



Reprocessing of phosphogypsum for recovery of REE

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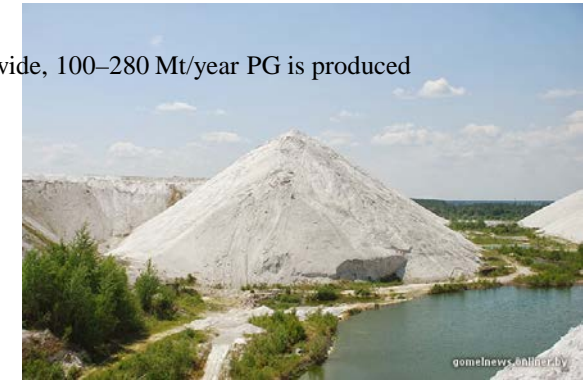
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Contents

- Phosphate rock process and phosphogypsum (PG)
- Phases of REE existing in PG
- Feasibility studies of REE enrichment by physical methods
- Chemical leaching of REE from PG – A Review

Phosphate rock process and phosphogypsum (PG)

Worldwide, 100–280 Mt/year PG is produced



Phosphate rocks (mainly in the form of mineral apatite) are mined, beneficiated and either solubilized (acid leach) to produce wet-process phosphoric acid, or smelted to produce elemental phosphorus.

The phosphate rock production in the world was 260 Mt in 2016, and most (82% of P₂O₅) was used for fertilizer. Phosphorites usually contain significant amount of rare earth elements (REE), approximately average 460 ppm.

Phosphogypsum (PG) is an by-product of the phosphoric acid wet-process and the main component is calcium sulphate dihydrate (CaSO₄•2H₂O) as showed in the following reaction equation:



During the wet-process REE are enriched in the PG* with only 20%–30% REE in the phosphoric acid leaching solution.

**Enrichment of REE into PG is caused by recrystallization of calcium sulphate from hemihydrate (CaSO₄•0.5H₂O) (85–105 °C) to dihydrate (CaSO₄•2H₂O) as temperature cools down (65–75°C).*



Phases of REE existing in PG

REE compositions of an European phosphogypsum (ppm) by ICP-MS.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
+75 µm	248.0	794.0	108.0	453.0	68.6	16.4	43.5	4.2	15.1
-75+45 µm	223.0	717.0	96.8	406.0	63.0	15.1	39.5	3.9	13.6
- 45 µm	414.0	1160.0	142.0	559.0	81.6	19.6	52.9	5.0	17.1
Overall	289.7	878.6	114.5	469.2	70.6	16.9	45.0	4.3	15.2
	Ho	Er	Tm	Yb	Lu	Sc	Y	TREE	
+75 µm	1.6	4.2	0.2	1.1	0.1		32.8	1791.0	
-75+45 µm	2.0	3.8	0.3	1.1	0.1	0.8	32.4	1618.3	
- 45 µm	1.8	3.4	0.2	0.8	<0.1	<0.5	28.7	2486.1	
Overall	2.1	4.3	0.3	1.1	0.1	<0.5	36.0	1948.0	

La, Ce, Pr, Nd, Sm, Eu, Gd, Dy and Y are found with relatively high concentrations. Other REE are in trace contents (<5 ppm). The content of total REE (TREE) is around 2000 ppm (0.2%). It is noted that the REE are not evenly distributed in the size fractions and the fine fraction (-45 µm) has higher content of REE.

Phases of REE existing in PG

Modal mineralogy of PG sample by the Mineralogical Liberation Analysis (MLA)

Mineral	Wt %				Mineral	Wt%			
	+75 µm	-75+45 µm	-45 µm	Average		+75 µm	-75+45 µm	-45 µm	Average
Gypsum	96.513	99.017	97.094	97.534	Monazite	0.011	0.017	0.119	0.046
Fluorite_mixer	1.249	0.212	0.867	0.784	Miner_REE_mix	0.031	0.015	0.051	0.032
Tremolite	0.334	0.136	0.149	0.211	Aeschnyite	0.000	0.000	0.004	0.001
Celestine	0.114	0.0515	0.376	0.17	Britholite	0.000	0.000	0.003	0.001
Celestine (Ba)	0.009	0.003	0.099	0.034	Other (silicates, Fe-oxide etc.)	1.121	0.493	0.938	0.843
Apatite	0.802	0.055	0.119	0.344	Total	100	100	100	100

