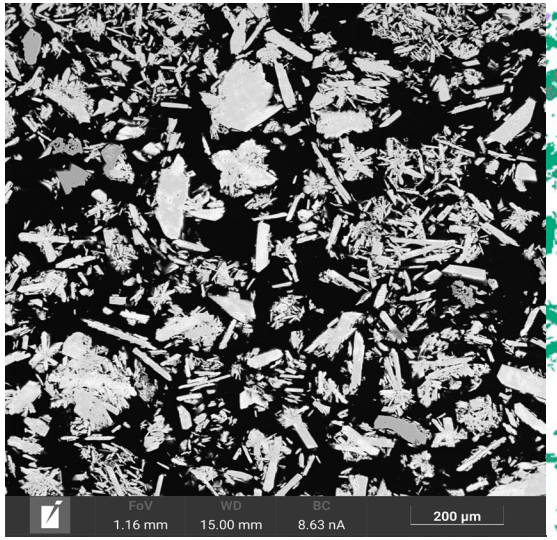
Major elements

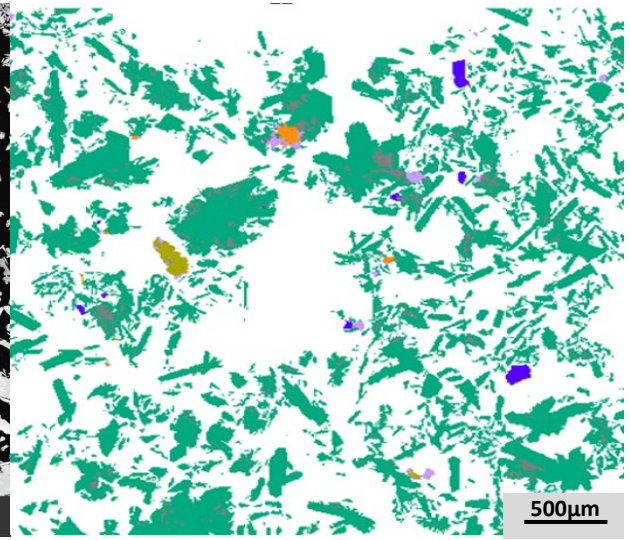


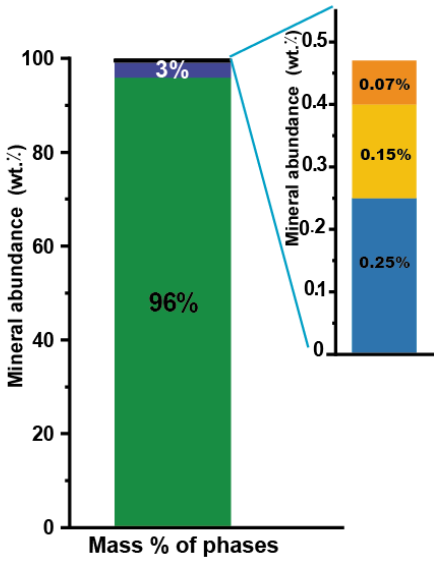
Minor and trace elements

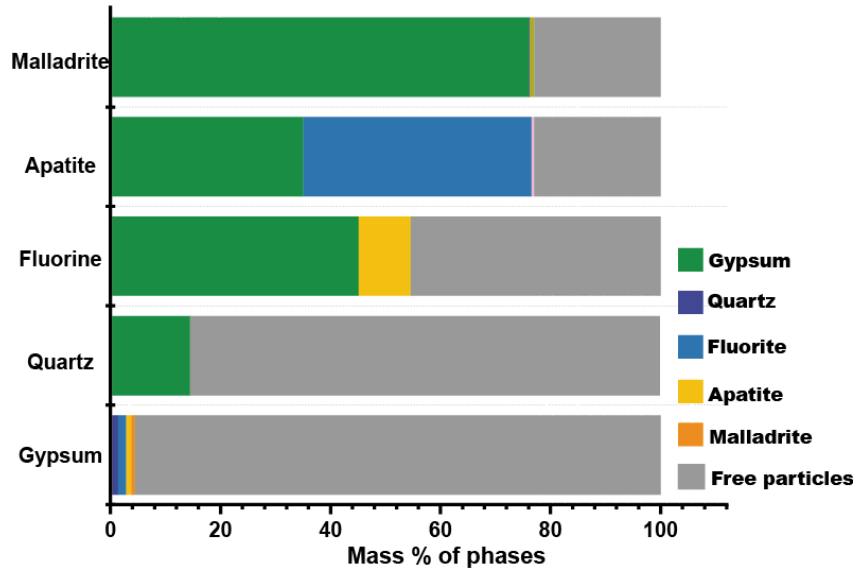
3. Integral characterization of phosphogypsum

