“Industrial and Mine Wastes as a Source of Technology Critical Elements”

Workshop of EIT RM Morecovery project- May 5th 2020

Leaching of REEs from phosphogypsum waste: Spain case

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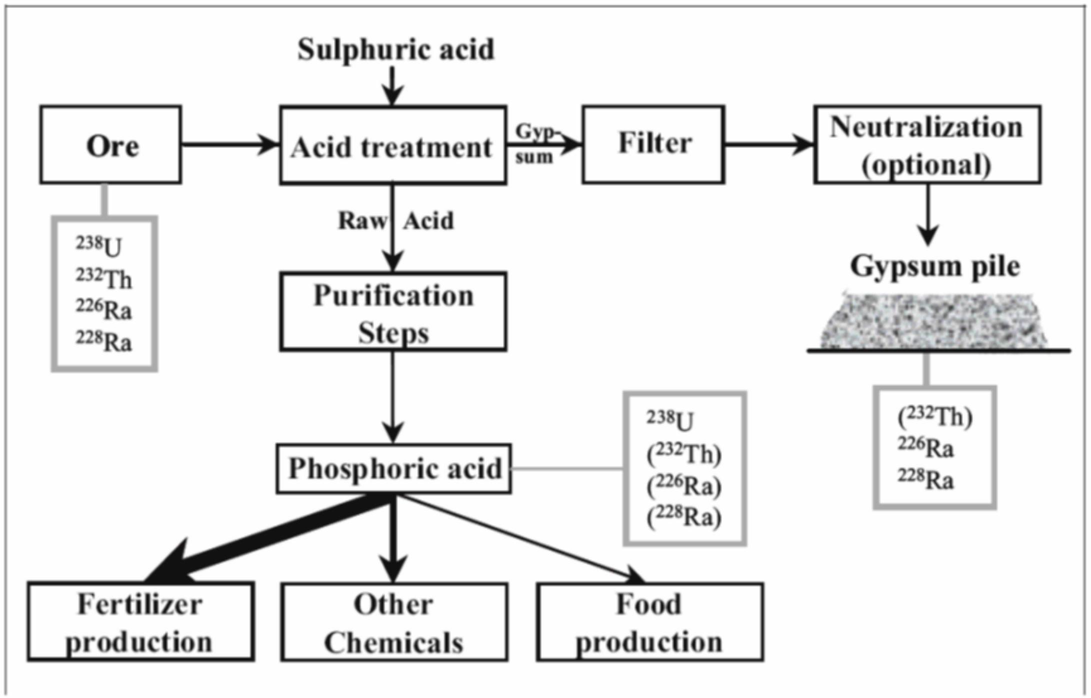
Phosphogypsum generation by the fertilizer industry worldwide

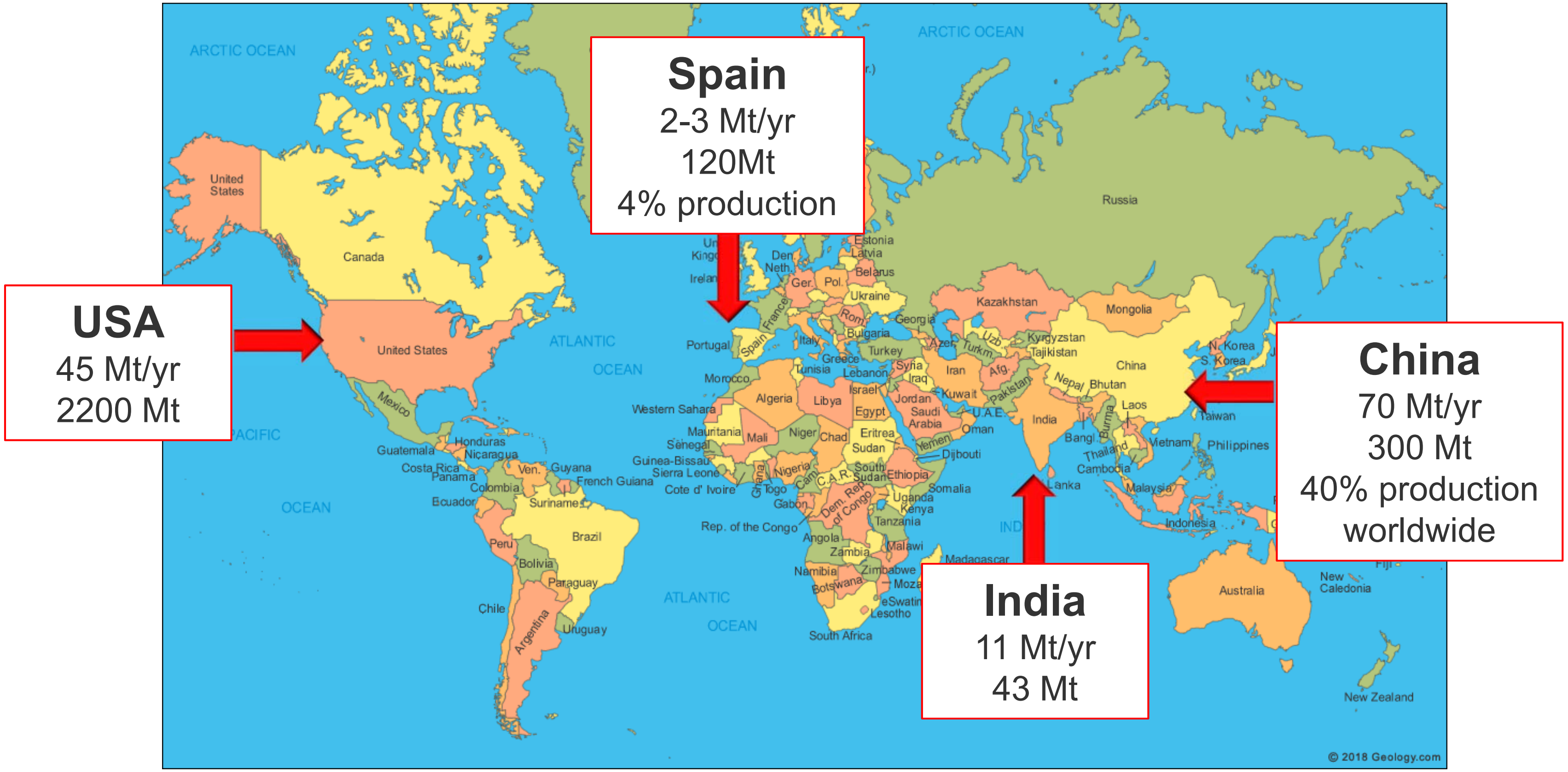


Production of H_3PO_4 for fertilizer manufacture

(Phosphate rock)		(Sulfuric acid)				(Phosphoric acid)		(Gypsum)		(Residual acids)

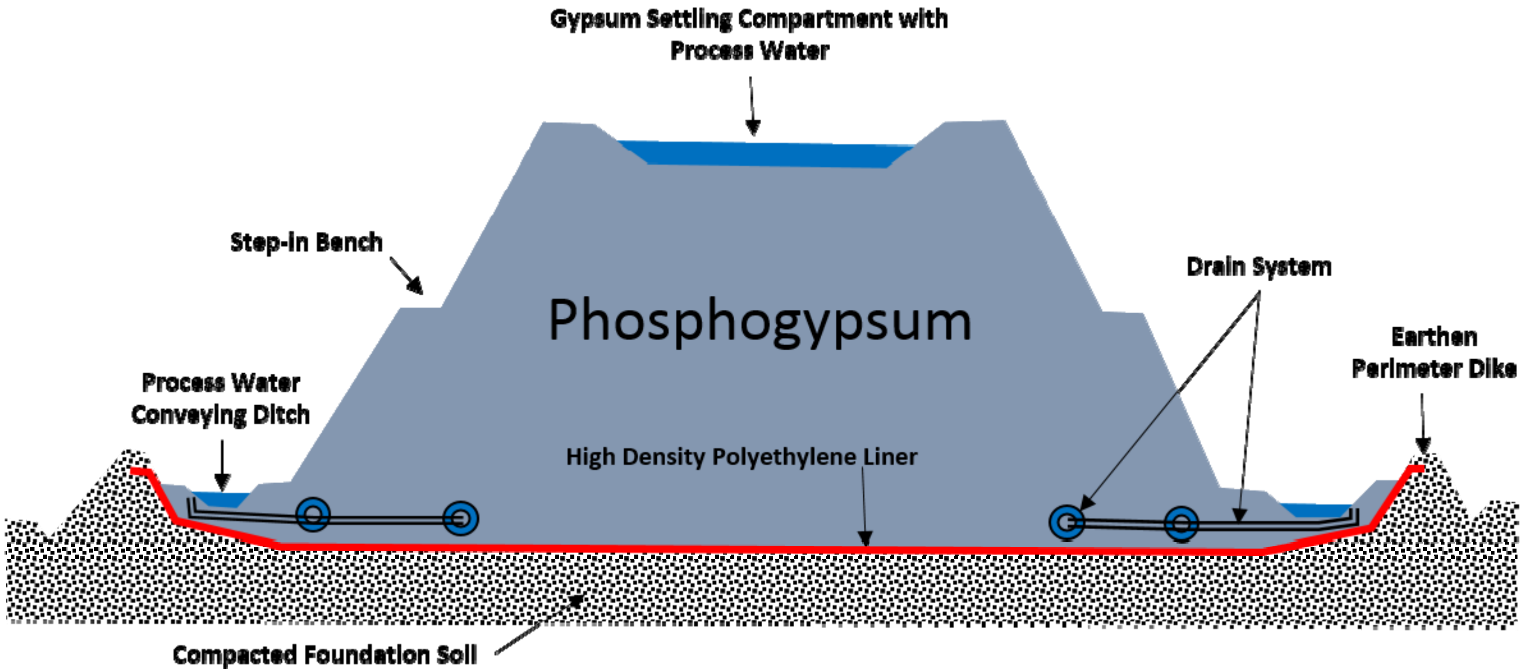
$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF$$