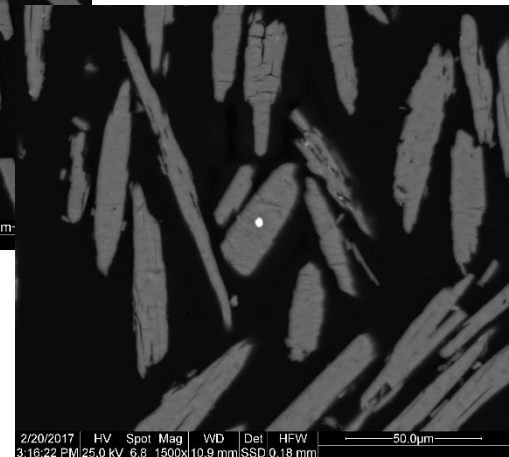
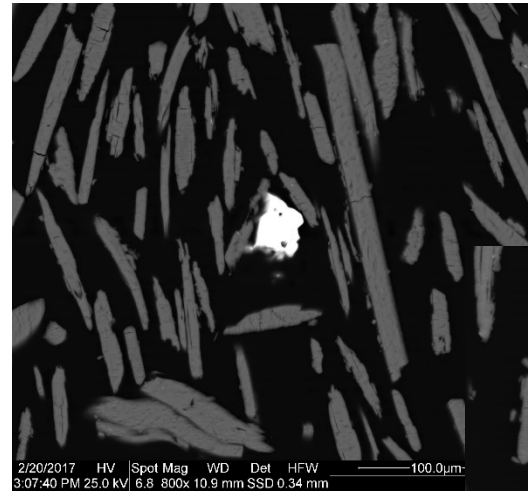
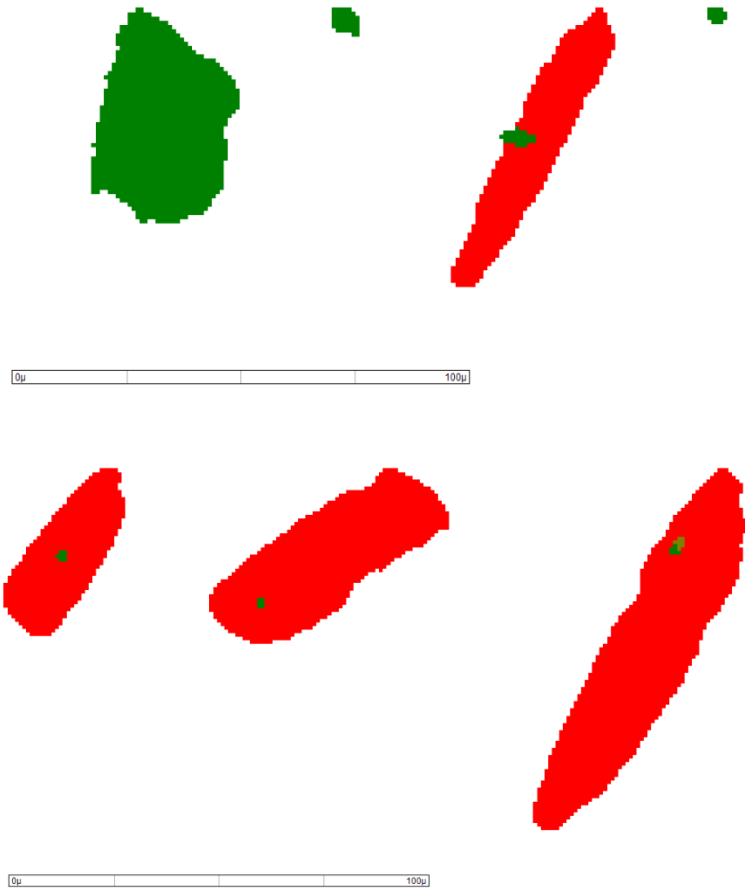
Gypsum ($\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$) is, naturally, the most common mineral (96.5-99.0%). REE minerals are monazite ($(\text{La,Ce,Nd})\text{PO}_4$), and aeschnyite ($(\text{Nd,Ce,Ca,Th})(\text{Ti,Nb})_2(\text{O,OH})_6$) and britholite ($(\text{Ce,Y,Ca})_5(\text{SiO}_4)_3(\text{OH,F})$) in trace amount. Meanwhile, another phase of REE was found by SEM which called “Miner-REEminer-mix”, a mixture of a REE-mineral and some other mineral(s) which can not identified by SEM. But the peaks of Ca, Sr, P and S indicate that these minerals might be gypsum, monazite and celestine etc.