Mineralogy of phosphogypsum

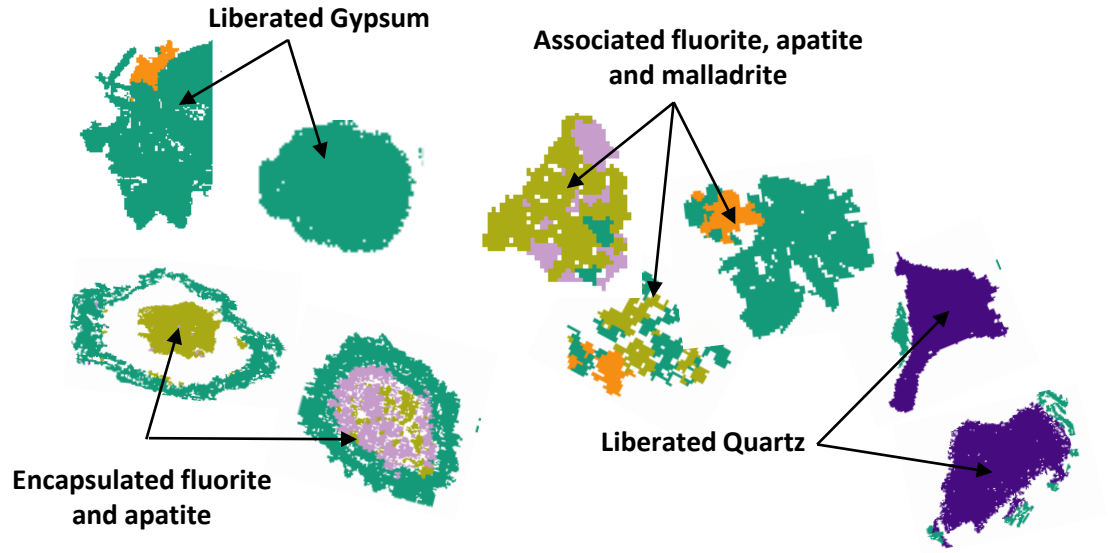






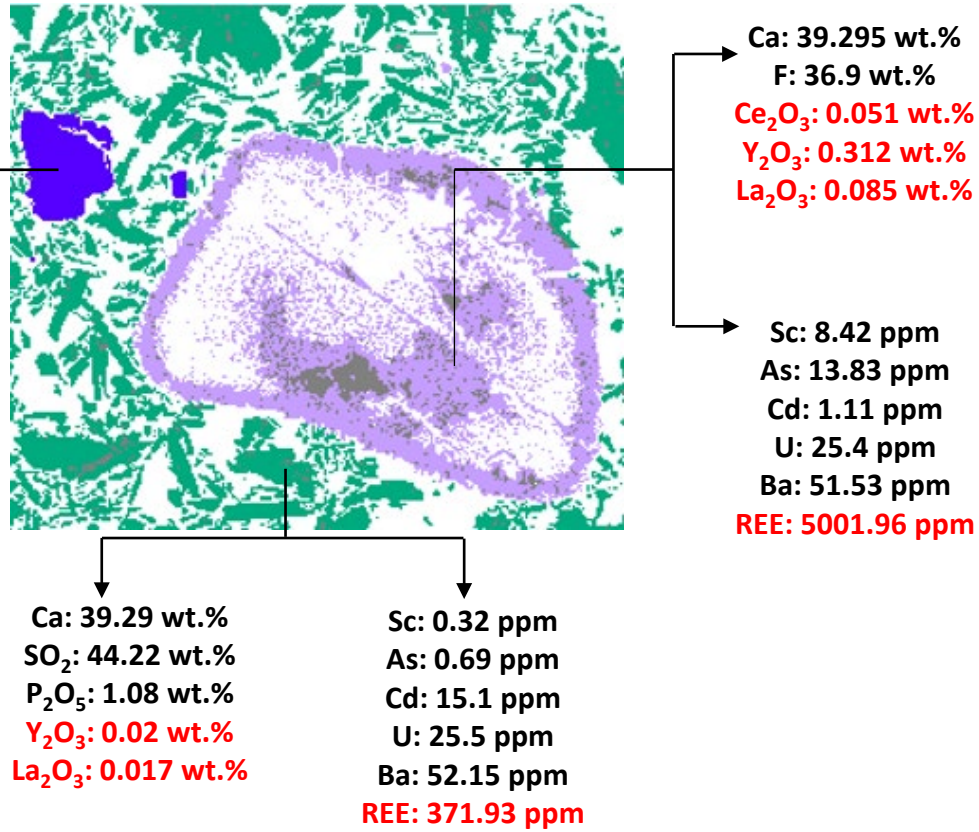


Do we need mineral processing ?



3. Integral characterization of phosphogypsum

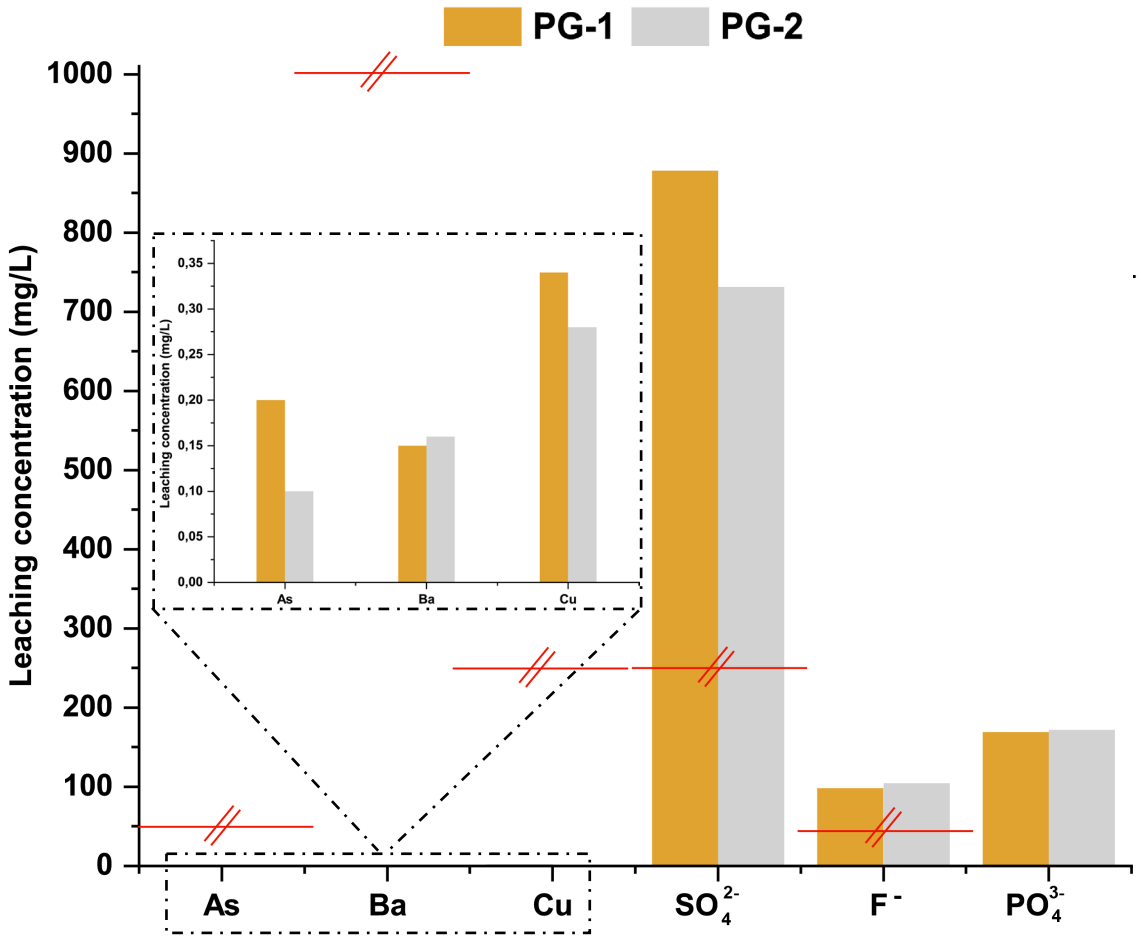
Microanalysis characterization: EPMA and LA-ICPMS