Phosphogypsum generation by the fertilizer industry worldwide



Phosphogypsum generation worldwide is not well reported: estimation based on H_3PO_4 production: ***5 tonnes of PG per ton of H_3PO_4*** (*generation of 175 Mt/yr*)

Phosphogypsum generation by the fertilizer industry worldwide

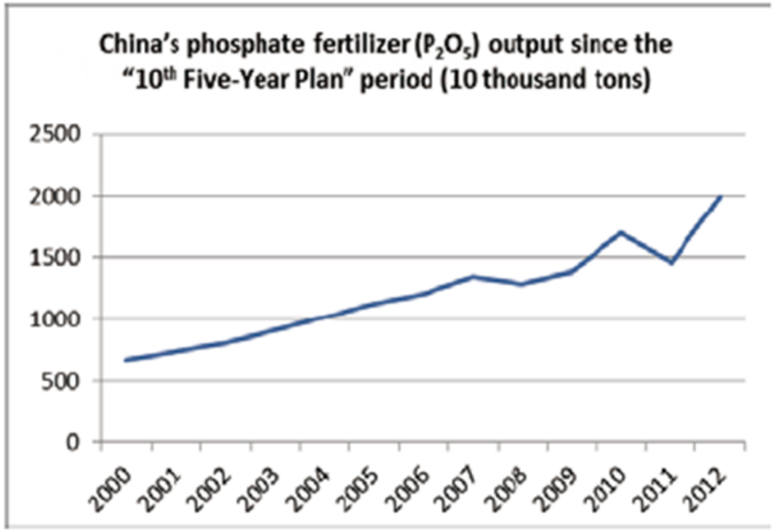


Around 6000 Mt of PG are deposited worldwide (> 50 countries such as USA, China, South Africa, Israel, Brasil, Spain, Poland, France, Greece, etc.).

PG stacks are located close to the factory and commonly in coastal areas

Phosphogypsum generation by the fertilizer industry worldwide

Living
with Danger
An Investigation of Phosphogypsum Pollution in the Phosphate Fertilizer Industry, Sichuan Province



Data Source: *Development plan on phosphate and compound fertilizer industry during the "12th Five-Year Plan" period*

Living with Danger report. Greenpeace (2013)

Huge stacks of phosphogypsum — solid waste pollution of phosphate fertilizer industry

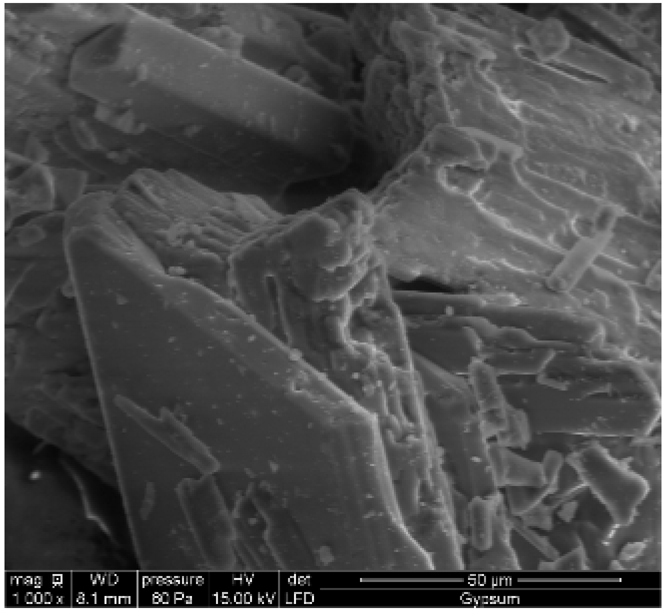
Phosphate fertilizer production is a high-polluting industry. Many of China's phosphate fertilizer production bases are located in environmentally fragile areas. As production capacity of phosphate fertilizer industry continues to expand rapidly in recent years, the environmental pollution of the industry, in particular phosphogypsum pollution, becomes more and more prominent.

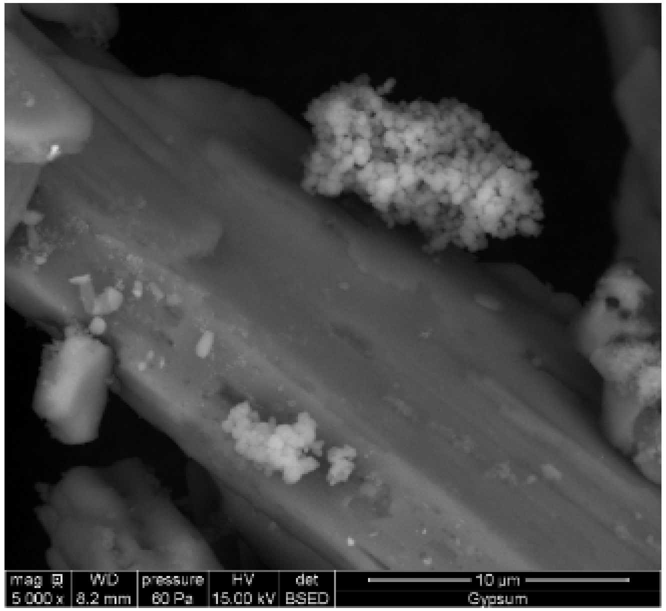
Phosphogypsum is the gypsum formed as a by-product of reacting phosphate ore (apatite,$Ca_5F(PO_4)_3$) with inorganic acid (including sulfuric acid, nitric acid, hydrochloric acid and phosphoric acid, mainly sulfuric acid), a process to turn phosphate ore into fertilizer with acid. a process reacting phosphate ore (apatite,$Ca_5F(PO_4)_3$) with inorganic acid (including sulfuric acid, nitric acid, hydrochloric acid and phosphoric acid, mainly sulfuric acid). Phosphogypsum commonly contains many harmful substances including fluoride, heavy metals and free acids, etc. Phosphogypsum stored in large stacks not only occupy large areas of land, but also bring with it many environmental risks. The harmful substances in phosphogypsum can cause pollution of groundwater and soil after rain, and when containing radioactive substances can even lead to radioactive contamination. [7] In addition to dust pollution, the stacks are prone to overflow and cause landslides during extreme rainfall.

Increasing tendency related to the growing demand worldwide!!

Phosphogypsum generation by the fertilizer industry worldwide

Scanning electron microscope images of PG



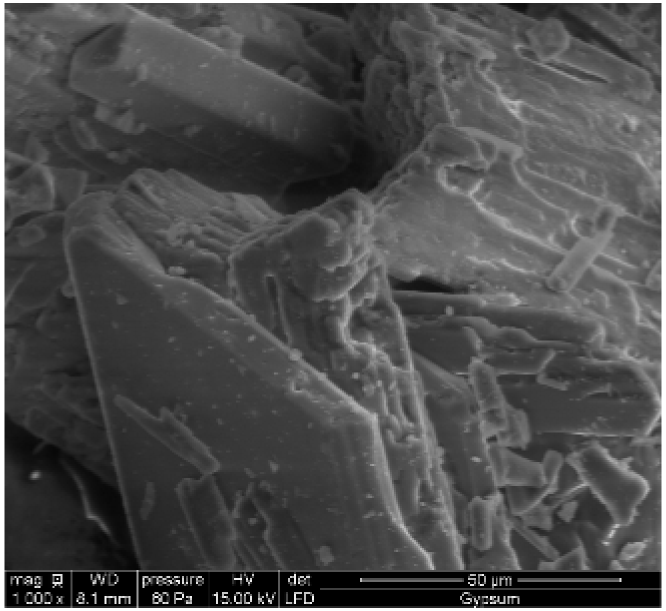


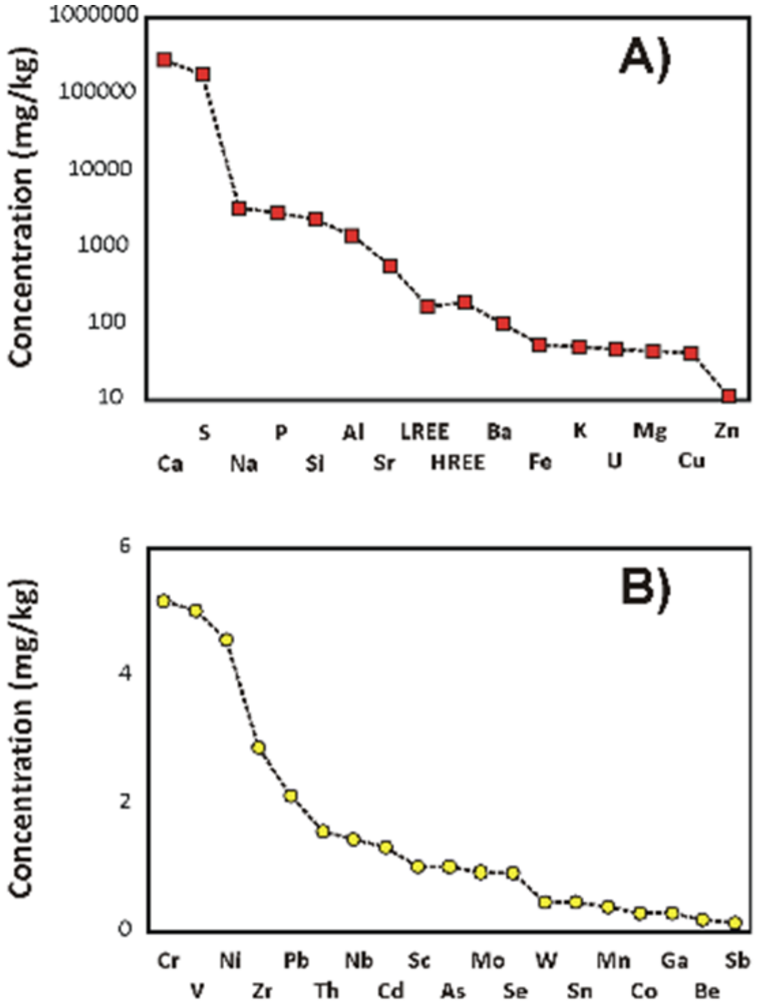
- 80-95% gypsum
- Unattacked rocks: phosphate, fluorophosphate
- Quartz
- Organic matter
- Fe oxides