Mineralogical analyses

MLA Images

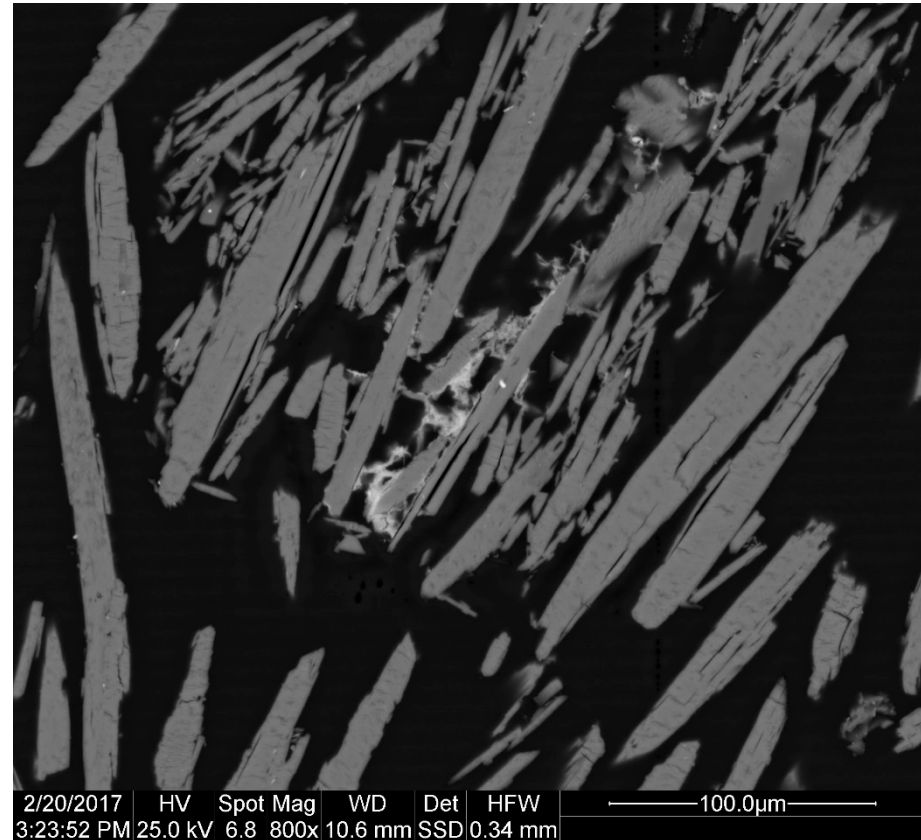
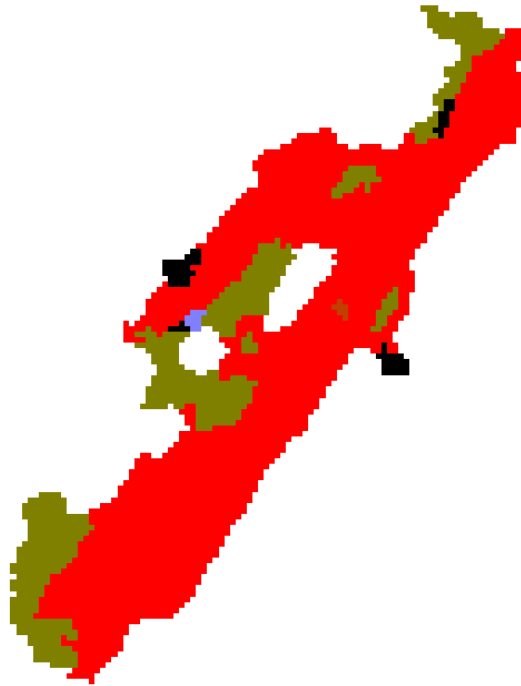
monazite (green) and gypsum (red).
Monazite occurs both as liberated grains and associated (locked) particles with other minerals.



Mineralogical analyses

MLA Images

mineral-REEmineral-mix (light green) and gypsum (red) are associated.



Complex phases of REE existing in PG

Monazite

Miner-REE-mix

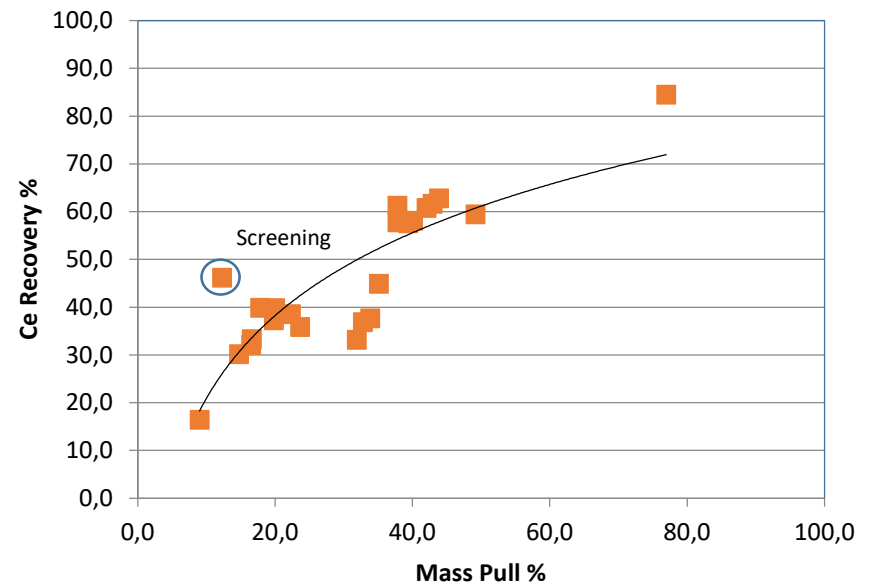
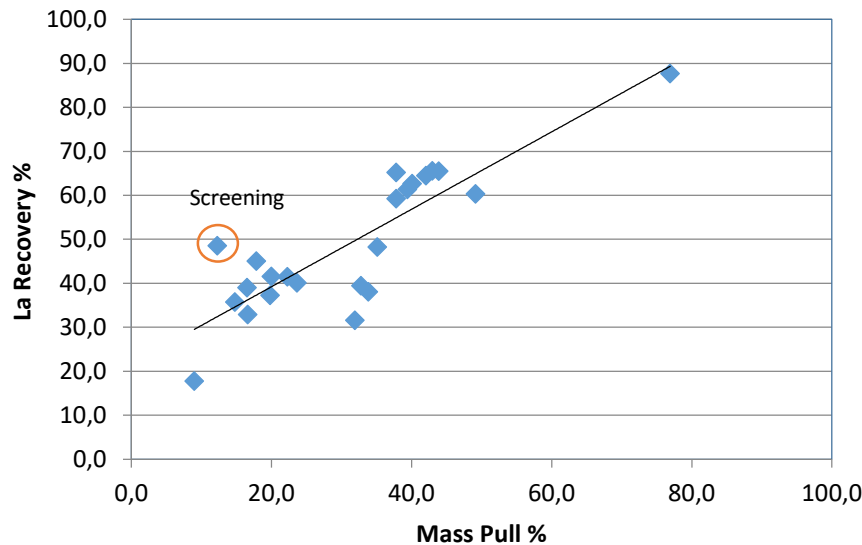


