ENHANCED REE EXTRACTION FROM PHOSPHOGYPSUM USING ACIDIC WASTE MATERIALS

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http://www.uhu.es/rensma/en/introduction-mga/

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RawMaterials
Connecting matters

REE recovery from Phosphogypsum wastes

Obtention of H_3PO_4 for fertilizer manufacturing

(Phosphorite)		(Sulfuric Acid)				(Phosphoric acid)		(Gypsum)		
$Ca_5(PO_4)_3F$	+	$5H_2SO_4$	+	$10H_2O$	$\rightarrow$	$3H_3PO_4$	+	$5CaSO_4 \cdot 2H_2O$	+	HF

<u>Some important figures:</u>

Around 5 tonnes of PG are generated per tonne of phosphorus pentoxide (P_2O_5)

6 billions tonnes of PG generated worldwide (until 2006)

Phosphate rock production increase by 2% per year: global population.

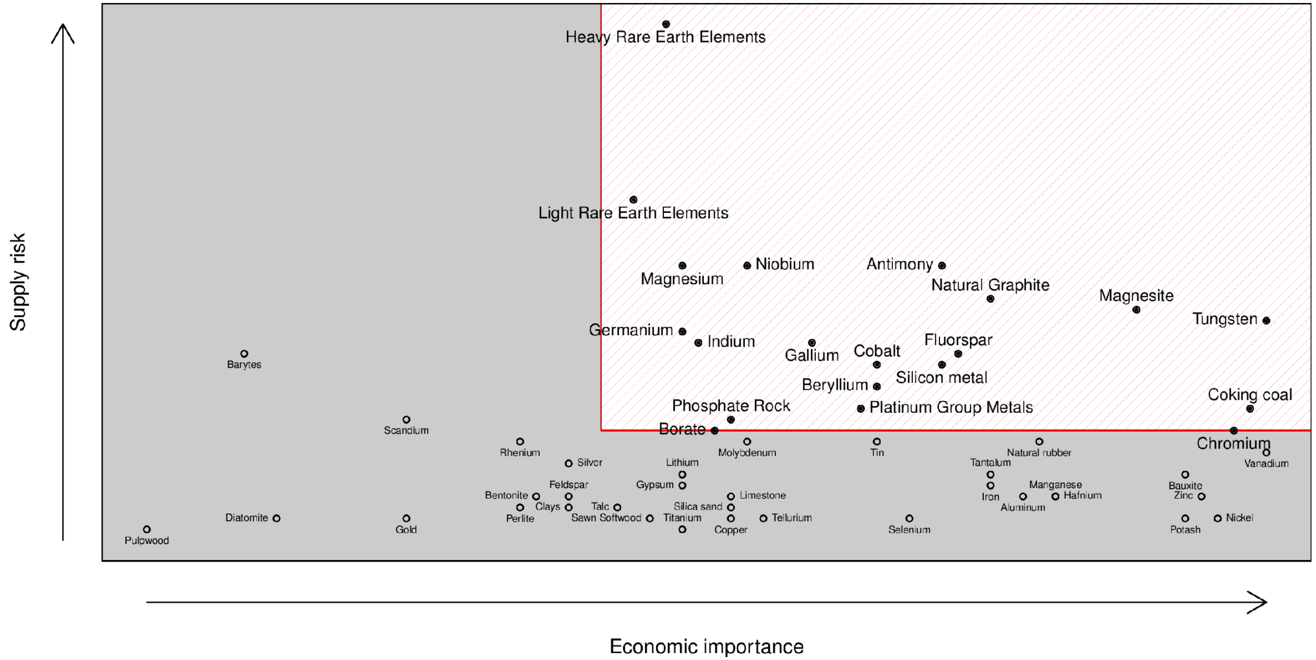
The production of PG is expected to increase in the near future!!

REE recovery from Phosphogypsum wastes

PG as source of elements of economic interest

The availability of raw materials in Europe is increasingly under pressure.

Strong dependence of supply: <u>China produce 85% of REE worldwide</u>



Seek of alternative REE secondary resources, i.e. End-of-Life products; less attention to industrial stockpiled wastes

REE recovery from Phosphogypsum wastes

PG as source of elements of economic interest

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Exploration of fertilizer industry wastes as potential source of critical raw materials

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A B S T R A C T

This paper explores the possibility of using wastes (i.e. solid phosphogypsum (PG), process waters and edge outflows) generated by a fertilizer plant in SW Spain as a source of elements of economic interest, estimating the available metal reserves and discussing the technological and economic pros and cons of this potential source of raw materials. In general, elements of economic interest are found in these wastes below of the grades commonly reported in conventional deposits. However, the huge tonnage of wastes stockpiled constitutes a significant secondary source of elements. Around 30,400 t of B, 28,000 t of rare earth elements (REE), 1800 t of U, 1400 t of Cr, 1300 t of V and lesser amounts of other elements of economic interest (e.g. Cu, Ni, Sc and Ga) are enclosed in the solid PG while lower amounts are found in process waters (e.g. 1360 t of Zn, 760 t of V, 630 t of U and Cr, 225 t of Cu, 160 t of Ni, 190 t of REE). Considering the market metal prices, the reserves contained in the Huelva PG stack have a potential value of around 8937 million USD, which mainly correspond to PG (97% of total value). The recovery of these elements is technically feasible, although intense research in refining processes is needed in order to increase the purity of the final product. The results of this study could be of interest in other PG stacks worldwide to provide more sustainable and cost-effective management of these wastes.

Could phosphogypsum be a source of elements of economic interest?

