



**Mineral and Energy  
Economy Research  
Institute**  
Polish Academy of Sciences

# Phosphogypsum - is it raw material or waste in Polish conditions?

Andrzej Jarosiński

Mineral and Energy  
Economy Research Institute  
Polish Academy of Sciences





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# Suitability of secondary raw materials

Determination of the suitability of secondary raw materials for a given production is assessed according to the following criteria:

1. technological (material properties such as chemical and mineral composition, humidity, mineral hardness, etc.)
2. economic and technical - resources (amount of waste), technical delivery possibilities, delivery conditions and others.

After recognizing the amount of resources of raw materials, technological criteria first decide about their use in a given technology.

In this speech, I will focus on some issues related to phosphogypsum (PG) and the question whether phosphogypsum in Polish conditions should be treated as waste or secondary raw material based on the example of recovery of rare earth elements.

# Phosphogypsum

The phosphogypsum is waste obtained in process of phosphoric acid production. It consists of calcium sulfates with different hydration ratio and traces of sulfuric, phosphoric and fluorosilicic acids as well as their salts and rare earth elements and radioactive elements.

The process of producing phosphoric acid is described by the following summary reaction:



where: n – amount of hydration waters connected with calcium sulfate.

According to technology used, hydration ratio is changing from hemihydrate to dihydrate and contents of rare earths from 0.6 to 0.3% respectively.

Raw materials are apatites and phosphate rocks, which in the EU are classified as critical raw materials.

Domestic demand for phosphate raw materials in total is covered by imports. Phosphate concentrates are mainly imported from Morocco, Tunisia, Togo and Syria, while the apatites come from the Kola in Russia.

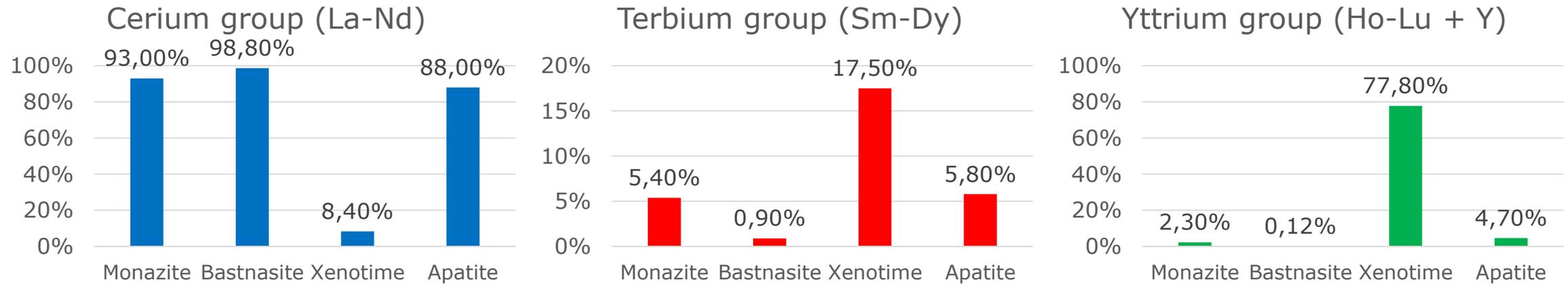
The processing of these raw materials involves a number of ecological problems.

# Share of rare earth elements in raw materials deriving from various deposits

Origin	Kind of phosphate raw material	Share of REE (% Ln <sub>2</sub> O <sub>3</sub> )
<b>Kola peninsula</b>	Apatite	0,8-1,0
<b>Florida</b>	Phosphate rocks	0,06-0,29
<b>Algeria</b>	Phosphate rocks	0,13-0,18
<b>Morocco</b>	Phosphate rocks	0,14-0,16
<b>Tunisia</b>	Phosphate rocks	0,14
<b>Al-Mahameed (Egypt)</b>	Phosphate rocks	0,028
<b>Lao Kai (Vietnam)</b>	Apatite	0,031

Among the raw materials for the production of phosphoric acid, apatites are the richest in rare earths (RE).