Mineralogical phases

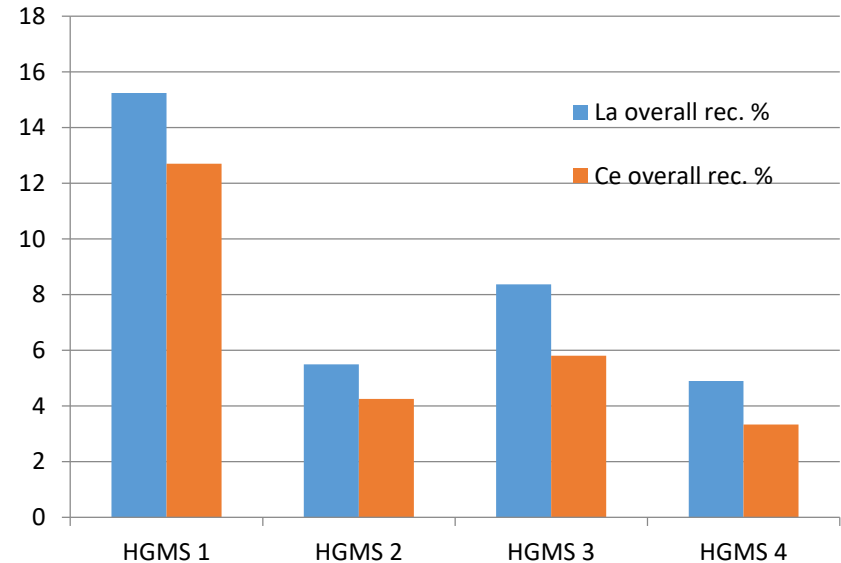
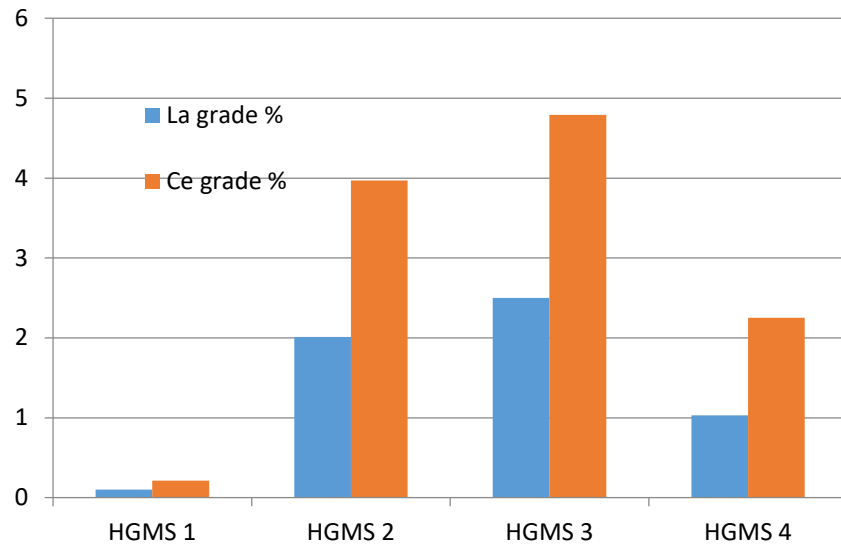
**REE ions substitution for Ca ions in gypsum CaSO_4
or adsorption on the surface**

Feasibility studies of REE enrichment by physical methods

Flotation test work using hydroxamate collectors under different conditions of grinding size, slurry pH and pre conditioning treatment were conducted. Flotation is not an efficient method comparing to screening for the enrichment of REE from the phosphogypsum.