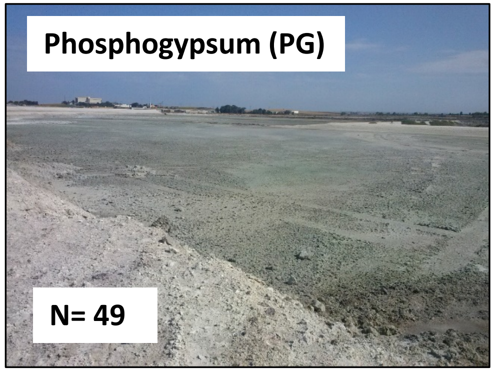
- *Determine the content of CRMs in PG*
- *Estimate their total valuation*

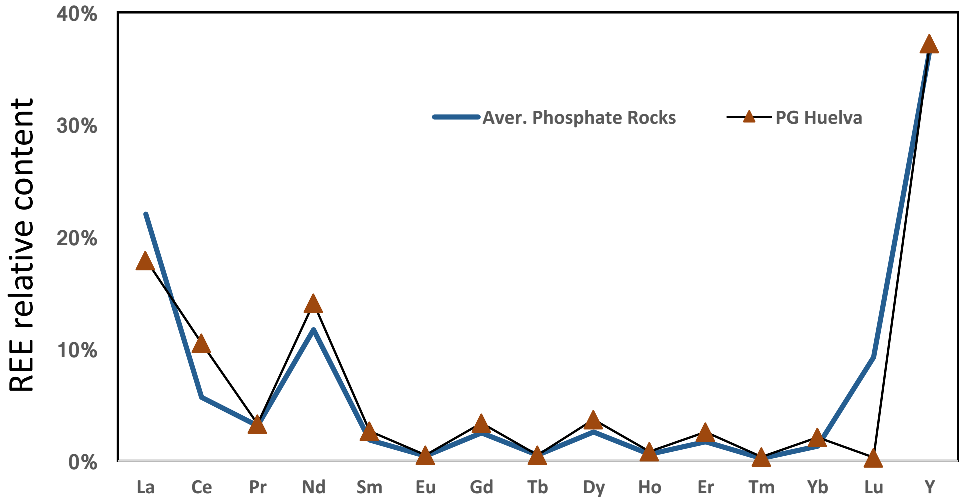
CRMs recovery from Phosphogypsum wastes

- **Are these elements in minable concentrations?**

Average content in heavy- and light-REE of 123 mg/kg and 160 mg/kg

Enriched in La (18%), Ce (11%), Nd (14%) and Y (37%)