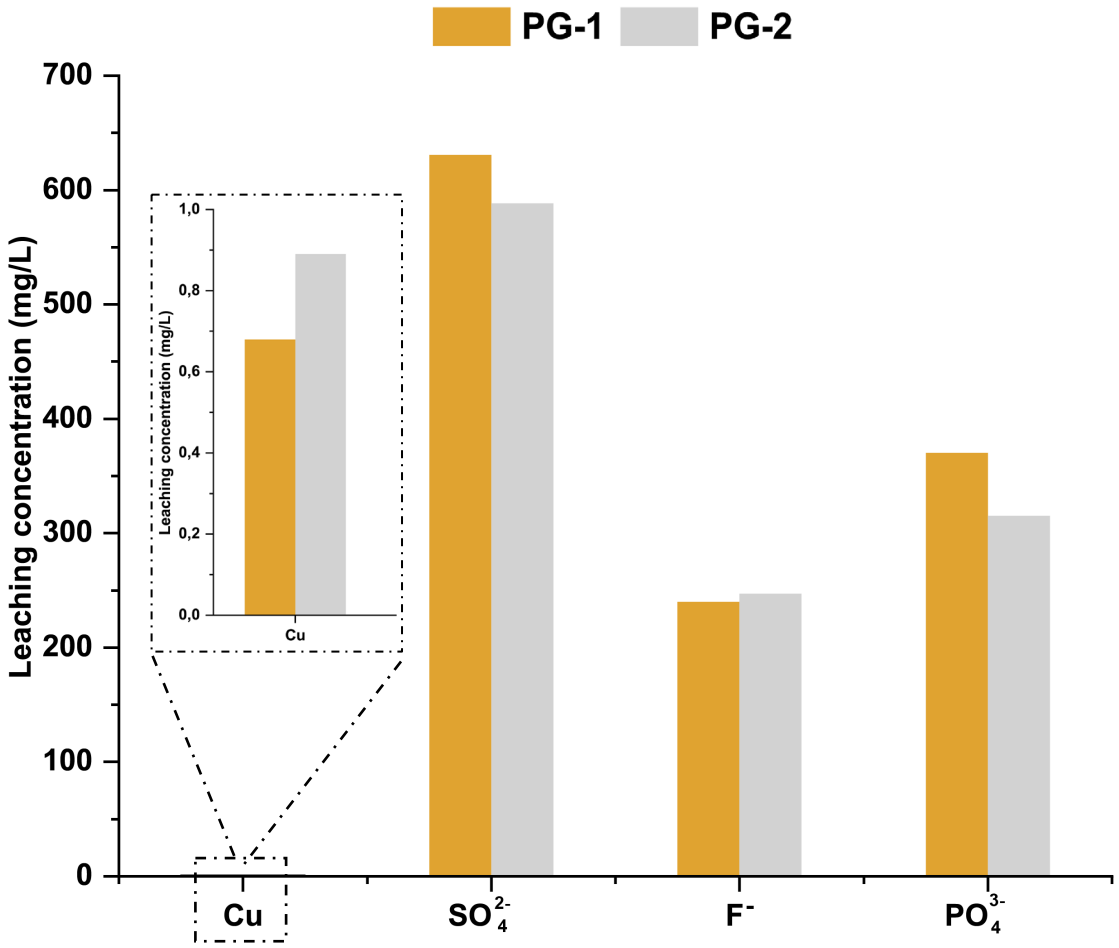
EPMA: Electron probe microanalyzer

3. Integral characterization of phosphogypsum

Toxicity Characteristic Leaching Procedure (TCLP) and the Synthetic Precipitation Leaching Procedure (SPLP)



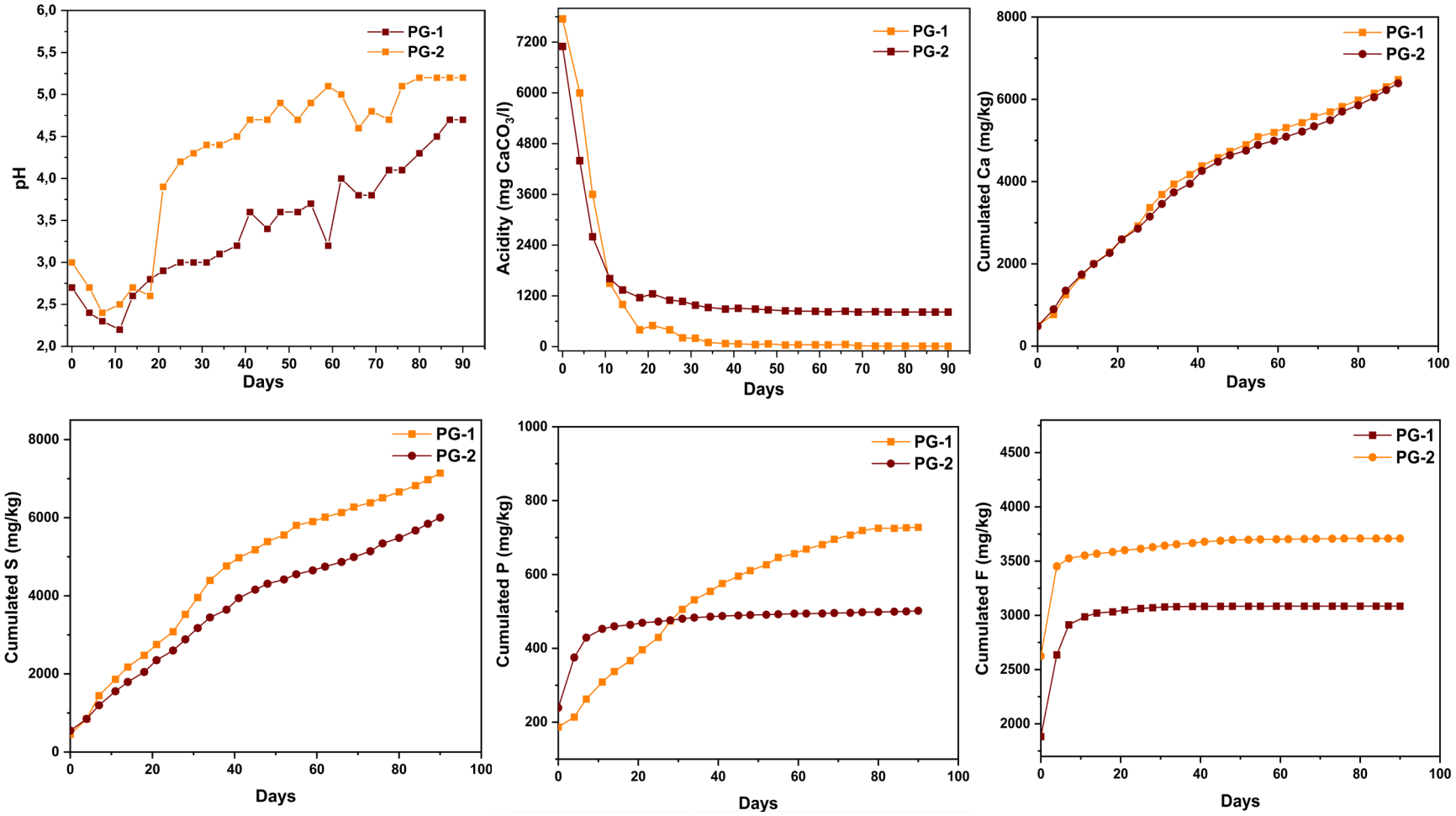
TCLP results test.