Feasibility studies of REE enrichment by physical methods

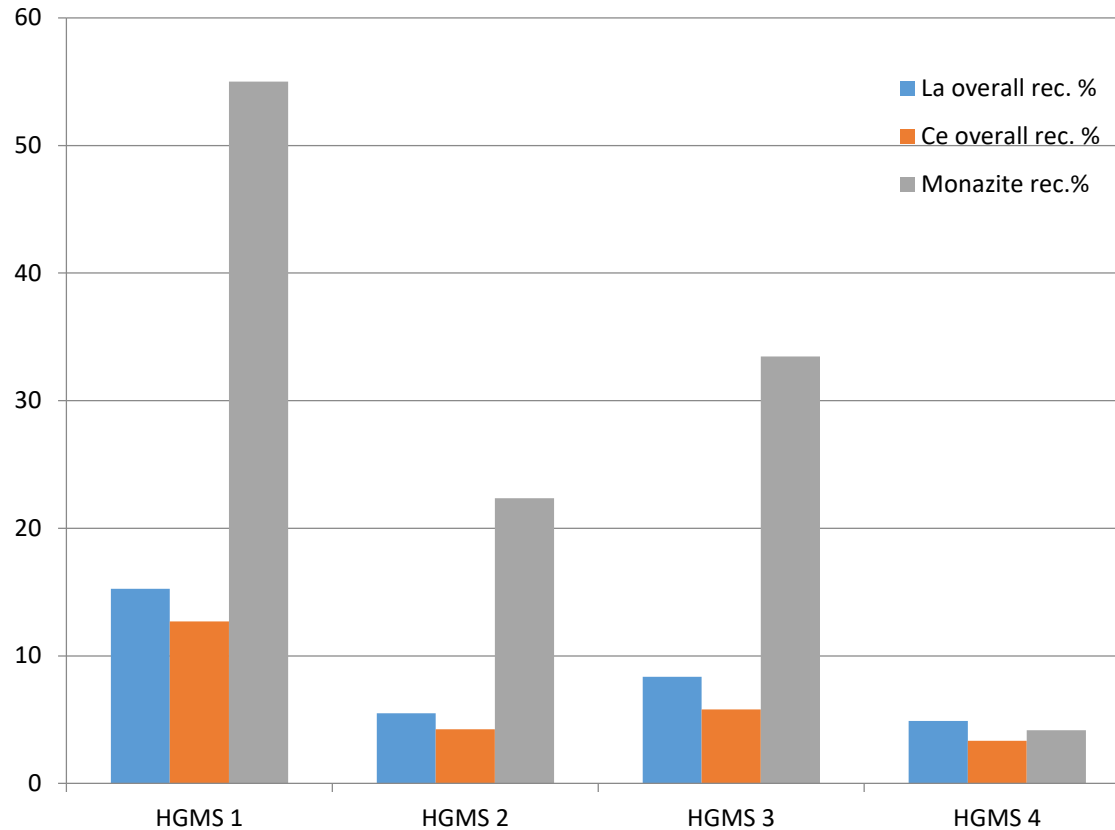


HGMS-1, original PG material with the size of P80=77 μm ; HGMS-2, flotation concentrate; HGMS-3, ground PG-flotation; and HGMS-4, the slimes of -16.7 μm .

Without pre-treatment the REE in the PG was hardly concentrated by magnetic separation, i.e. low concentrate grade in HGMS-1. By pre-treatment, either flotation, grinding-flotation or desliming, the REE was effectively enriched, i.e. high grades of La and Ce were obtained for HGMS-2, HGMS-3 and HGMS-4. In the test HGMS-3 the grades of La and Ce reached 2.50% and 4.79%, respectively. But their recoveries were extremely low, i.e. the overall recoveries are 4.9-8.5% for La and 3.3-5.8% for Ce.