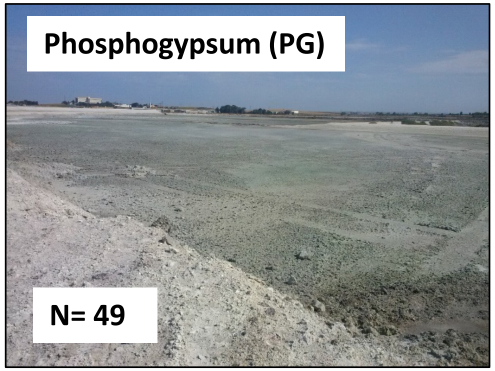




REE oxide grade of 0.034%

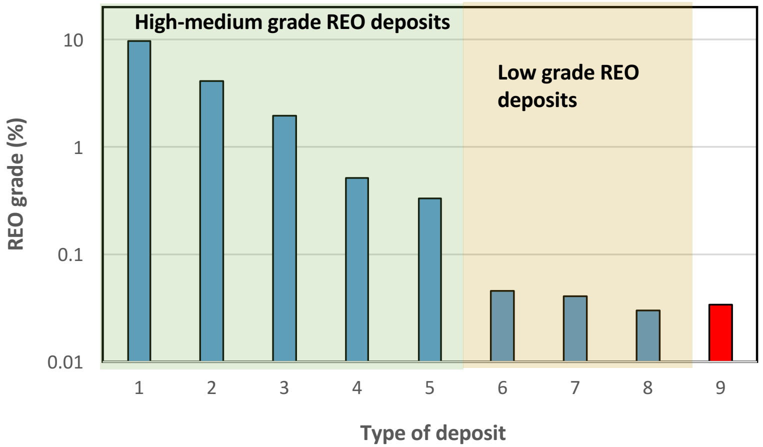
CRMs recovery from Phosphogypsum wastes

- **Are these elements in minable concentrations?**



Average content in heavy- and light-REE of 123 mg/kg and 160 mg/kg

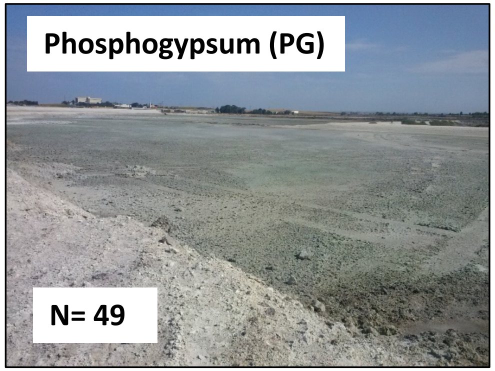
<u>REE oxide grade (REO) of 0.034%</u>



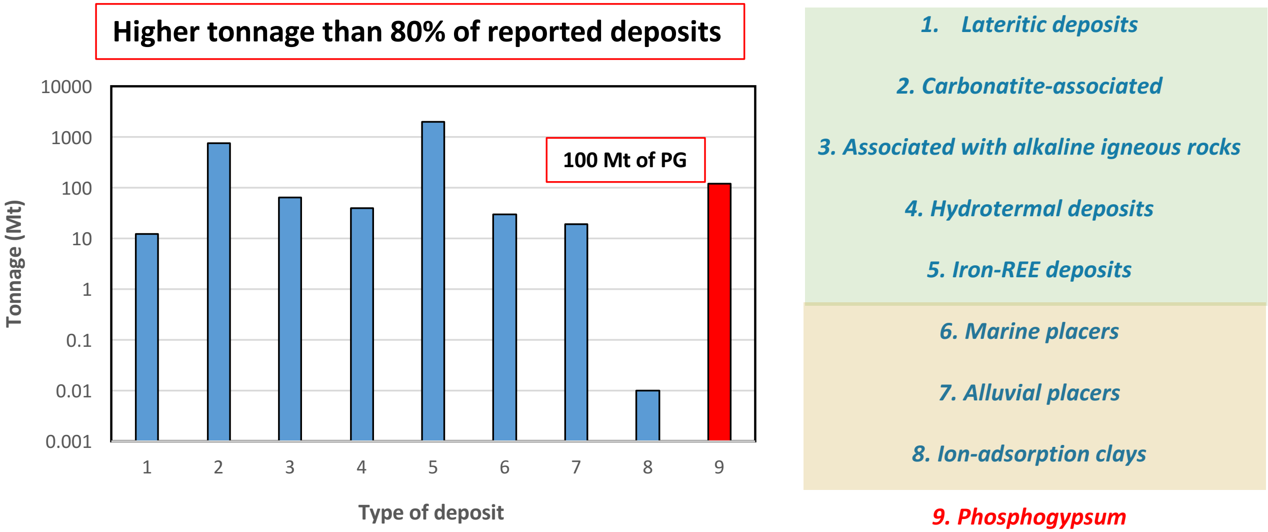
1. *Lateritic deposits*
2. *Carbonatite-associated*
3. *Associated with alkaline igneous rocks*
4. *Hydrotermal deposits*
5. *Iron-REE deposits*
6. *Marine placers*
7. *Alluvial placers*
8. *Ion-adsorption clays*
9. *Phosphogypsum*

CRMs recovery from Phosphogypsum wastes

- **Are these elements in minable concentrations?**



*<u>REE valuation in Huelva PG stack according to LME market is **1700 million USD**</u>*
(assuming 100% recovery and 99% of purity)



REE recovery from Phosphogypsum wastes

PG as source of elements of economic interest

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Leaching of rare earth elements (REEs) and impurities from phosphogypsum: A preliminary insight for further recovery of critical raw materials

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A B S T R A C T

Phosphogypsum is a pollutant waste generated by the fertilizer industry. Managing this pollutant is challenging due to the large volumes generated worldwide. A promising route is the valorization of phosphogypsum to recover rare earth elements. However, optimized recovery schemes are needed to create a cost-effective and environmentally friendly process. This paper studies the extraction efficiency of rare earth elements from phosphogypsum and the release of impurities during leaching in a variety of solutions and different working conditions. The best leaching performance was obtained using a 3 M nitric acid (above 80%) solution that achieved a dissolution rate of 63% of the gypsum originally present. In contrast, using 0.5 M sulfuric acid extracted between 46% and 58% of the rare earth elements contained in phosphogypsum, dissolving less than 6% of the gypsum. This higher dissolution of gypsum led to a higher release of impurities by nitric acid. Increasing reaction times from 2 h to 8 h yielded an improvement of leaching efficiency of around 8% for both leaching solutions, while also promoting an increase of 6% in the release of impurities. Adding DTPA resulted in poor leaching performance (from 13% to 22%). Pretreating phosphogypsum with water can remove a significant fraction of the impurities without scavenging rare earth elements. Mineralogical and chemical evidence suggests unreacted phosphate and fluoride are the most probable minerals hosting rare earth element minerals in phosphogypsum. The results of this study could contribute to optimizing recovery methods to extract rare earth elements from phosphogypsum worldwide, thus helping achieve the goals of the circular economy.

Could REE be efficiently leached from PG?

- *Efficiency of REE extraction*
- *Release of impurities*

CRMs recovery from Phosphogypsum wastes

Step 1: *acids at diferent Tª and C*

HNO_3, HCl, H_2SO_4

0.5, 1, 2 and 3M

20, 40, 60 and 80ºC

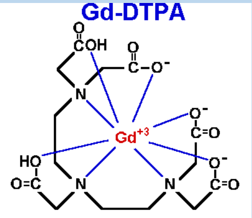
S:L ratio 1:20

Step 2: *use of chelants*

DTPA

0.05M DTPA from pH 3 to 5.