SPLP results test.

3. Integral characterization of phosphogypsum

Kinetic leaching test: Weathering cells

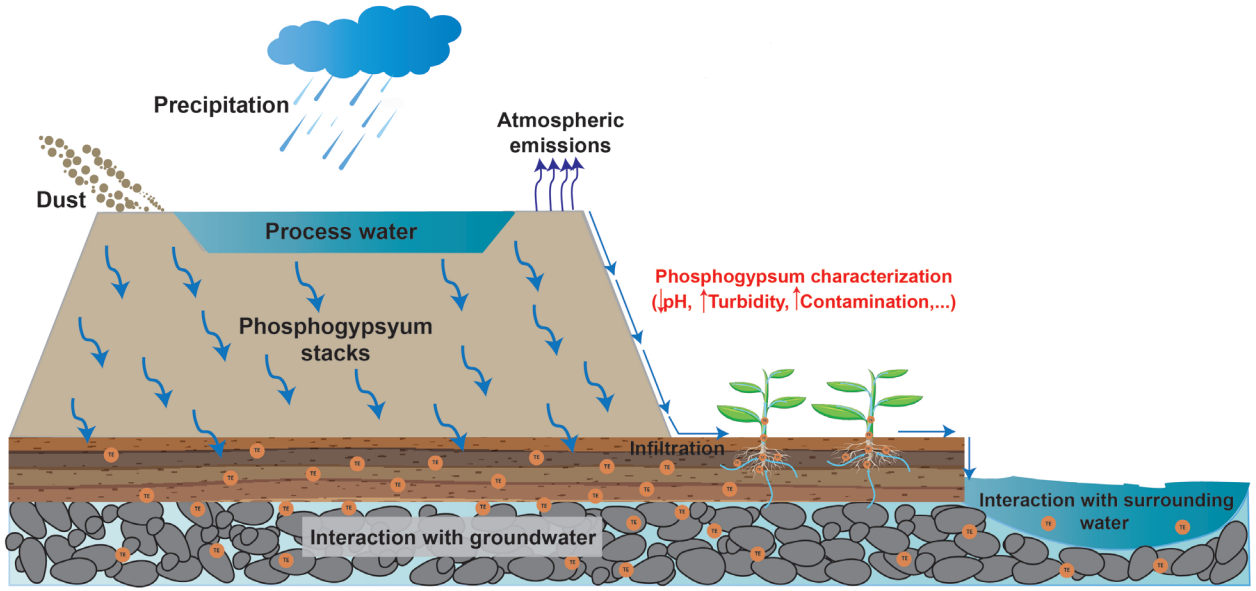


Evolution of pH, conductivity, and cumulative concentration of Ca, S, F, and P of the phosphogypsum samples using weathering cells.

- ✓ **High acidity** of the phosphogypsum samples in the first leaching days caused by **the presence of intrinsic residual acid.**
- ✓ A **significant cumulative concentration** of **sulfate, phosphate and fluorite** over time was observed.

3. Integral characterization of phosphogypsum

Geochemical modeling using PHREEQC



- ✓ **A non-hazardous** material regarding trace chemical species**.**
- ✓ **High residual acidity.**

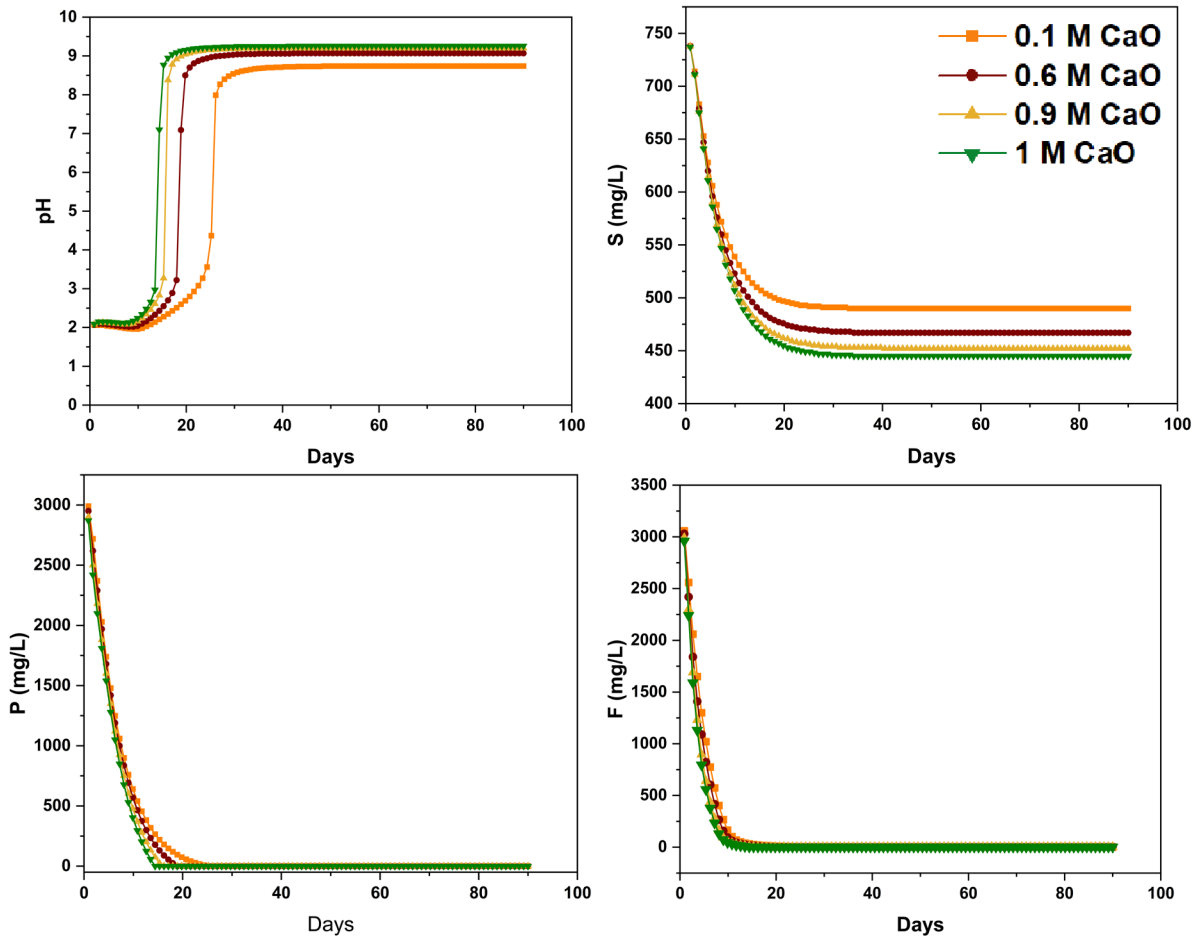
Phosphogypsum must undergo treatment before being stored on the surface.