Feasibility studies of REE enrichment by physical methods

Comparison of recoveries of monazite and REE (La, Ce) of HGMS concentrates

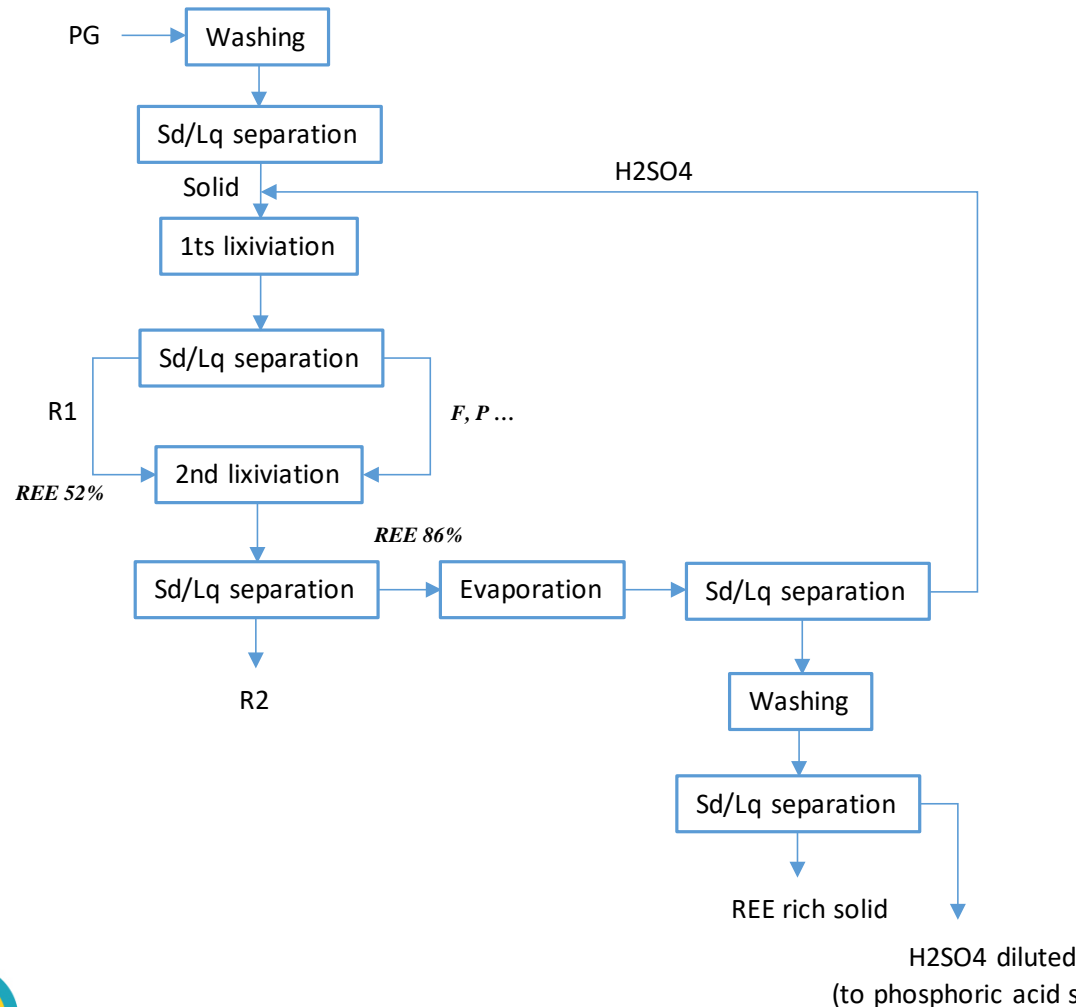


Although quite high recoveries of monazite (22-55%) were obtained, REE (La, Ce) recoveries were still very low.

According to the mineralogical analysis by MLA the main REE mineral is monazite in the sample but the content of monazite is less than 0.05%. Most of REE are carried by gypsum and celestine in the phases of mineral-REE mixtures which are difficultly enriched by physical methods such as magnetic separation and flotation.

Chemical leaching of REE from PG – A Reveiw

A two-step leaching (double sulfuric leaching) method (Hammas-Nasri et al., 2016)



double leaching with a sulfuric acid solution (10%) at 60 °C, for 1–2 h of continuous stirring, with a weight ratio (liquid/solid) about 1.3.

After a first lixiviation (leach) with the acid solution, the residue (R1), obtained after filtration, was **remixed** with the same leach liquor. Then, after a solid–liquid separation, **evaporation** of the final filtrate at 100 °C resulted in a solid crystallization.

Analytical results (XRD, ICP-MS) showed that the first acid leaching allowed essentially to impurities dissolution (such as fluorides and phosphates) and so rare earths enrichment in the residue (about 52%), whereas the second leaching led to the dissolution of such elements in the sulfuric acid liquor (about 50%). The crystallized solid obtained after the evaporation stage corresponds to a mixture of anhydrite (CaSO₄) and monetite (CaHPO₄) phases with a total rare earths enrichment of about 86%. The analytical results showed that a double lixiviation is more efficient than a single one as it allowed a better solubilization of the rare earth elements as well as a further purification of the calcium sulfate which can be used in many types of industries.

Chemical leaching of REE from PG – A Reveiw

Acid leaching of REE using HCl, HNO₃, and H₂SO₄ was compared (Walawalkar et al., 2016):

PG sample from Redwater Fertilizer plant in Alberta, Canada.

Y, La, Ce, Nd, Sm, and Pr were detected in both elemental as well as oxide form by TOF-SIMS (time-of-flight secondary ion mass spectrometry) (a surface-sensitive analytical method);

The results showed that the leaching efficiency of REEs using H₂SO₄ was significantly lower than that of HCl and HNO₃ and the reason is because solubility of gypsum in H₂SO₄ is much lower than in HCl. It was observed that at 80 °C the solubility of gypsum in H₂SO₄ about 40 times lower than that in HCl (0.075 M vs. 0.3 M, respectively) (Azimi et al., 2007, 2008).

Similar results with HCl and HNO₃ were obtained that the average leaching efficiency (only considering REEs with highest concentration in the PG sample: Ce, La, Nd, Sm, and Y) after 20 min is 57% for the case of HNO₃ and 51% for the case of HCl, both at 1.5 M concentration, 80 °C, S/L ratio of 1/8, and 500 rpm agitation. The leaching results showed that 80 °C, 1.5 M concentration, S/L of 1/8 and 20 min are the most suitable operating conditions for three acids.

Chemical leaching of REE from PG – A Reveiw

Z.H. Ismail et al. (2015):

Leaching of different lanthanides using HCl, H₂SO₄ and HNO₃;

PG from Abu-Zaabal Company in Egypt. by The total lanthanides content in the PG was found to be about 480 ppm. Parameters of the acid concentration, the mixing time, and acid to PG ratio (L/S) as well as temperature were tested. The highest leaching efficiency was obtained using 3.0 M HNO₃, at L/S = 3.0, mixing time of 3.0 hr and room temperature (25°C). After three cycle of leaching, the leached out lanthanides from PG was more than 66 %. It was found that the leaching efficiency is different for individual lanthanide and La has the highest leaching efficiency, that is, 73.4% La, 68.0 % Ce, 62.3 % Er, 55.1 % Y and 39.5 % Pr.