S:L ratio 1:20



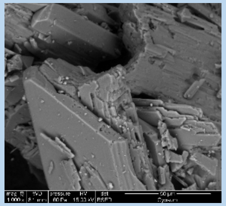
Step 3: *use of water*

H_2O

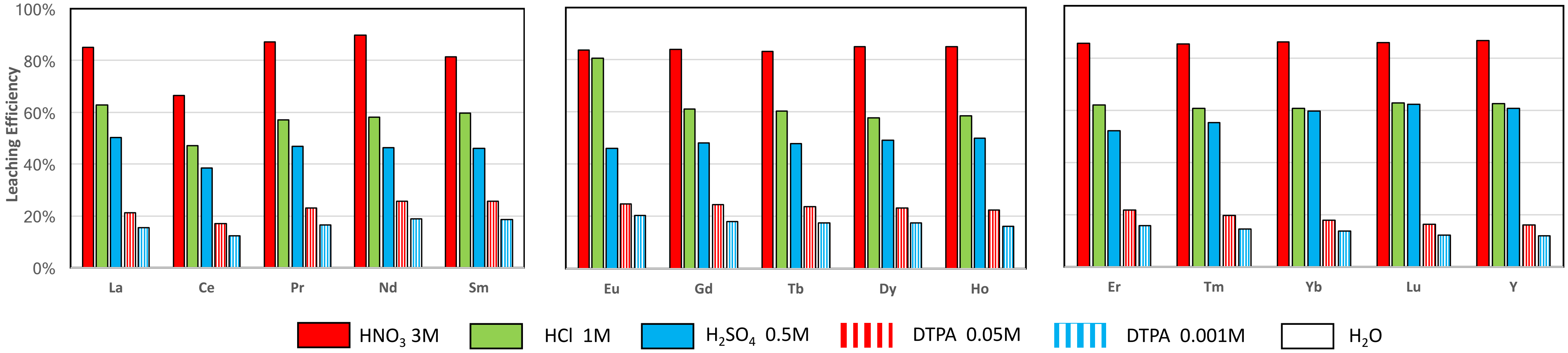
S:L ratio 1:20

Step 4: *Mineralogical study*

Raw and treated samples studied by SEM and XRD



CRMs recovery from Phosphogypsum wastes



Higher REE extraction with acids (around 80% with HNO_3 3M, 65% with HCl1M and 50% with H_2SO_4 0.5M

Lower extraction with quelants, around 20%, and no extraction with water.

The highest gypsum dissolution rate was achieved by HNO_3 (67%), followed by HCl (32%), DTPA, water (15-20%) and H_2SO_4 7%).

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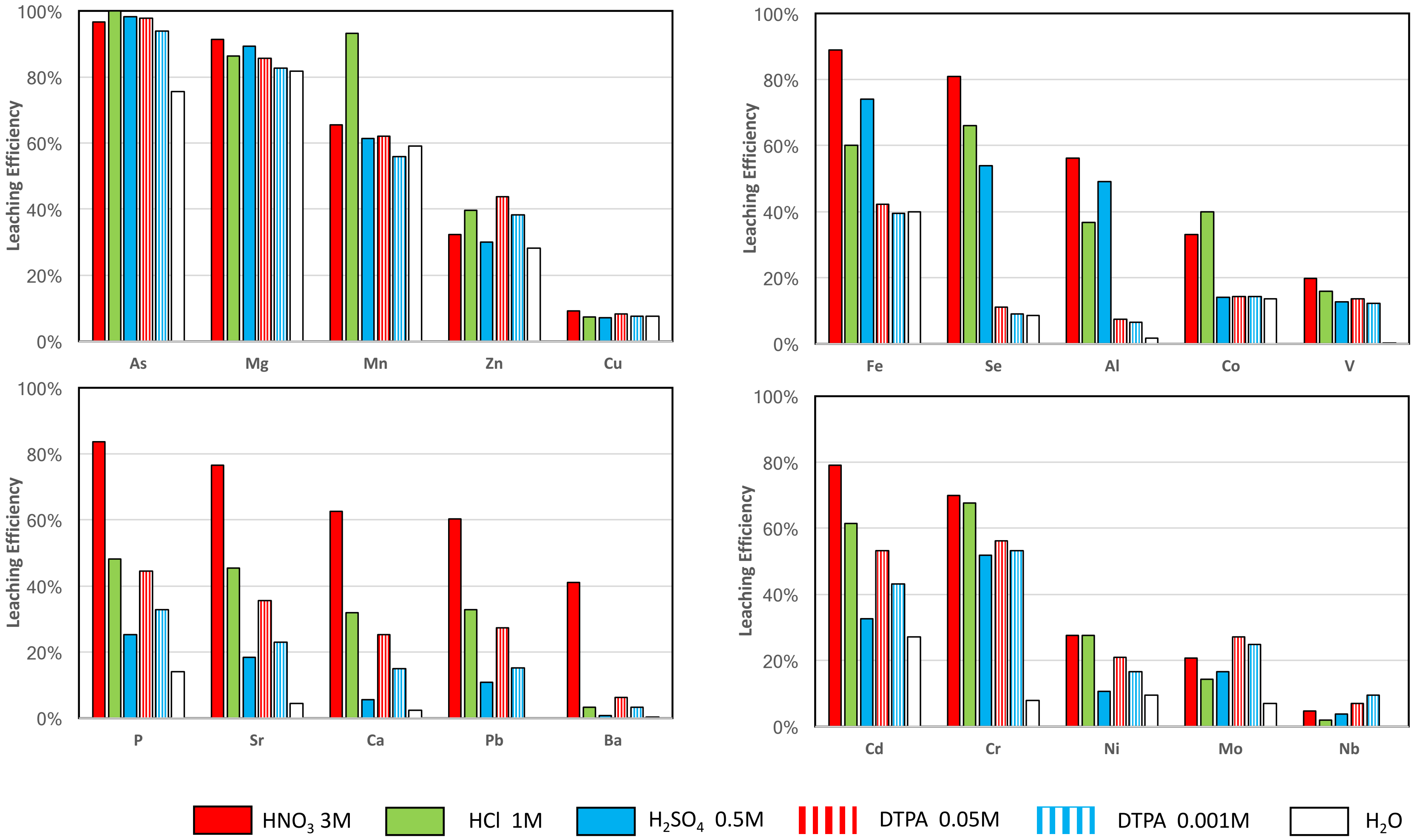
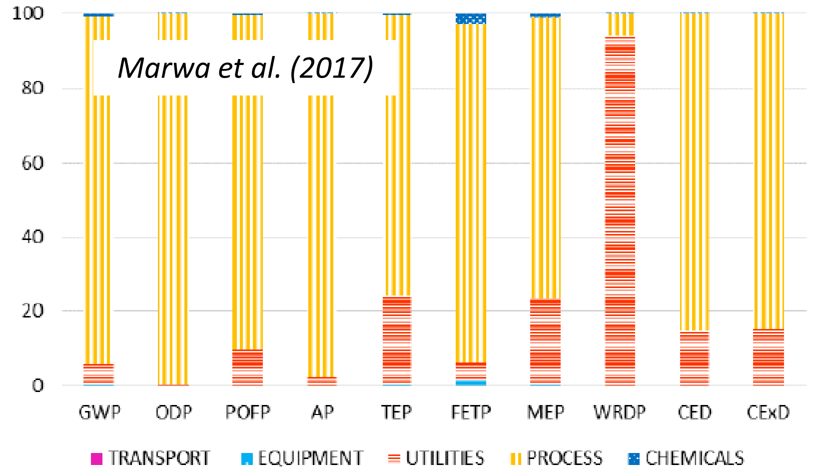
CRMs recovery from Phosphogypsum wastes