- ❑ **$Ca(OH)_2$-DAS or MgO-DAS**
- ❑ **Alkaline chemicals reagent**
- ❑ **Multi-stage precipitation**
- ❑ **Acid leaching**

DAS: Dispersed alkaline substrate technology

3. Integral characterization of phosphogypsum

Conceptual geochemical model



Simulation of various scenarios underlining the effect of different concentrations of CaO on leachate quality

✓ **This simple treatment** method demonstrated **encouraging outcomes** to **mitigate and minimize the environmental impact of PG on the surrounding areas.**

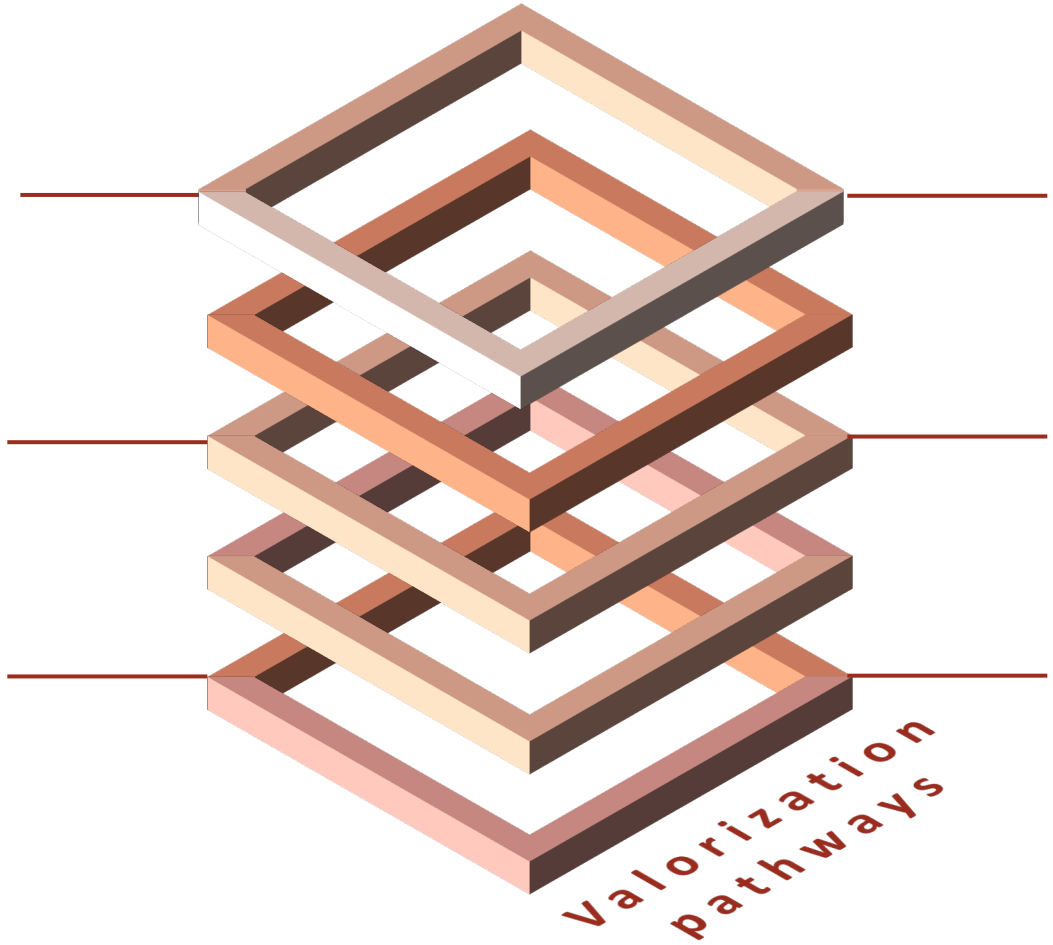
4. Phosphogypsum conversion and trace elements monitoring

To address this issue, the **International Fertilizer Association (IFA**) proposes two approaches for **100%** legacy waste elimination for PG: **Utilization and Prevention.**

Agriculture Valorization
Several advantages limiting by the presence of hazardous impurities and acidity of phosphogypsum.

REE extraction
Promising routes for PG as a secondary source of REE.

Chemical transformation
Promising valorization route to obtain raw materials of economic interest.



Thermal decomposition
Decomposition of phosphogypsum into its primary components, CaO and S. And for the extraction of K from K-feldspar.

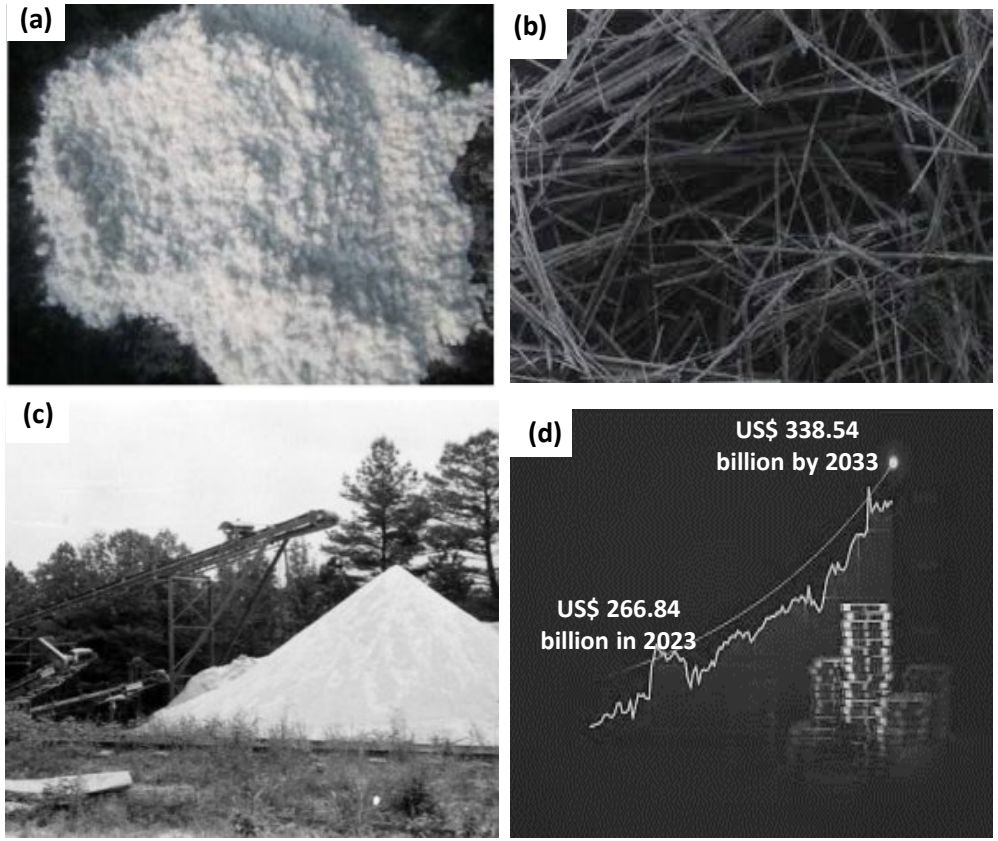
Environmental application
An inexpensive alternative for the CO_2 sequestration and metal removal from industrial wastewater.