# Content of rare earth elements of the cerium, terbium and yttrium groups in various minerals



This data indicates that apatite is rich both in the REE of the cerium group and other groups. For these reasons, apatite is one of the alternative raw materials of rare earths. In general, prices of REE raw materials are higher for raw materials rich in elements of yttrium and terbium.

# Content of radioactive elements in PG

Element	Typical content in phosphate phosphogypsum	Maximum values in PG	Apatite (PG) derived from Kola peninsula	Maximum values in apatite (PG)
<b>K-40</b>	60	300	146	300
<b>Ra -226</b>	390	1100	41	85
<b>Th -232</b>	20	160	15,5	30

In general, apatite concentrates contain REE and are poorer in radioactive elements compared to phosphate rocks.

The phosphogypsum chemical-mineral composition depends on:

1. the initial composition of the used phosphate rocks or apatite,
2. the method used for the production of extraction phosphoric acid,
3. the level of impurities in the liquid phase (in the acid production process),
4. the effectiveness of washing the sludge (phosphogypsum) on the filter.

It is estimated that 145 million tons of PG are generated per year, of which only a maximum of 5% is utilized. In Poland, about 2 million tonnes of PG are generated annually.

# Plants producing phosphoric acid in Poland

1. Zakłady Chemiczne „Police” S.A.,
2. Gdańskie Zakłady Nawozów Fosforowych „Fosforyty” S.A.
3. Zakłady Chemiczne „Wizów” S.A. till 2006
4. Zakłady Chemiczne „Alwernia” S.A.

The first three plants produce "extraction phosphoric acid", while Z.Ch. "Alwernia"- "thermal phosphoric acid".

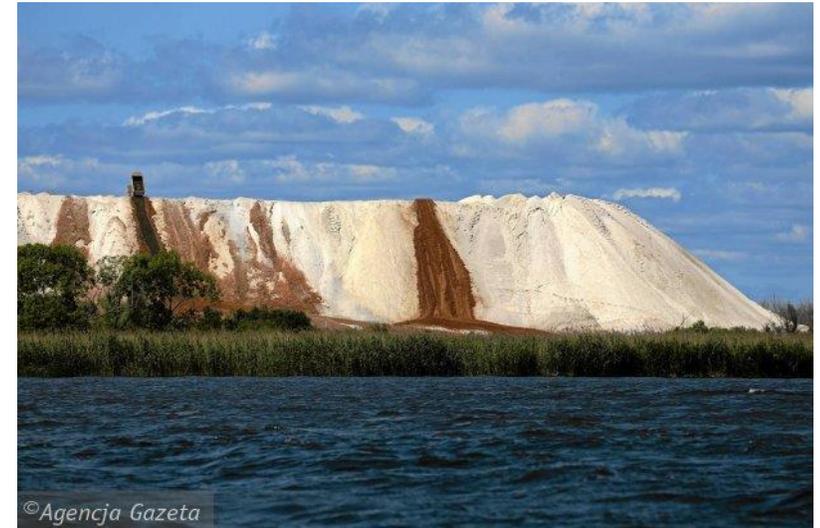
At landfills in Poland in 2016, about 140 million Mg of phosphogypsum was stored.

Plants	Area [ha]	Amount of waste [mln Mg]	Processed raw material
ZCh. „Police”	295	113	Phosphate rocks and apatites
GZNF	26	22	Phosphate rocks
ZCh. „Wizów”	-	5	Apatite

# Z.Ch. "Police" - landfill

- The landfill site occupies 295 ha, annual growth of the heap - about 3 ha
- Amount of collected waste (phosphogypsum together with energy and other waste, phosphogypsum deriving from processing apatite as well as phosphate rocks)
- Monitoring of leachate is carried out
- The amount of leachate - about 2 million m<sup>3</sup> / year
- Total loads (SO<sub>4</sub><sup>2-</sup>, F-,P) – 6,5 ·10<sup>3</sup> Mg/year
- pH of leachate -3,5- 4
- Surface water monitoring

The lack of selective storage of apatite caused loss of about 2,000 Mg of Ln<sub>2</sub>O<sub>3</sub> (Ln= La, Ce, Pr, Nd ....) per year and makes their recovery in the future impossible.