Mineralogical composition of phosphogypsum

Phosphogypsum generation by the fertilizer industry worldwide

Scanning electron microscope image of PG





- Fine grained: <0.08 mm
- High reactivity
- Residual acidity: acid and metal rich pore water
- Low permeability and karst processes

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Connecting matters

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Phosphogypsum generation by the fertilizer industry worldwide

Element fractionation during the production of H_3PO_4

Phosphate rock

Radionuclide, REE, Y

+

Sulfuric acid

Trace metals

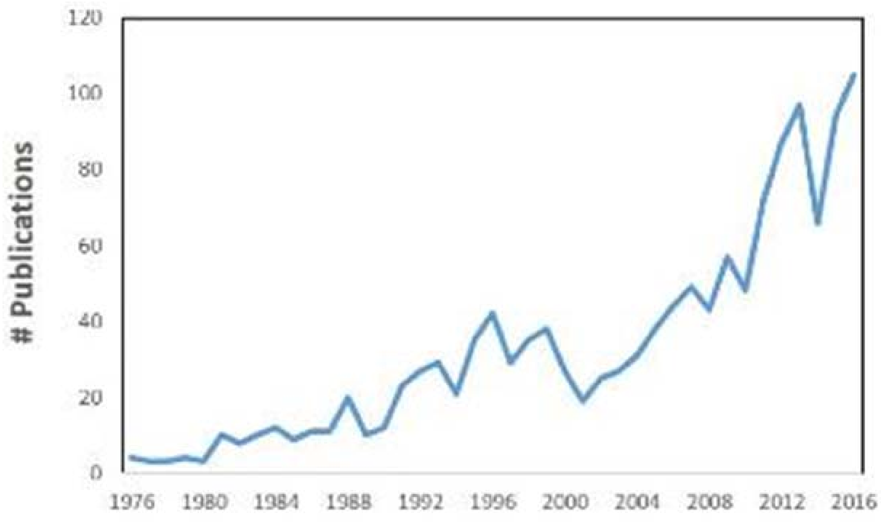
~ ^{210}Po and ^{226}Ra
~ REE + Y

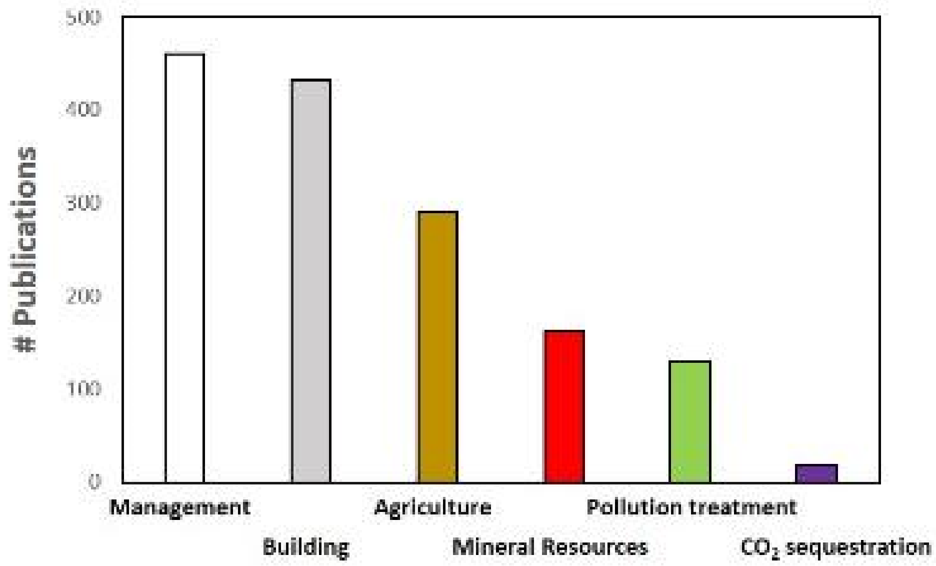
~ As, Cd, Cu, etc.
~ U and ^{210}Pb

Phosphogypsum

Phosphoric acid

Waste valorization





- Valorization routes to absorb the huge volumen of PG produced worldwide: *circular economy*
- Growing interest to valorizate this waste
- Main valorization focused on building and agriculture.
- Promising routes: source of critical raw materials

Waste valorization

~ 80% U y ^{210}Pb in acid

~ 90% ^{210}Po and ^{226}Ra in PG

~ 70-80% REY in PG

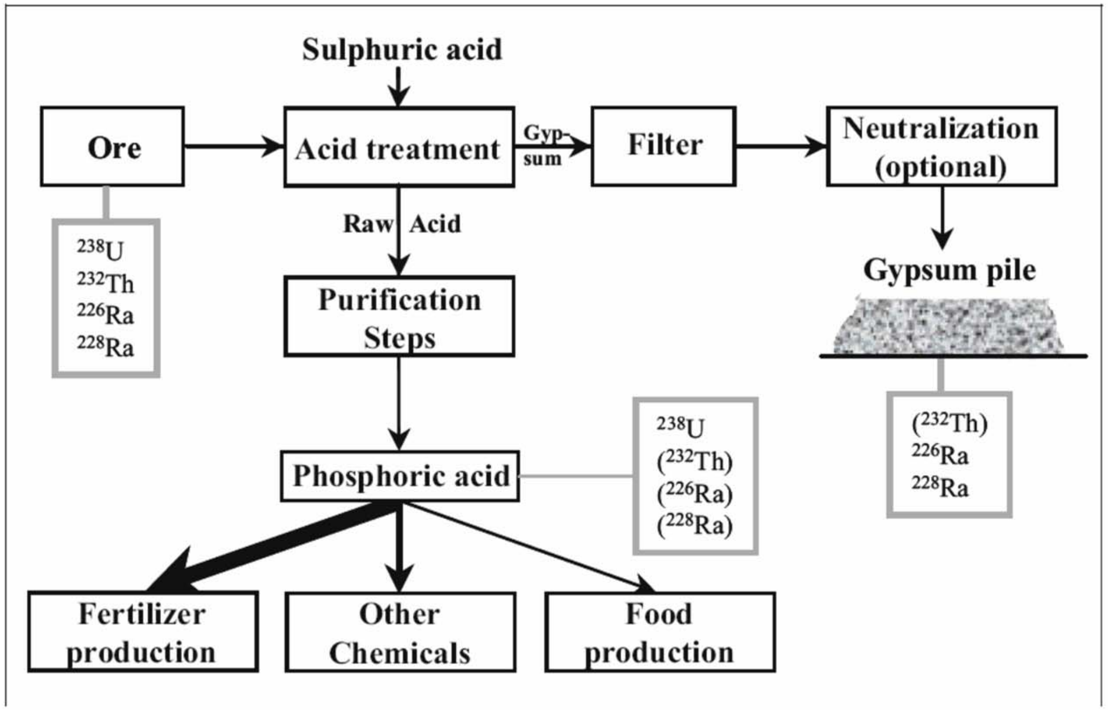
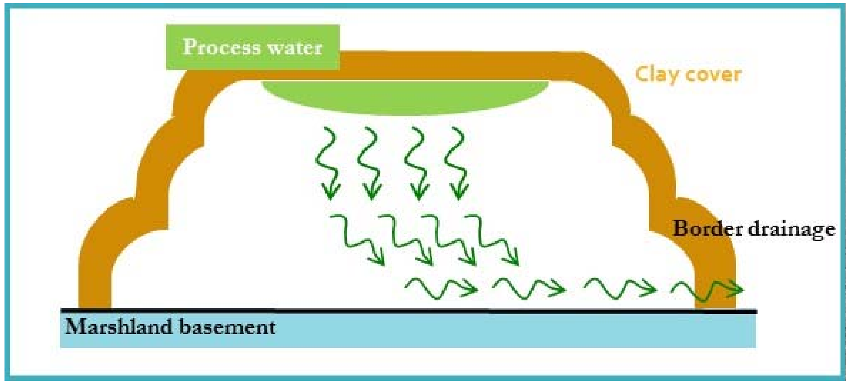


Fig. 1. Flow diagram of the sulphuric acid P-extraction process (IAEA 2003).