Construction and building materials
An important valorization pathway consuming a huge quantity of PG.

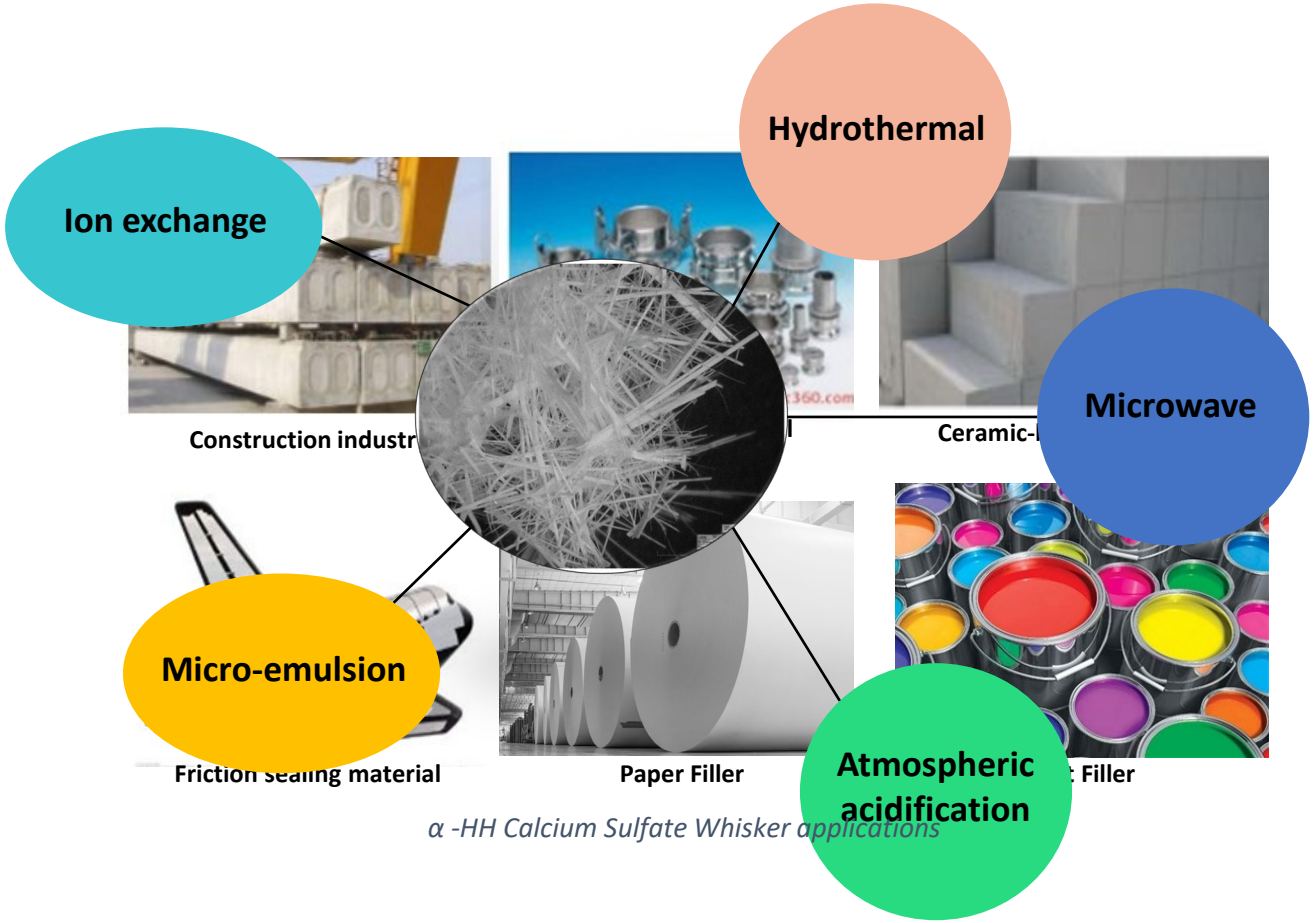
(Akfas et al., 2024), (Luz et al., 2009), (Singh and Garg, 2005), (IFA Report 2020)

4. Phosphogypsum conversion and trace elements monitoring

What is α-hemihydrate calcium sulfate whisker?



(a) Microstructure of CSW (b) CSW products (c) Gypsum mining (c) Market prices .