# Gdańskie Zakłady Nawozów Fosforowych „Fosforyty” S.A.

- The landfill site is located in Wiślinka near Gdańsk (PG from processing of phosphate rocks).



# Z.Ch. "Wizów"

Z.Ch. "Wizów" is one of the inactive plants, where approx. 5 million Mg of apatite phosphogypsum have been deposited, including about 20 000 Mg rare earth.

The heap is practically devoid of any troublesome in processing of the thorium.



# Concepts of limiting the amount of phosphogypsum:

1. production of nitrophosphates (phosphates are dispersed in nitric acid),
2. partial or total reduction of the production of phosphoric acid.

The following options are considered:

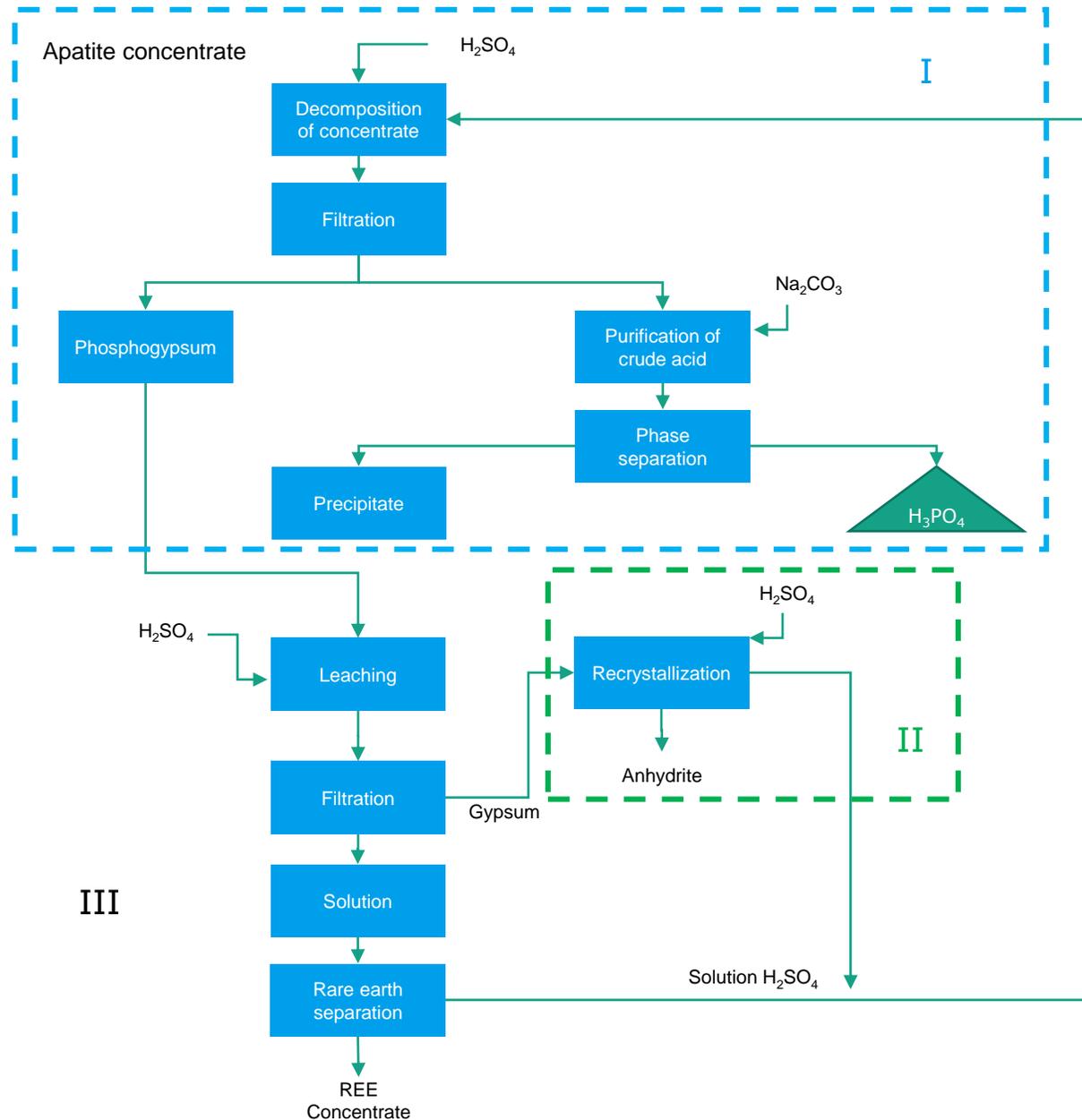
- a) 50% of the demand for phosphoric acid will come from import and 50% will come from domestic phosphoric acid plants.
- b) Complete abandonment of acid production - 100% import.