Waste valorization limited due to PG impurities

Leaching of REEs from phosphogypsum waste: Spain case

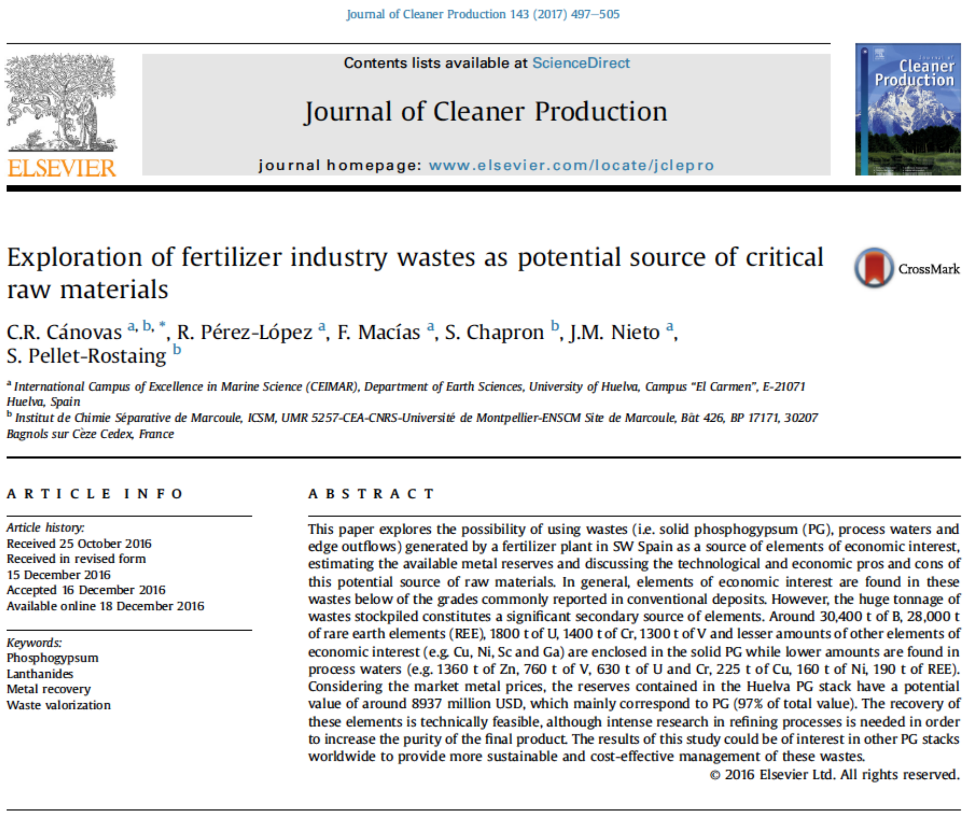


120 Mt deposited in a coastal area for 50 yr period

Huelva PG stack not properly isolated, <u>high pollution to the estuary</u>: 42 ton/yr of Fe, 12 of Zn, 6.9 of As, 4.2 of U, 3.5 of Cr, 1.8 of Cu, 1.6 of Cd among others.

A restoration plan is designed: isolation of the stack.

Leaching of REEs from phosphogypsum waste: Spain case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Exploration of fertilizer industry wastes as potential source of critical raw materials

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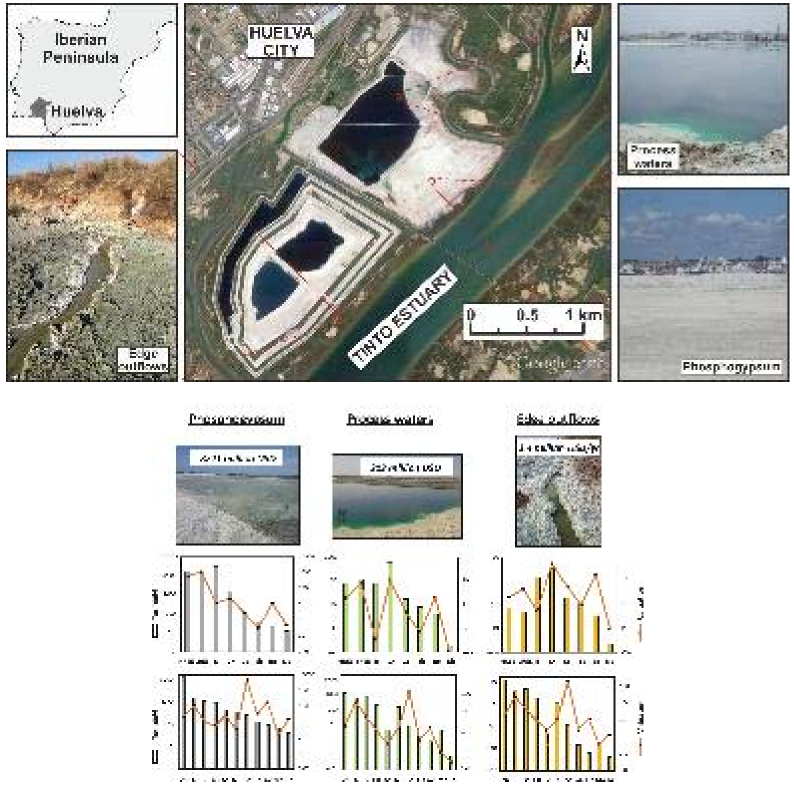
ABSTRACT

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.



However, a more sustainable solution may be achieved: the recovery of critical raw materials (CRMs)….

Leaching of REEs from phosphogypsum waste: Spain case

Key questions:

1. Are elements of economic interest in minable concentrations?

Estimation of metal grades in phosphogypsum and comparison with conventional deposits

2. Are these metal pools valuable enough to be exploited?

Economic estimation of metal deposits in phosphogypsum (London Exchange Metal Market).

3. Is technically feasible to extract these metals?

Assessment of technical requirement to extract and convert these metals into a commodity.

4. Economic, legal and social barriers for phosphogypsum recycling

Assesment of economic, legal and social barriers that could preclude phosphogypsum recycling

Leaching of REEs from phosphogypsum waste: Spain case

Methodology

- Collection of samples in surface and depth (n= 49)
- Mineralogical analysis (SEM, XRD, µXRF, XANES)
- *Aqua regia* digestion
- Total composition by ICP-AES and ICP-MS.
- Leaching with comercial acids (S:L ratio 1:20): *HCl, HNO_3 and H_2SO_4.*
- Aided-extraction by chelation and ultrasound

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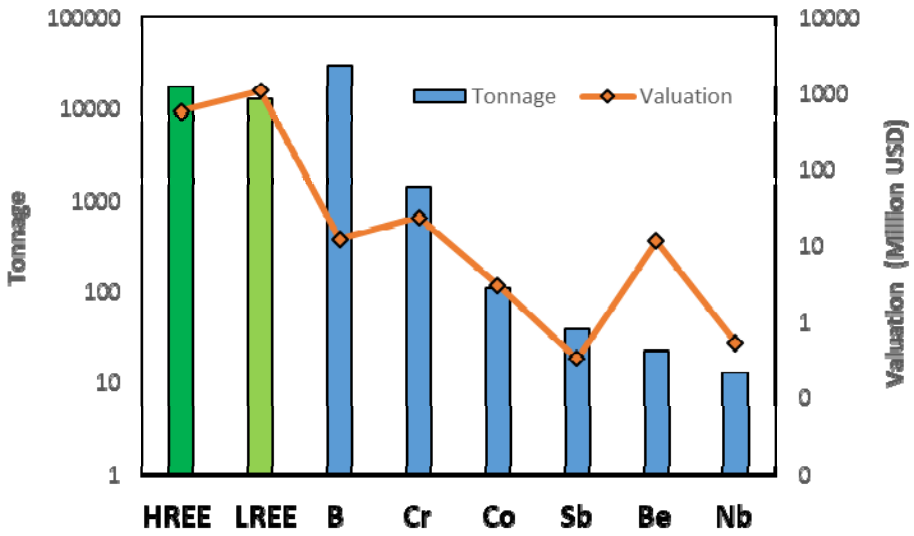
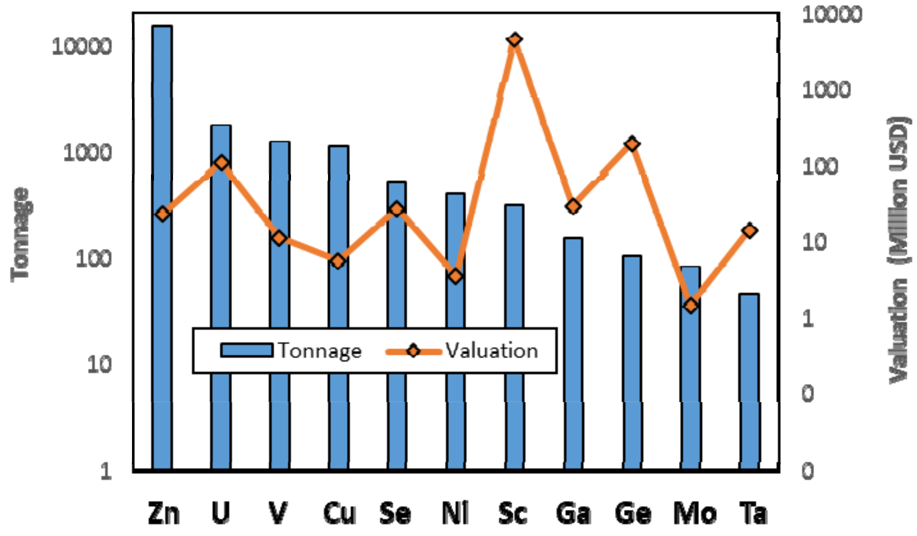
Leaching of REEs from phosphogypsum waste: Spain case