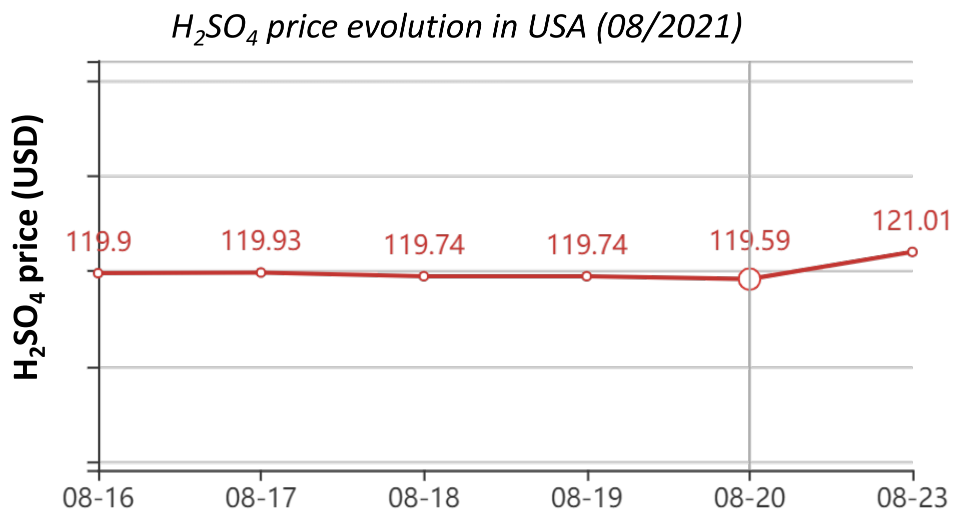


Best relationship *REE extraction:release of impurities* using sulfuric acid!!

REE recovery from Phosphogypsum wastes

Environmental and economic constraints of using H_2SO_4





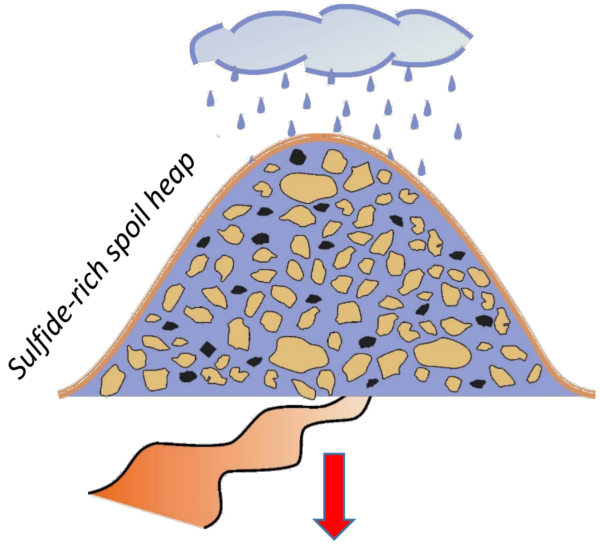
1 ton H_2SO_4 = 83.26 kg of CO_2, 3.92 mol H^+ eq, and 9624 MJ for CED

0.14 m^3 of H_2SO_4 per 1 m^3 of phosphogypsum = **13 €**

Considering a price of 90 € /m^3 of H_2SO_4

REE recovery from Phosphogypsum wastes

A more sustainable and cheap H_2SO_4 is available?



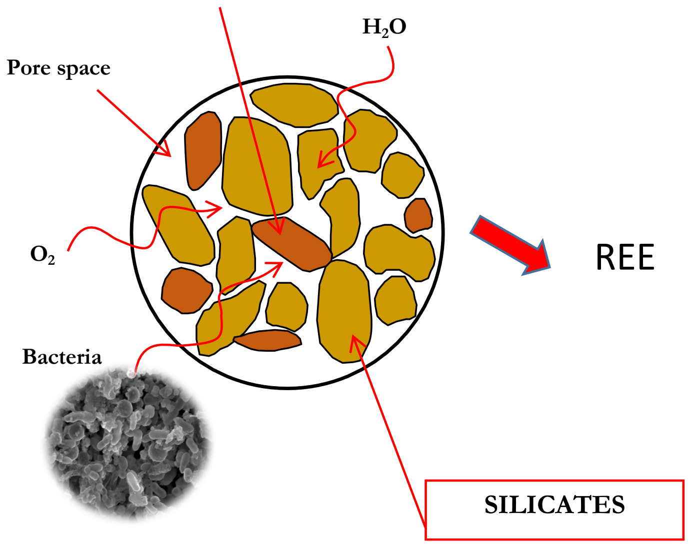
AMD

Sulfide-rich mine wastes

SULFIDES

Pyrite
Chalcopyrite
Sphalerite
Galena
Arsenopyrite

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
$$CuFeS + 4O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2SO_4^{2-}$$
$$ZnS + 2O_2 \rightarrow Zn^{2+} + 2SO_4^{2-}$$
$$PbS + 2O_2 \rightarrow Pb^{2+} + 2SO_4^{2-}$$
$$4FeAsS + 11O_2 + 6H_2O \leftrightarrow 4Fe^{2+} + 4H_3AsO_3 + 4SO_4^{2-}$$