# Examples of contemplated conceptions of PG utilization in Polish conditions



No.	Conception
1	Processing of PG for binder and gypsum elements, use in the cement industry as a mineralizer or cement setting time regulator, anhydrite cement (self-leveling floor layers) and the like.
2	The use of PG in the production of sulfuric acid and cement clinker.
3	Manufacture of fertilizer chalk and ammonium sulphate by converting PG with ammonia in the presence of CO <sub>2</sub>
4	The use of phosphogypsum in road engineering as it blends with fly ash.
5	Obtaining of gypsum binders with simultaneous recovery of rare earth elements (REE)
6	Preparation of anhydrite cement from apatite phosphogypsum with simultaneous recovery (REE) and phosphates.
7	Investigation on the possibilities of producing fertilizers based on urea and phosphogypsum adducts

# Schematic diagram of the complex processing of apatite



In order to obtain a binding material, it is necessary to remove phosphates and also to significantly reduce REE. The purpose is achieved by treatment PG with solutions of sulfuric acid.

## Flowsheet of complex processing of Kola apatite concentrates on phosphoric acid.

- I – main process ( $H_3PO_4$ )
- II – process associated with obtaining anhydrite II
- III – main process associated with obtaining anhydrite II and rare earth elements concentrate (circular economy)

# Remarks

Based on my own research and literature analysis, the following remarks arise:

1. from the technological point of view, apatite phosphogypsum from both the hemihydrate and dihydrate processes is useful for the recovery of rare earths,
2. phosphogypsum resources on the ZCh. "Wizów" amounts to about 5 million Mg, including 20,000 Mg REE,
3. the proposed technologies may be waste-free in connection with the working installation of apatite decomposition system with sulfuric acid
4. (no possibility today),
5. preference is given to obtaining a pre-concentrate by concentrating sulfuric acid after leaching
6. phosphogypsum is a material with a different chemical and mineral composition,
7. methods of PG utilization should take into account their variability of properties.

# Remarks (continued)

8. apatite PG is an alternative secondary raw material of rare earths, which is classified as critical raw materials,
9. average content of rare earth elements in the apatite phosphogypsum is 0.6% or 0.4% Ln<sub>2</sub>O<sub>3</sub> (depending on way processing phosphate rocks) and is relatively rich in elements of both the yttrium group and the terbium group,
10. the advantage of phosphogypsum from ZCh. "Wizów" in contrast to phosphogypsum of phosphate origin is the low content of radioactive elements,
11. the presence of impurities in both apatite and phosphate phosphogypsum eliminates their direct application to the production of gypsum and anhydrite binders. These impurities disrupt the process of dehydration and re-crystallization of gypsum and, as a consequence, reduce the mechanical properties of calcium sulphate based adhesives,
12. REE recovery methods developed in Poland make it possible to obtain concentrates comparable to concentrates obtained on an industrial scale, eg from monazite or bastnaesite raw materials,
13. obtaining of REE pre-concentrate from phosphogypsum includes: leaching of PG in purpose pass of REE into solution, precipitation of REE pre-concentrate, e.g. by concentration of acid after leaching and separation of rare earth hydroxides from the concentrate of the so-called hydroxide method,
14. above all, a method should be considered, including the production of anhydrite and the use of sulfuric acid after the process of recrystallization of gypsum to anhydrite and sulfuric acid after separation of the REE concentrate (circular economy).

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Thank you for your  
attention