1. Are metals in minable concentrations?

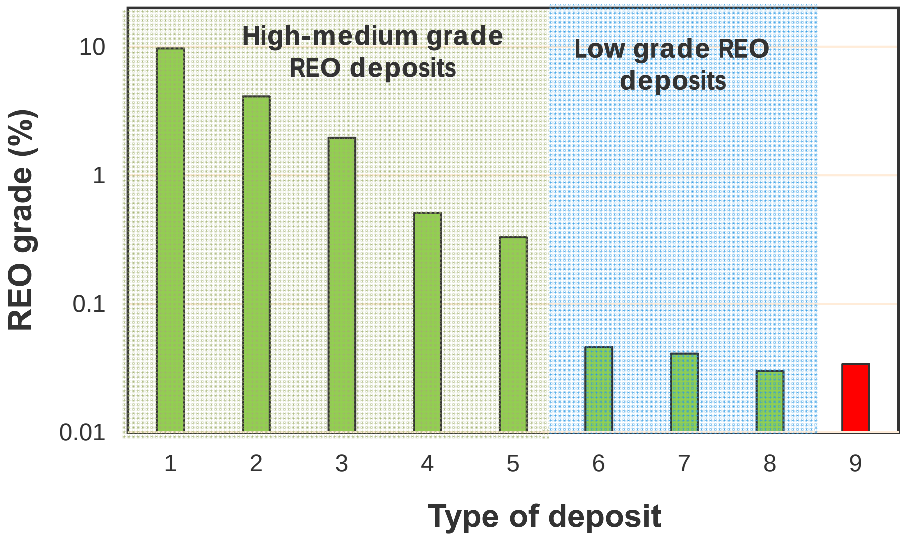




The most abundant critical raw materials (CRMs) were B (304 mg/kg), light REE (LREE, La-Sm; 160 mg/kg), heavy-REE (HREE, Eu-Lu e Y; 123 mg/kg) and other trace metals (e.g. Cr, Co, Sb o Be).

Leaching of REEs from phosphogypsum waste: Spain case

1. Are metals in minable concentrations?



Conventional deposits

High-medium grade

1. *Lateritic deposits*
2. *Carbonatite-associated*
3. *Associated with alkaline igneous rocks*
4. *Hydrotermal deposits*
5. *Iron-REE deposits*

Low grade

6. *Marine placers*
7. *Alluvial placers*
8. *Ion-adsorption clays*

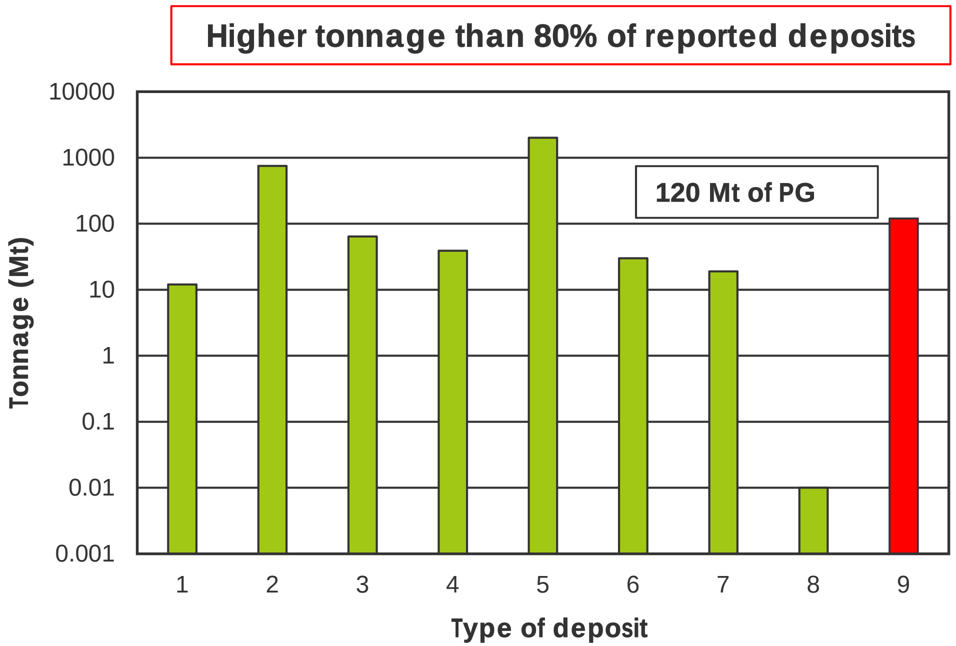
9. ***Phosphogypsum***

REO grade in PG of 0.034%

REO grade several orders of magnitude lower than high-medium REO deposits, but similar to low-grade deposits

Leaching of REEs from phosphogypsum waste: Spain case

1. Are metals in minable concentrations?



Conventional deposits

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Low grade

6. *Marine placers*
7. *Alluvial placers*
8. *Ion-adsorption clays*

9. *Phosphogypsum*

However, PG deposits have similar or higher tonnages than most conventional deposits.

Leaching of REEs from phosphogypsum waste: Spain case

2. Are these metal pools valuable enough to be exploited?

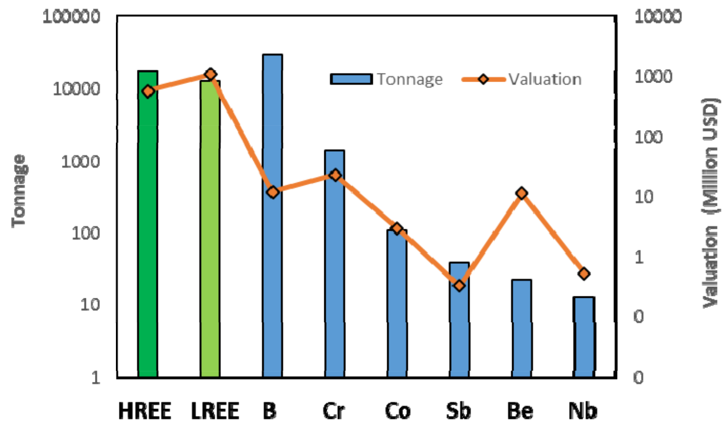
Theoretical valuation:

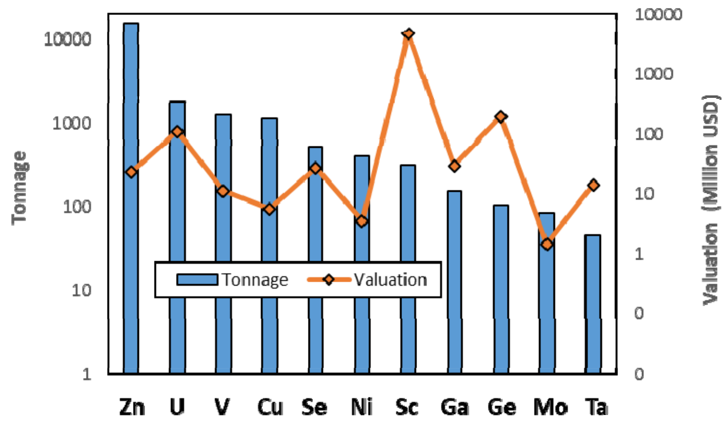
<u>8721 millones USD</u>

<u>Assuming total extraction of elements and the obtaining of pure markeatable products:</u>

Leaching of 70-99% for REE, Cr, Sb, Be, Se and Sc.

A correction factor should be applied (30% of market values)