REE recovery from Phosphogypsum wastes

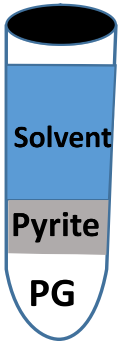
REE extraction from phosphogypsum based on circular economy principles

3 different solvents

Distilled water (pH 6) (REE 0 mg/L)

Mine water (pH 1.9) (REE 8.9 mg/L)

PG process water (pH 1.1) (REE 1.4 mg/L)



Agitator / incubator

3 different solid ratios:

75% py + 25% PG
50% py + 50% PG
25% py + 75% PG

3 different S:L ratios:

1:2.5, 1:5, 1:10

4 different times:

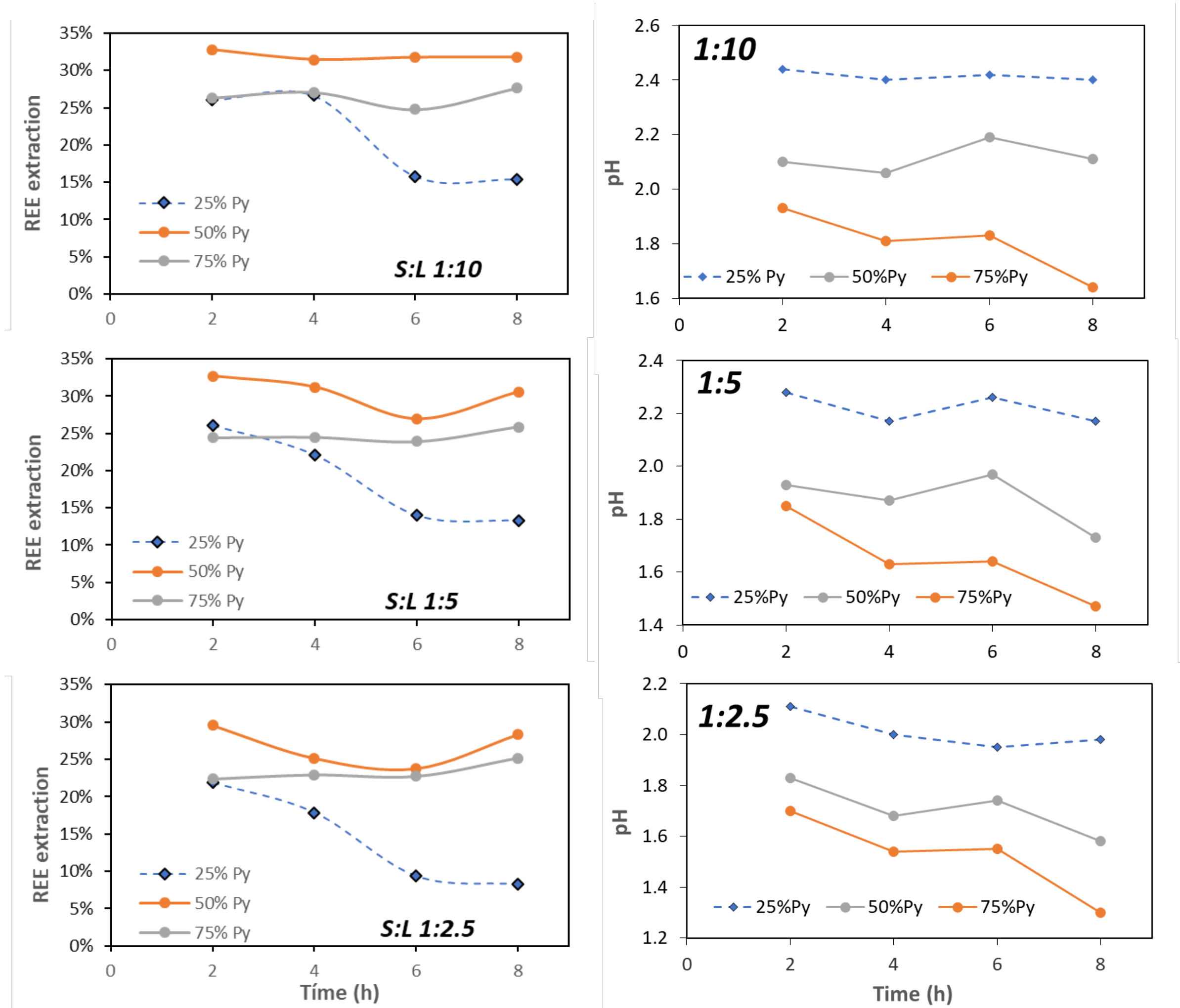
2, 4, 6, 8 hours

3 different temperatures

20, 40, 60ºC

REE recovery from Phosphogypsum wastes