Chemical leaching of REE from PG – A Reveiw

Z.H. Ismail et al. (2015):

the addition of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) to nitric acid solution was found to increase the leaching efficiency of lanthanides, e.g. as $\text{Ca}(\text{NO}_3)_2$ concentration increases from 0.0 – 1.0 M in 3.0 M HNO_3 the % L increases from 47.4 to 59.5 % then it remains almost constant with further increase in $\text{Ca}(\text{NO}_3)_2$ concentration up to 2.0 M. The addition of NaNO_3 or $\text{Mg}(\text{NO}_3)_2$ in the concentration range from 0.1 – 2.0 M has no effect on % L.

Preston et al. (1996):

the leaching of the rare earth values from the PG of a South Africa apatite ore by dilute nitric acid was considerably enhanced by the addition of $\text{Ca}(\text{NO}_3)_2$ to the lixiviant, enabling recoveries of up to 85% to be achieved. The mechanisms could be that the addition of calcium ions lowers the concentration of free fluoride ion (it was observed that the concentration of rare earths the leach liquors might be dependent upon the various fluoride-related equilibria), or the high calcium concentration in solution naturally tends to displace the rare earths from the solid phase, in which they are heterovalently substituted for calcium ions.

Chemical leaching of REE from PG – A Reveiw

Kouraim and Fawzy (2014):

Leaching of lanthanides from PG using Nonyl Phenol Ethoxylate (NPE) associated with HNO₃ and HCl; PG sample from processing of Abu-Tartur phosphate ores in Egypt with TREE 1387 ppm highly concentrated in the fine size fraction (< 20 μm);

The total lanthanides in PG was and Leaching of lanthanides from PG was carried out using either free acids HCl and HNO₃ or these acids associated with Nonyl Phenol Ethoxylate (NPE). Based on the experimental results relative to the corresponding free acids the leaching efficiency of lanthanides was **increased by 30 %** using even small concentrations of NPE (>4 % wt/v) at temperature 25 °C. The factors affecting the leaching process were optimized. Also the kinetics of the leaching investigated as a function of temperature.

However, using Nonyl Phenol Ethoxylate (NPE) could cause high risk to the environment such as the concentration in the water should be less than 6.6 ppm. This is the drawback of the process.

Chemical leaching of REE from PG – A Reveiw

El-Didamony et al., 2012, 2013:

Treatment of PG using suitable organic extractants was investigated using a PG sample from Egypt.

Different types of organic extractants, such as Tributylphosphine (TBP), trioctyl phosphine oxide (TOPO), triphenyl phosphine oxide (TPPO), and di-ethyl-hexyl phosphoric acid (DEHPA), dissolved in kerosene were experimented to investigate the effect of different solvents on the removal efficiency of radionuclides and REE from PG. Using 0.1 M from each solvent, the processes were carried out at room temperature (25 °C); contact time = 1 h; and liquid: solid ratio = 1. The results showed that, **the highest E% of REE was obtained by using TBP**. By the addition of TBP, 46% of REE was removed.

The leaching conditions for treatment of PG using TBP in kerosene optimized by experiments are: contact time of 2 h; concentration of TBP in kerosene 0.5 M; liquid: solid ratio 1:1 (TBP in kerosene vol./PG wt.); temperature of 55 °C (depending on the vapor pressure of the used solvent). At the conditions leaching efficiency of **68.5% REE** was obtained.

The method was improved by using mixtures of TBP and TOPO (trioctylphosphine oxide) in kerosene instead of pure TBP mixtures. In this case the recovery of the rare earths **equalled 80%**.

Chemical leaching of REE from PG – A Reveiw

Reid, 2017:

The effect of **microwaving PG** as the pre-treatment on acid leaching was investigated. It was found that microwave radiation results in the dielectric heating of water molecules in the crystals and vaporization, causing the formation of breaks and pores in these particles as the vapour escapes.

Todorovsky et al., 1997:

The influence of **mechanoactivation by grinding** on the overall solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and of phosphogypsum **in water and in diluted acids** (10% HCl, 7% H_2SO_4) as well as on the leaching of rare earths from phosphogypsum have been studied. The PG sample was from Kola apatite processing. The REE content was 3700 ppm including La, Ce, Pr, and Nd. The grinding is performed in a centrifugal ball mill in air and in suspension with the acids. The results showed that the leaching of rare earths from phosphogypsum was **improved by the activation in air, water and acids** but additional experiments are required to give a fully satisfactory explanation of the results.

Laurino and Mustacato, 2015:

REE recovery from phosphogypsum by leaching using a patented leaching solution (PX- 107) followed by REE extraction with a polymer (Chelok®) was reported. PG sample was milled using a rod mill for 10 minutes. The leached REE was increased after being milled for almost all the REE.