Leaching of REEs from phosphogypsum waste: Spain case

3. Is technically feasible to extract these metals?

Route 1: *acids at different T and M*

HNO_3, HCl, H_2SO_4

0.5, 1, 2, 3M

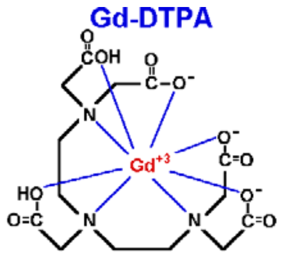
20, 40, 60 y 80ºC
Ratio S:L 1:20

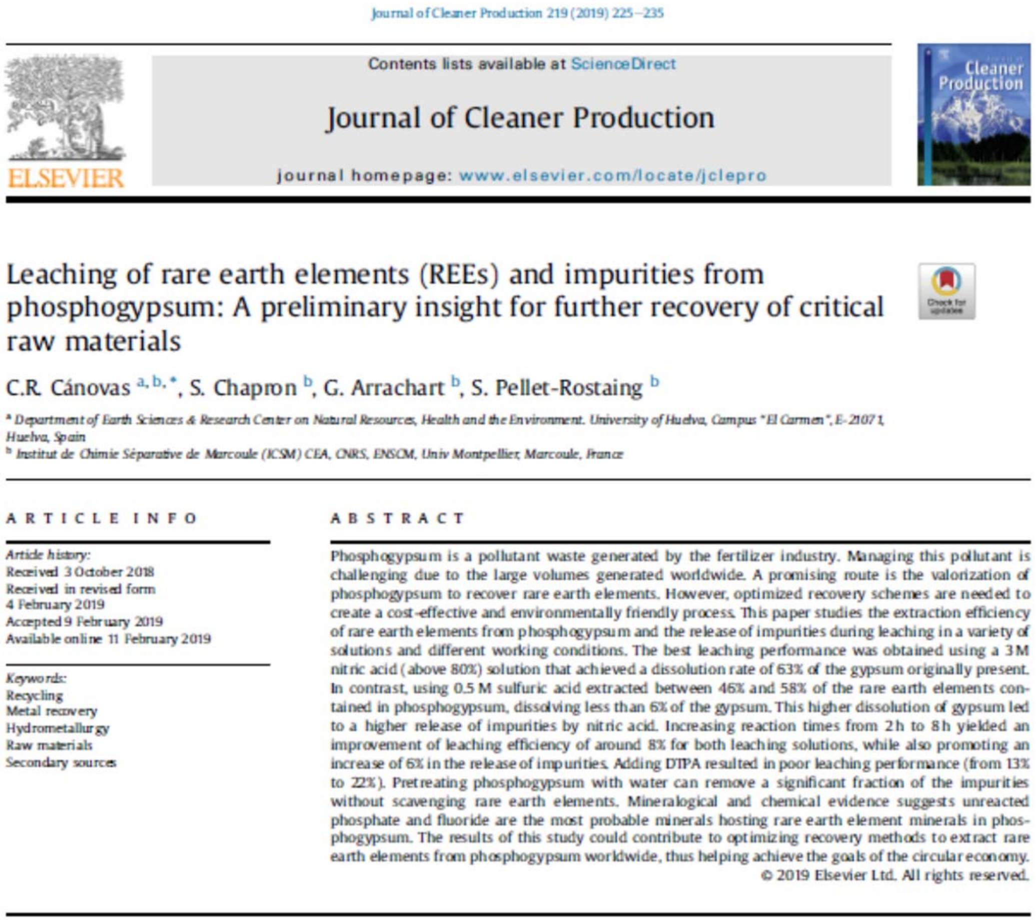
500 rpm

Route 2: *DTPA at different pHs*

DTPA

0.05M DTPA
pH 3 to 5.

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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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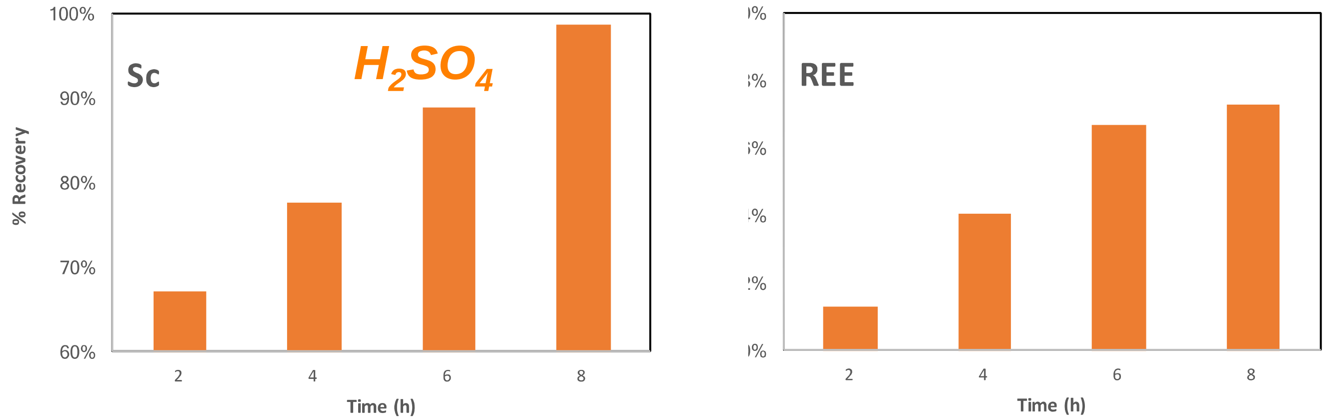
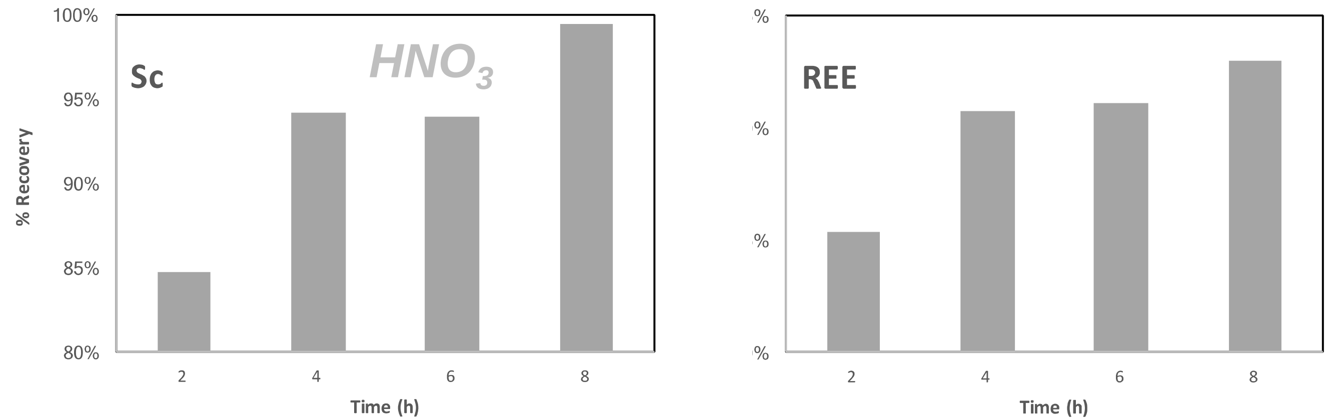
ABSTRACT

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 3M 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 2h to 8h 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.

Leaching of REEs from phosphogypsum waste: Spain case

3. Is technically feasible to extract these metals? ***Effect of extraction time***

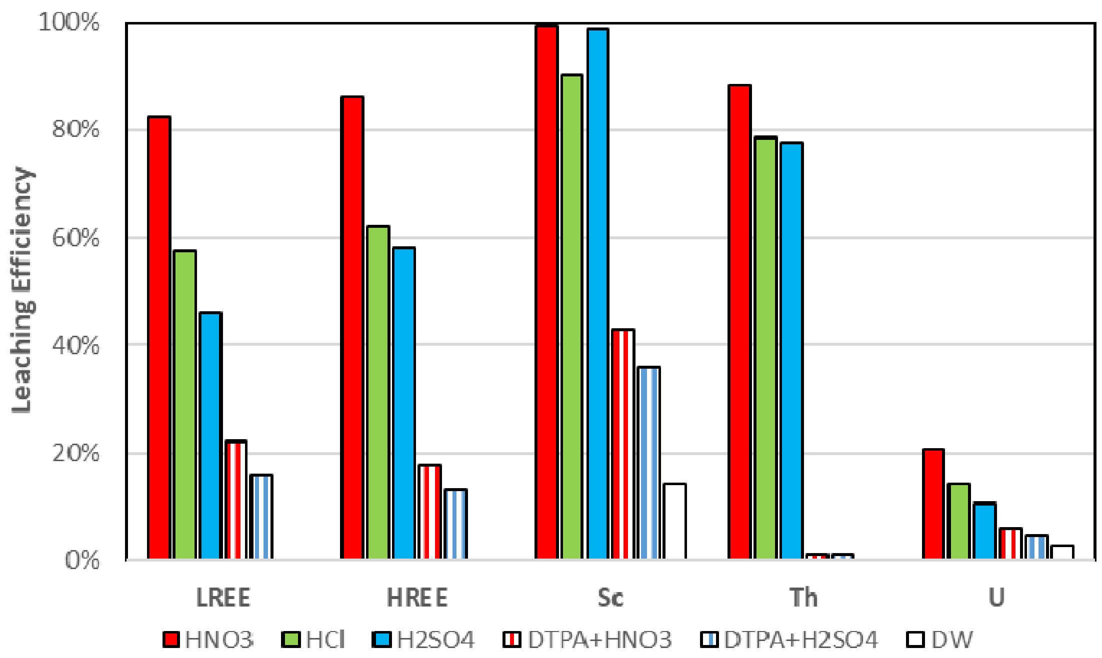




Extraction of target elements increased with time….. But also impurities

Leaching of REEs from phosphogypsum waste: Spain case

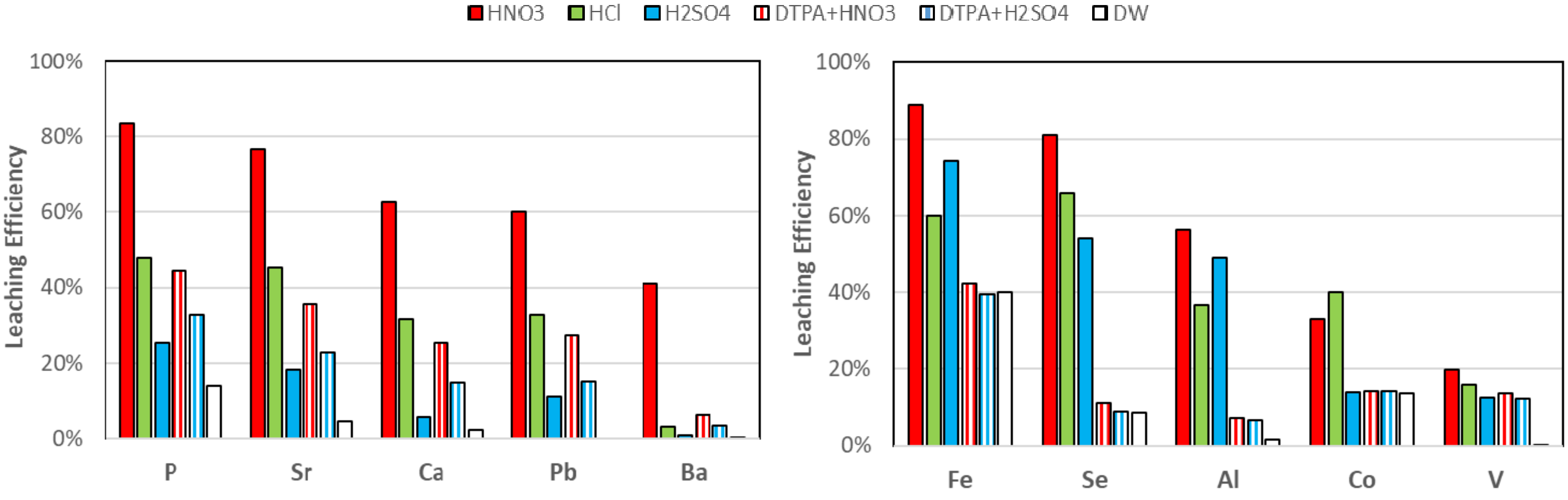
3. Is technically feasible to extract these metals? ***Effect of extracting agent***