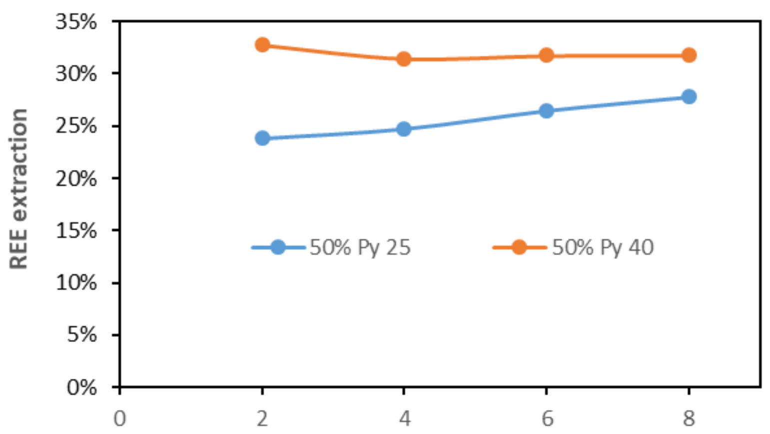
Results: Distilled water

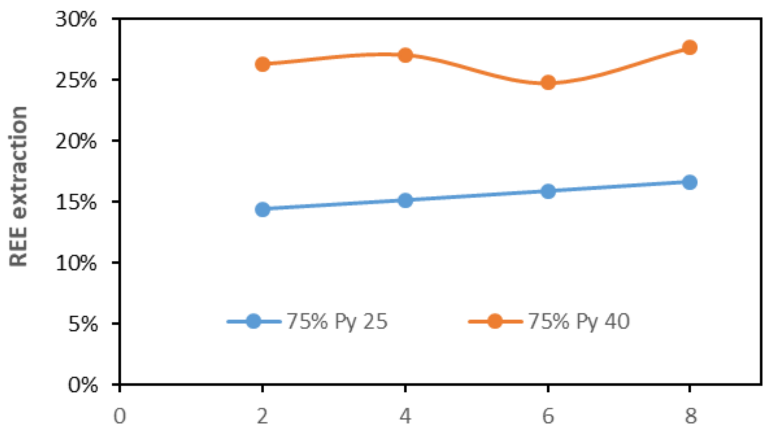


- Lower REE extraction (< 35%) than using H_2SO_4 0.5M (55%).
- Differences may be related to pH of the solvent (pH 0.3 for H_2SO_4 0.5M and pH >1.2 using pyrite + distilled water).
- Re-precipitation processes of REE initially released were observed with time using 25% of pyrite.

REEE recovery from Phosphogypsum wastes

Results: Distilled water





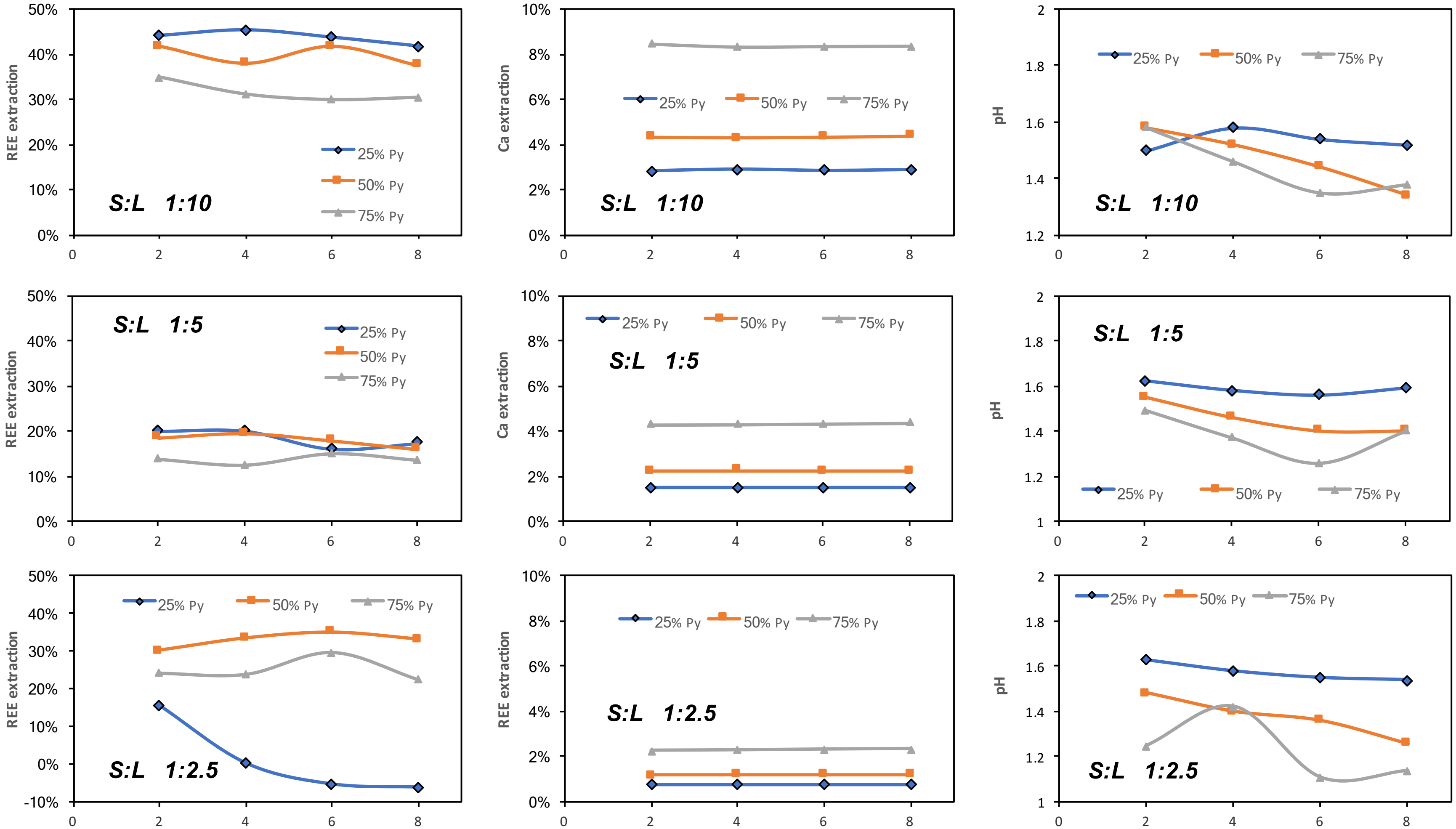
Effect of temperature on the REE extraction rates