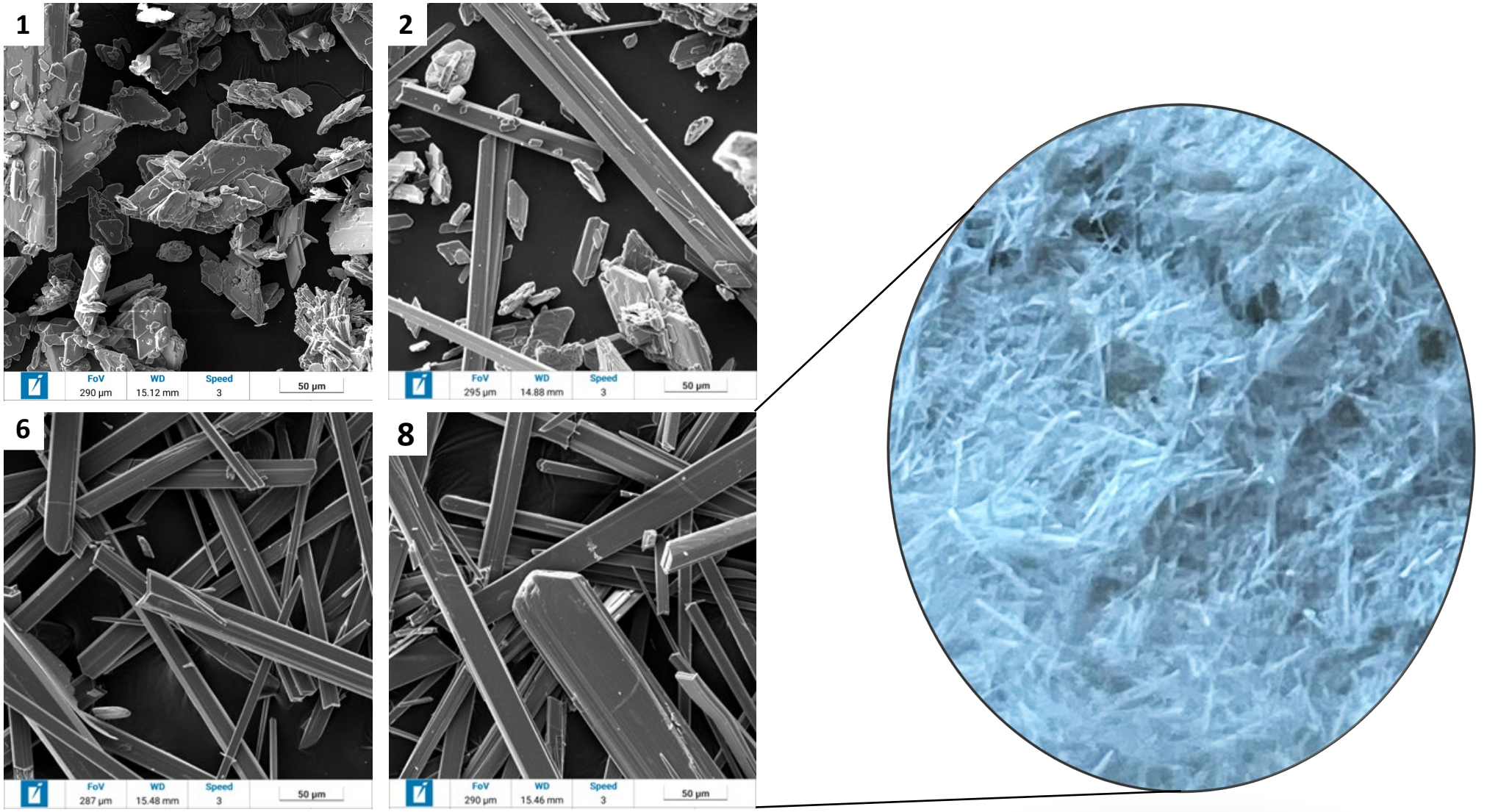


α -HH Calcium Sulfate Whisker applications

α -HH Calcium Sulfate Whisker synthesis methods

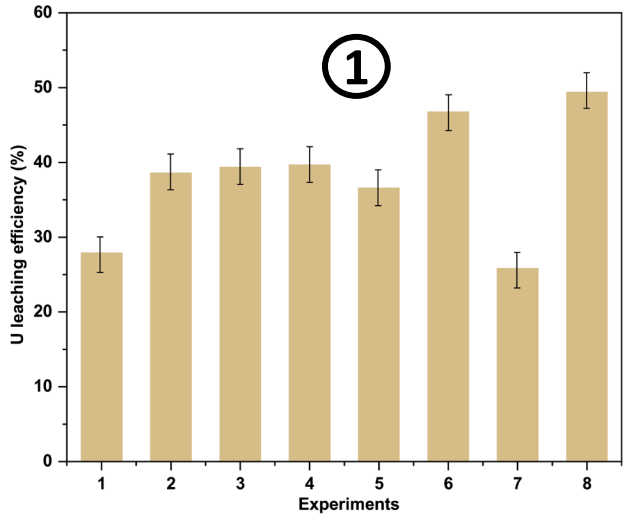
4. Phosphogypsum conversion and trace elements monitoring

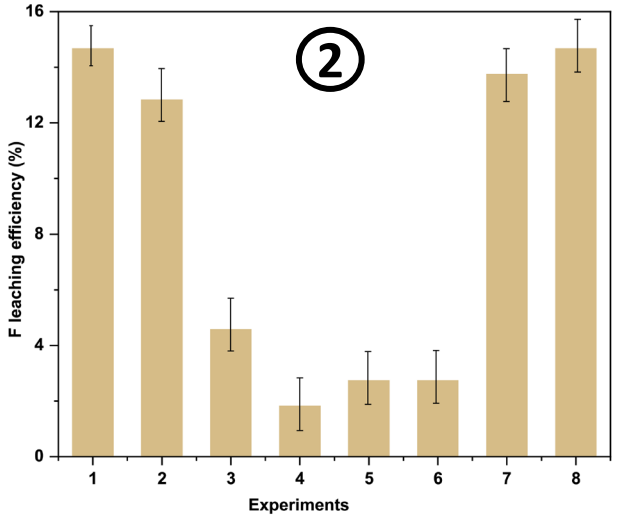
Properties of the prepared α-HH whiskers

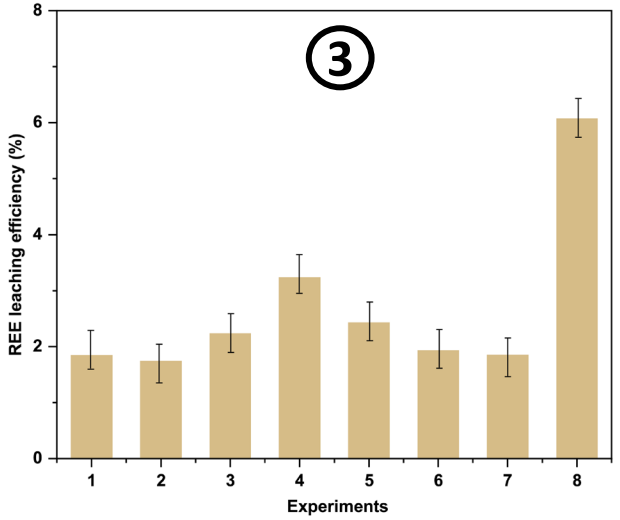


4. Phosphogypsum conversion to α-hemihydrate whiskers

The release of incorporated elements during the dissolution recrystallization process







① Notable leaching efficiency was observed for U. The leaching efficiency of U reached 50%.

② F leaching efficiency around 16%.

③ REE leaching efficiency remained below 6%.