Higher extraction with HNO_3 (>80%), followed by HCl (60%), H_2SO_4 (55%), DTPA-acids (20%) and water (<5%)

Leaching of REEs from phosphogypsum waste: Spain case

3. Is technically feasible to extract these metals? *Effect of extracting agent*



Higher release of impurities using HNO_3 and HCl than with H_2SO_4

Better performance REE extraction:gypsum dissolution for H_2SO_4 (55%-6%) than for HNO_3 (80%-69%)

EIT RawMaterials — Connecting matters

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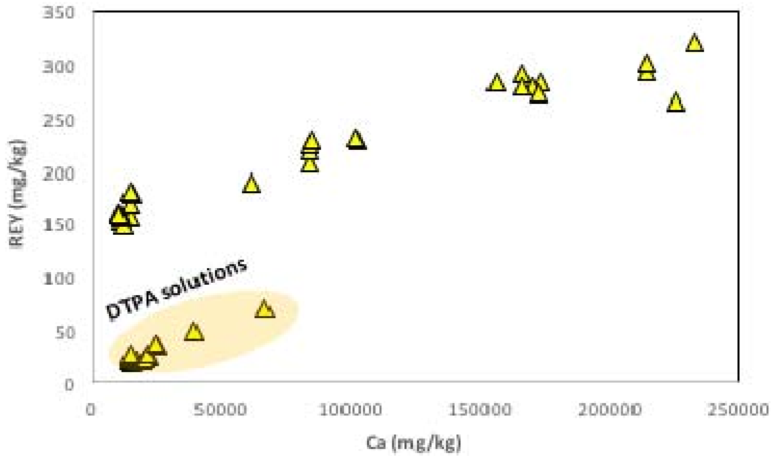
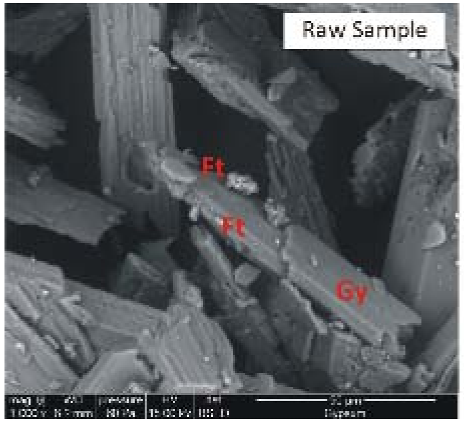
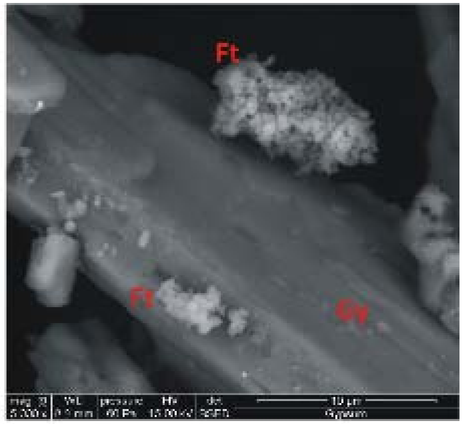
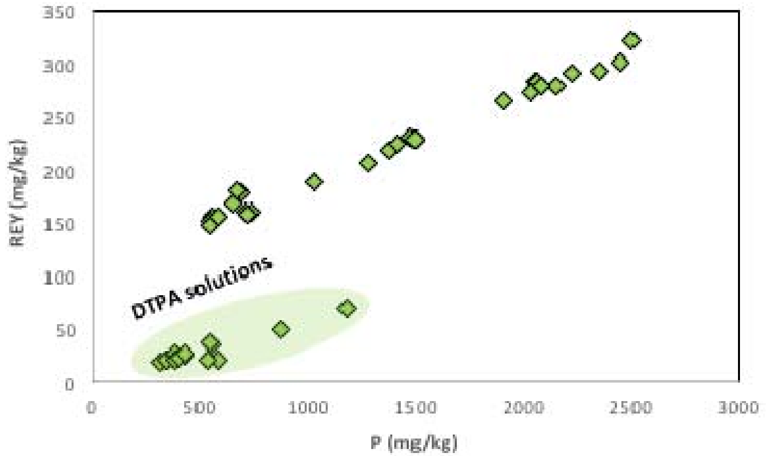
Leaching of REEs from phosphogypsum waste: Spain case

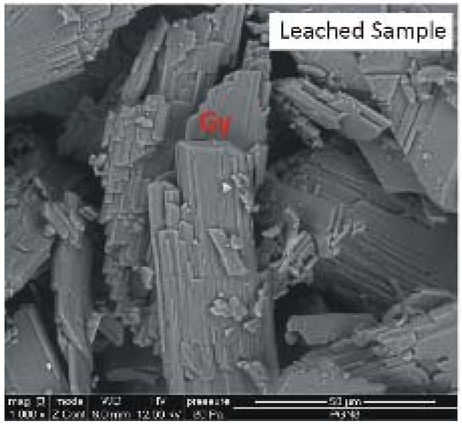
3. Is technically feasible to extract these metals? *Mineralogical control on REE release*

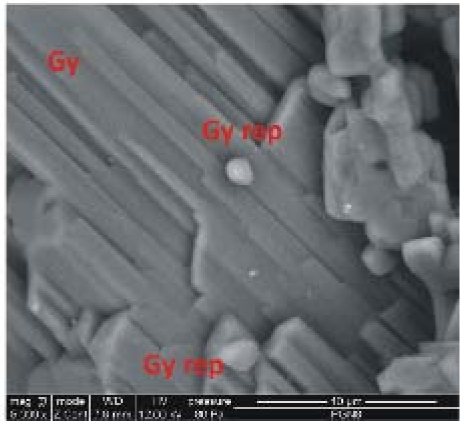












Leaching of REEs from phosphogypsum waste: Spain case

3. Is technically feasible to extract these metals? *Mineralogical control on REE release*

ID21 - X-RAY MICROSCOPY BEAMLINE

µXRF mapping: detect high-resolutions element associations with REE.

µXANES - micro X-ray absorption near-edge structure: Ce speciation

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Decision of the Committees

Please inform your co-proposer(s)

EV-358
"UNRAVELLING RARE EARTH ELEMENTS (REE) MOBILITY IN PHOSPHOGYPSUM: ENVIRONMENTAL AND ECONOMIC IMPLICATIONS"

Beamline	Round	Beam time allocated
ID21 (C07)	4/2018	9 shift(s)

Review Committees' comments (if no comment appears from a committee, none has been given):

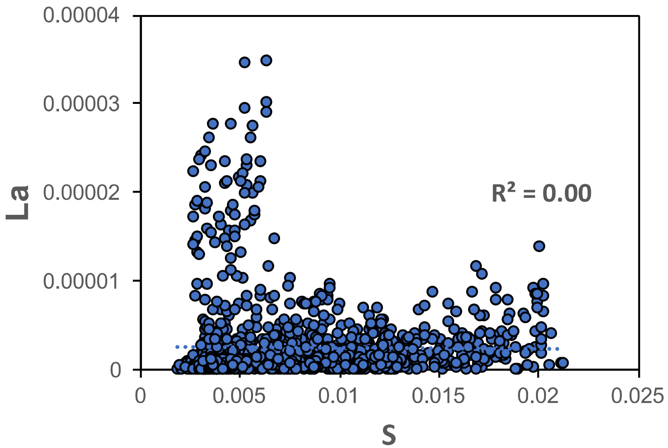
- C07 : Given the ongoing refurbishment of ID21, beam time cannot yet be guaranteed. However should the beam time be available, the panel has selected your proposal for allocation of beam time as indicated. The beamline staff will contact you in due course to confirm the allocation if the beam time is available. The panel further commented: A good proposal. Beam time is granted but results must be published and the list of publications in future proposals must be updated.

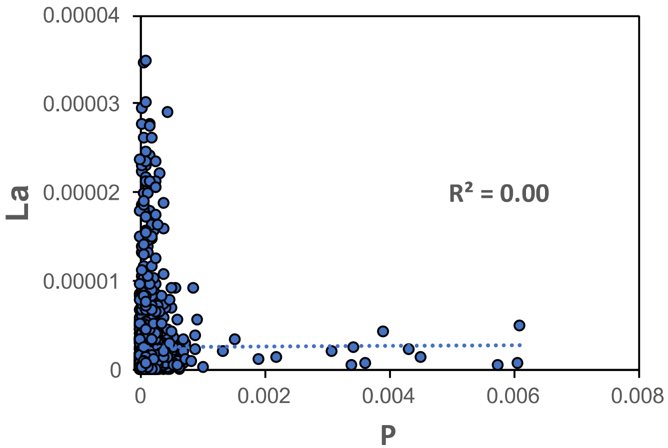
For up to date information, please consult our Website (http://www.esrf.eu) under "Users and Science/User Guide" and then "Applying for beamtime".