- Higher REE extraction rates were observed at 40ºC than at 25ºC.

- More intense re-precipitation processes at higher temperatures when pH values are above 2.

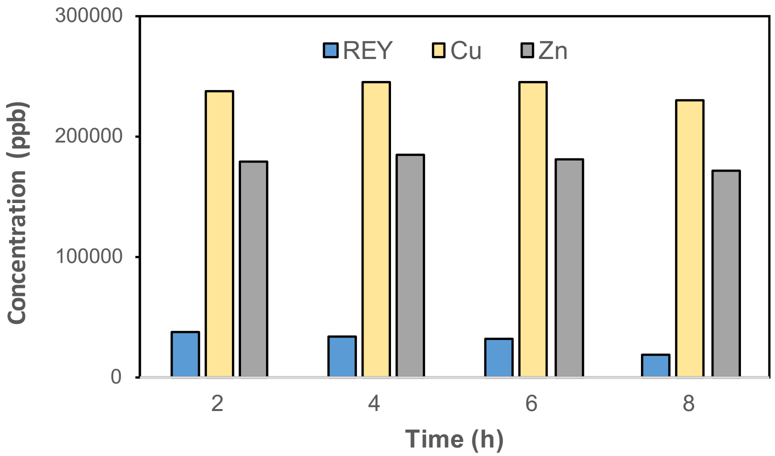
REEE recovery from Phosphogypsum wastes

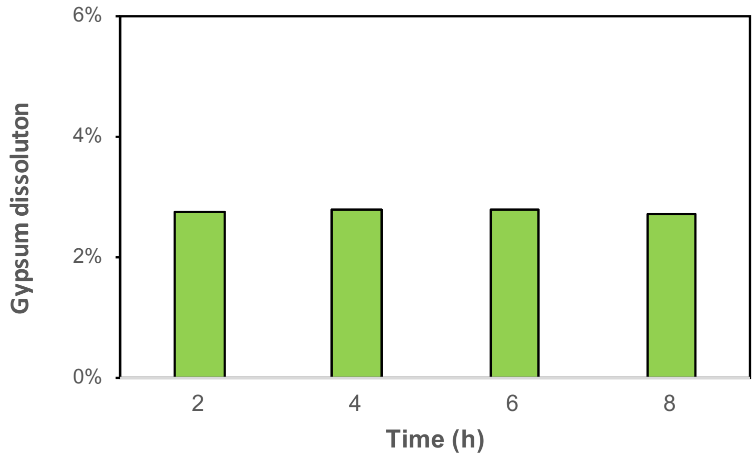
Results: acidic and REE-rich mine water



REE recovery from Phosphogypsum wastes

Results: acidic and REE-rich mine water





Extraction liquors with high concentrations in valuable elements:

Concentrations of Cu and Zn close to 200 mg/L
Concentrations of REY close to 50 mg/L

Low level of impurities released from the gypsum: ***< 3% of gypsum dissolution***

REE recovery from Phosphogypsum wastes

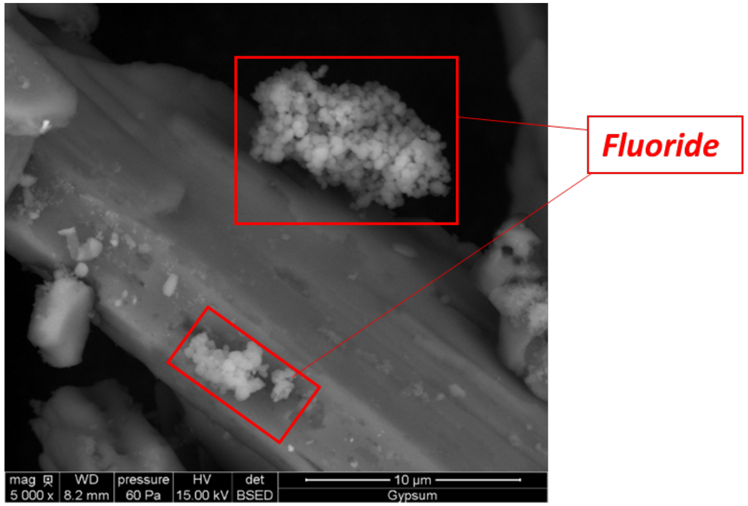
Concluding remarks and pending works

- REE extraction from phosphogypsum may be controlled by the dissolution of accesory minerals (e.g., oxide, fluorides, phosphate) , which in turn depends on the acidity of the leaching solution.

- Enhanced oxidation of pyrite wastes yielded low pH values (down to 1.2), however REE extraction rates were moderated (lower than 50%).

- High concentrated metal leachates were obtained combining mine and phosphogypsum wastes.

- High resolution mineralogical studies on PG are needed to know the fate of REE during the extraction.



REE recovery from Phosphogypsum wastes

Thanks for your attention!!!

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