4. Phosphogypsum conversion to α-hemihydrate whiskers

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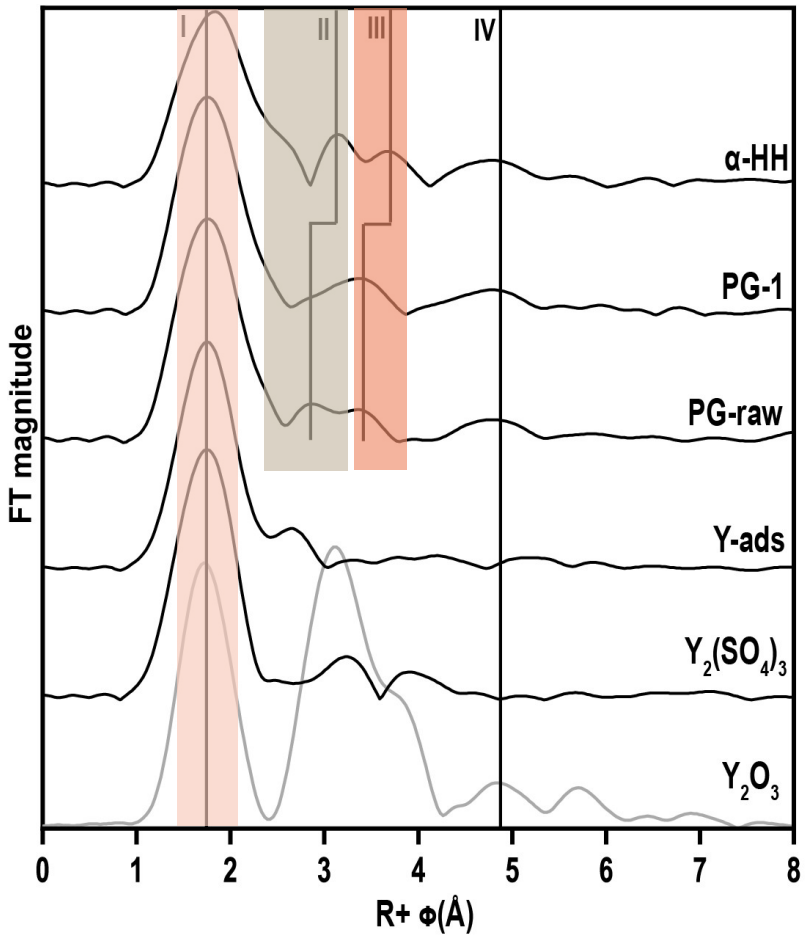
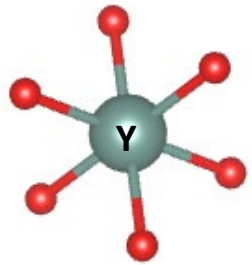


Fourier transform at the Y K-edge for Y_2O_3, $Y_2(SO_4)_3$ and Y-ads model compounds, and PG, PG-1 and α-HH samples.

- **Since Y** is **expected to crystallize** within the PG structure with a **+3 charge,** maintaining **structural electroneutrality** requires **coupled substitution mechanisms.**

1. **The presence of a monovalent cation: $Y^{3+} + Na^{+} = 2Ca^{2+}$**
2. **The presence of a vacancy site: $2Y^{3+} + \square$ vacancy $= 3Ca^{2+}$**
3. **The calibration of the structure by the presence of another anion: $Y^{3+} + O^{2-} = Ca^{2+} + F^{-}$**



Y_2O_3

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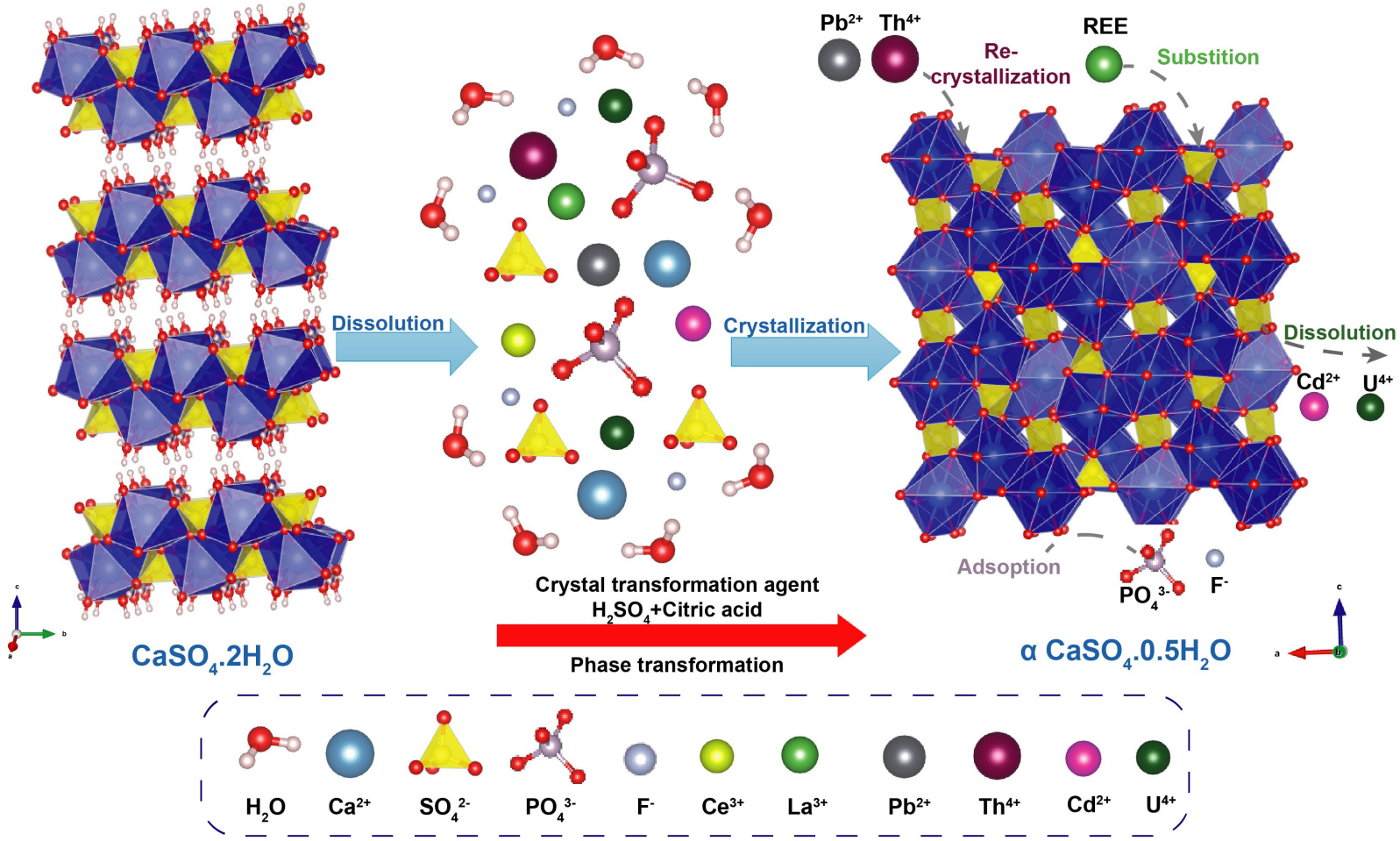
The release of incorporated elements during the dissolution recrystallization process



The conceptual model of the dissolution-crystallization of α-HH and the release of incorporated elements in phosphogypsum.

5. Concluding remarks

- ✓ In few years, PG may be the largest ‘orebody’ of REE (*low grade/high tonnage ore?*),
- ✓ Phosphogypsum re-use/elimination requires the implementation of an ecosystem of several valorization pathways; there is no unique magical solution,
- ✓ More efforts are needed in terms of regulations regarding PG reuse (TENORM),
- ✓ Management and/or valorization scenarios of PG must be adapted to its characteristics (data availability vs. data uncertainty),
- ✓ Disposal taxes ?

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Thank you for your attention

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