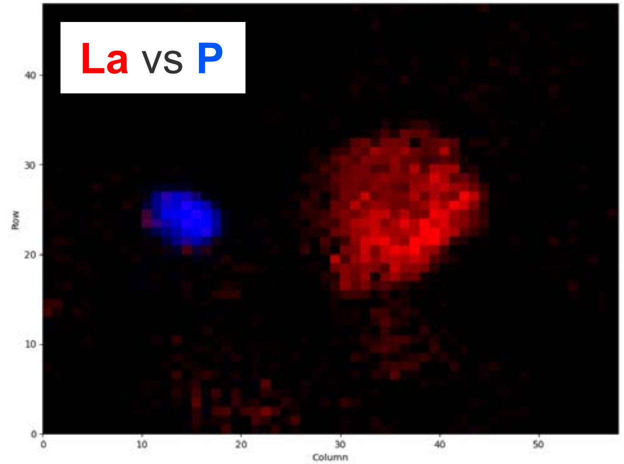
Leaching of REEs from phosphogypsum waste: Spain case

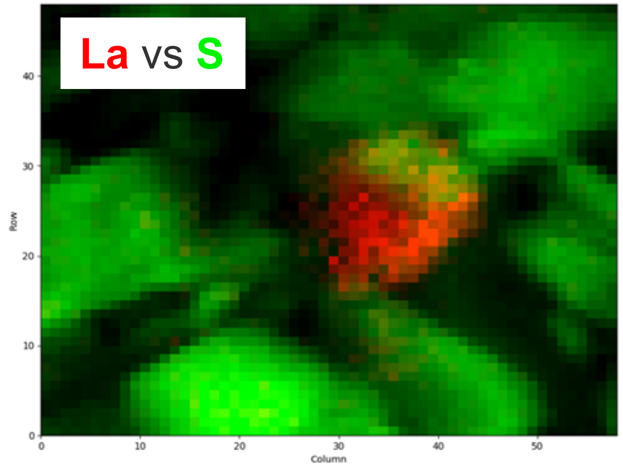
3. Is technically feasible to extract these metals?

Synchrotron µXRF mapping



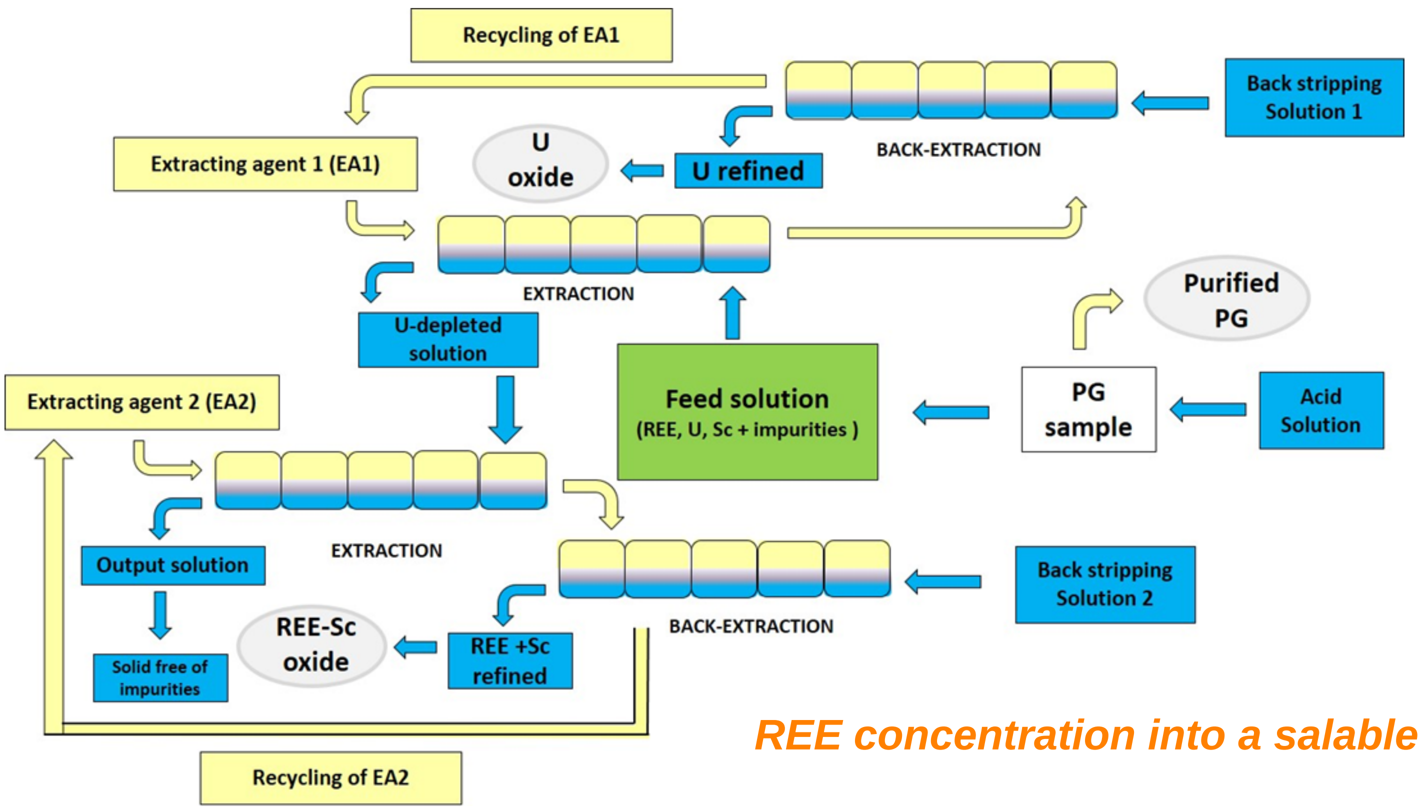






Leaching of REEs from phosphogypsum waste: Spain case

3. Is technically feasible to extract these metals?



REE concentration into a salable product

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4. Economic, legal and social barriers for phosphogypsum recycling

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Evaluation of the recovery of Rare Earth Elements (REE) from phosphogypsum waste – case study of the WIZÓW Chemical Plant (Poland)

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ABSTRACT

More than 5 million tons of apatite phosphogypsum, a waste derived from the production of phosphoric acid, have been tipped on the waste tip of the Wizów Chemical Plant (Poland). This waste contains Rare Earth Elements (REE) which are on the list of 'critical' raw materials in the EU and other countries. This paper presents an evaluation of the industrial waste management solutions in the Wizów plant. Technology has been developed that enables one to eliminate the landfilling of the phosphogypsum by converting the waste into commercial products: anhydrite and REE concentrates (wasteless technology). In this study, the impacts of landfilling (1st variant) and the implementation of improvement – REE recovery (2nd variant) were explored taking into account both economic and environmental aspects. The two variants of waste management in Wizów were assessed using the Life Cycle Assessment (LCA) method. The functional unit was 1 Mg of waste. Analyses were performed using the generic data ('input' and 'output') from the existing plant and from a technological plan proposed for REE recovery. The identification of factors affecting the environment was the basis for determining the environmental and developmental target and the basis for exploring modified technological solutions. The Eco-Indicator 99 (EI'99) method was applied. The evaluation of economic efficiency using the LCNPV method was based on calculations of technological plans, cost estimates and the market prices of raw materials. For validation, the results of exergy assessment were also proposed. The results of the analyses carried out using EI'99 indicate that disposal of waste has much less impact on the environment (Pt 4.58) than the proposed technology for processing it (Pt 8.28), even though in the new technology one takes into account the potential beneficial environmental impacts associated with the new materials: REE concentrates and anhydrite. The technology developed requires significant investment, but it can provide additional raw materials due to the possibility of REE recovery. There are considerable ecological benefits for plants generating phosphogypsum waste since the utilisation of all current production wastes would end phosphogypsum storage and turn the manufacturing process for extracting phosphoric acid into a low-waste production process, which is consistent with the targets of a circular economy. Moreover, the technology proposed in this paper should help to incentivise the global recovery of REE and facilitate the launching of new production activities due to the possibility of its application in other plants generating a large amount of phosphogypsum waste.

Limitations for upscaling

Table 3
Unit costs of energy for a new technology in the Wizów plant.

Energy carrier	Unit cost [PLN]	Unit
Electrical energy	0.19 (~0.05 EUR)	kWh
Gas	0.85 (~0.2 EUR)	Nm^3
Steam	24.00 (~6.0 EUR)	GJ
Compressed air	0.02 (~0.005 EUR)	m^3

Table 4
Unit costs of raw materials for a new technology in 'Wizów' plant.

Description	Unit cost [PLN]	Transport cost [PLN]	Unit
Phosphogypsum	0.00 (~0.00 EUR)	5.00 (~1.25 EUR)	Mg
Sulphuric acid	50.00 (~12.50 EUR)	6.00 (~1.50 EUR)	Mg
Turoszów ashes	10.00 (~2.50 EUR)	15.00 (~3.75 EUR)	Mg
Calcium oxide	109.00 (~27.25 EUR)	20.00 (~5.00 EUR)	Mg
Water	3.40 (~0.85 EUR)	0.00 (~0.00 EUR)	m^3

- This solution is cost-effective
- High investment requirement
- High risks: fluctuation on REE prices
- Environmental impact??? Life cycle analysis

"Industrial and Mine Wastes as a Source of Technology Critical Elements"

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Thanks for your attention!!!!

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