Chemical leaching of REE from PG – A Review

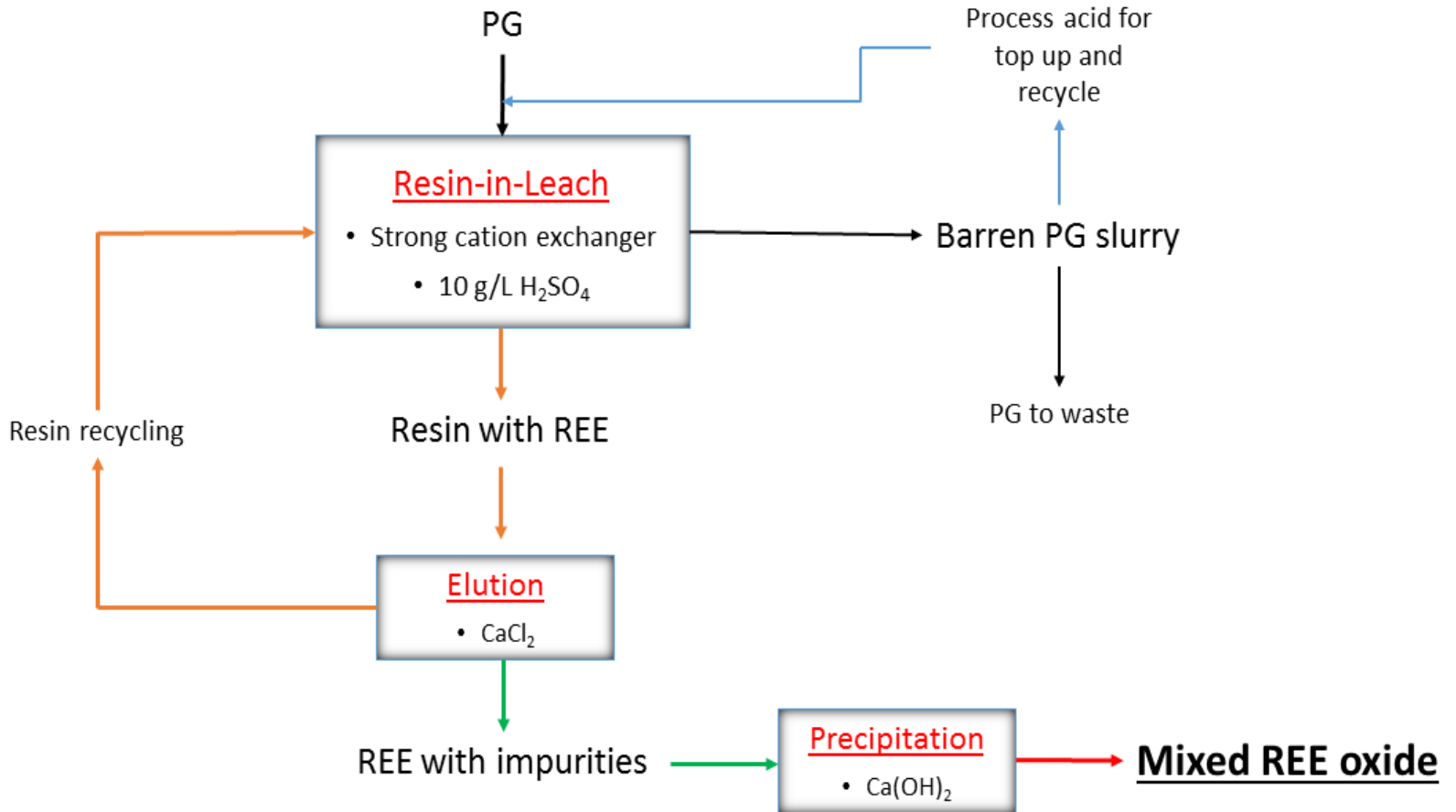
Padayachee

The use of ion exchange resin-in-leach

The optimization of the process for processed PG was feasible

Koopman and

investigated the use of ion exchange resin for the recovery of REE from phosphoric acid. They found that with 25% gypsum. Dependent on the percentages of exchange resin, hydrochloric or nitric acid solutions.



Summary

1. As the phases of REE in PG are complex, being carried by monazite and mineral-REE mixtures, and in the form of REE ions substitution for Ca ions in gypsum and surface adsorption, enrichment by physical methods is difficult.
2. Direct leaching with mineral acids or some organic agents for extraction of REE from PG has been studied and indicated it is technically feasible;
3. The PG reprocessing for the extraction of rare earths (REE) and other valuable elements has not been industrially realized. The economic infeasibility could be one of the main reasons:

Some other trace elements such as Strontium (Sr), Barium (Ba), Silicon (Si), Phosphorus (P), Iron (Fe), Aluminium (Al), Titanium (Ti), Uranium (U), and Thorium (Th) etc. are contained in PG which considered one of the main environmental concerns. For safe disposal or utilization of PG the removal of these impurities needs to be considered.

PG uses: agriculture; roads; construction; landfill

Radiation safety

Acknowledgement

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Thank You for your Attention!

