

Potencial management of waste phosphogypsum with particular focus on recovery of rare earth metals

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Phosphogypsum is a noxious industrial waste contributing to global environmental and economic problems. This publication focuses above all on phosphogypsum resulting from the processing of apatite as a phosphorus bearing compound, since it contains considerable amounts of lanthanides due to its magma origin. The possibilities of its waste-free processing are large, however they require the application of suitable technologies, frequently expensive ones, and allowing for the individual characteristics of the given waste. The research works conducted so far confirm the possibility of applying phosphogypsum for the recovery of lanthanides, and the process enhances the removal of remaining impurities, thanks to which the purified calcium sulphate (gypsum) may find application for the production of construction materials.

Keywords: phosphogypsum waste, phosphogypsum conversion, rare earth elements, environmental threats.

INTRODUCTION

Phosphogypsum is a by-product generated during the process of obtaining phosphoric acid with the wet method. Depending on the conditions, in which the process is conducted, calcium sulphate is present in the form of anhydrite, hydrate and dihydrate, and its participation in the final product amounts to 1:4 ($H_3PO_4/CaSO_4$ mass ratio)¹. The most important threats connected with phosphogypsum storage, include the possibility of leaching dangerous substances (phosphates, fluorides, heavy metals, radioactive elements) that constitute a threat to the fauna and flora of local water bodies². A considerable amount of waste generated during the process as well as the problem of its management resulted in gradual discontinuing of domestic production and a partial replacement by importing H_3PO_4 . In 2012 the costs of phosphogypsum waste storage in Poland amounted to 10.70 PLN/Mg, which leads to the amount of PLN 18 million per annum, considering the current scale of production. Projections for the following years do not indicate a decrease in the amounts of generated phosphogypsum waste. On the contrary, an increase of as much as 10 per cent is anticipated within the next 10 years³.

At present only Grupa Azoty Zakłady Chemiczne "Police" SA, a chemical plant near Szczecin, is involved in processing of phosphorus bearing raw material by applying both phosphorites and apatites in the production of phosphoric acid with the extraction method. Although production has been terminated at both Zakłady Chemiczne "Wizów" S.A., a chemical plant near Bolesławiec, and Gdańskie Zakłady Nawozów Fosforowych "Fosfory" S.A. (a plant in Gdańsk), the plants have accumulated significant amounts of phosphogypsum waste, which at present are stored for recultivation as refuse heaps. However, only a heap in Zakłady Chemiczne "Wizów" S.A is fully created from waste after apatite processing and is the main point of our research interest.

Any efficient method of phosphogypsum neutralization during the current production has been found until today – therefore, it is justified to search for alternative methods of management of the existing and ever grow-

ing phosphogypsum heaps in Poland. Processing the phosphogypsum waste is undoubtedly beneficial, as it contributes to the natural environment protection and additionally permits to obtain valuable secondary raw materials, such as rare earths concentrates, which have been widely applied in metallurgical, glass, motor, and even pharmaceutical industries. Since 2010 import of lanthanides has become more and more difficult, due to the situation on the global raw material market. China, the principal potentate in this field, controlling as much as 31 per cent of global resources of these metals, dramatically decreased their export at the same time increasing a unit price and the shipment costs. Such actions have resulted in protests from the US and Russian governments and EU representatives. Petitions have been sent to the World Trade Organisation against China's actions, which, however has not bring about the intended effect. In 2010 the demand for the rare earths reached 134 000 Mg, however China exported only 8 000 Mg annually in spite of the extraction level ensuring continuous production⁴⁻⁶. As a result, the lanthanides reserves have dropped dramatically, reducing many producers' production capacity.

LANTHANIDES APPLICATION

The research on alternative raw materials for Lanthanides production have been applied among others in modern technologies, the so-called high-tech. Cars produced at present, e.g. Toyota Prius, may contain in their mass up to a dozen or so kilograms of rare earths, which exert a beneficial influence on metallic elements enhancing their hardness, crack resistance and general wear. In cars mechanics REE (Rare Earth Elements) compounds are applied in the production of electrical engines (hybrid NiMH battery – contains lanthanum and cerium additives; engine – contains terbium, dysprosium, neodymium, praseodymium), vehicle catalysts (lanthanum, cerium), UV windscreens (cerium), front light glasses (neodymium) and LCD screens (europium, yttrium, cerium)⁷⁻⁸. Nanoparticles of cerium borate, with a diameter of 50 nm, are applied as oil additives, thus

beneficially influencing the coefficient of friction and anti-wear properties of oil⁹.

In metallurgy REO (Rare Earth Oxides) are widely applied to enhance an alloy resistance to welding. They cause spheroidization of carbides (combining good casting properties of cast iron and plasticity of cast steel¹⁰), which as a result enhances the quality of a produced alloy. Rare earth elements are also added to the material of rolls used in the process of steel rolling thanks to which the steel ignition point is lowered, and the rolls become more resistant, not only to mechanical damage but also to high temperature. In this case REO do not affect the phase system of carbides, but only reduce their need in steel¹¹. It has also been confirmed that metals doped with cerium compounds (Ce_2O_3 , $\text{Ce}_2\text{O}_2\text{S}$) or lanthanum compounds (LaAlO_3) have a beneficial impact on resistance to abrasion, cracking, plastic deformations and scratches¹²⁻¹³. Investigations are carried out on the possibility of replacement of beryllium admixtures with yttrium compounds, which in magnesium alloys enhance resistance to oxidation, and in zinc alloys the tensile strength and elongation resistance are improved¹⁴.

Yttrium oxysulphides as luminophores have been applied in the production of colour TV sets and flat panel displays, electronic thermometers, or fluorescent lamps¹⁵⁻¹⁶.

Lanthanum carbonate has been applied in biotechnology and medicine, and thanks to its ability to bind phosphates, it may be applied while treating hyperphosphatemia, a chronic kidney disease, leading to the disturbance of calcium-phosphate regulation. The medicament known on the market as Fosrenol® has been considered safe, and additionally, it has been proved that it has a protective influence on the osseous system¹⁷⁻¹⁸. It was discovered, while conducting previous research work, that also dysprosium compounds possess protective properties with regard to the osseous system – osteogenic effect on bone marrow cells¹⁹.

In China investigations have been carried out on the properties of HGCE fibres containing such ingredients as gelatine and a cerium additive. Improved hydrophobic and mechanical properties of the fibre have been confirmed, and their smooth surface, compact structure, antibacterial properties and good biocompatibility, permit to assume that these fibres may find an application in biomedicine²⁰.

THE USE OF WASTE PHOSPHOGYPSUM IN THE WORLD

Among the studies conducted so far on waste phosphogypsum utilization, the wide possibilities of its use in construction materials: brick, Portland cement and clinker, should pay attention. Such solutions mainly use waste phosphogypsum, as well as combinations of phosphogypsum and granulated blast-furnace slag with limestone³⁴. In most cases, phosphogypsum requires preliminary treatment, aimed at reducing the content of P_2O_5 and fluorine compounds, which could adversely affect the strength of the final products.

In some research, dehydration and recrystallization was used to remove impurities from phosphogypsum. These actions allow to strengthen the microstructure

of the bricks, which significantly affect their strength. Bricks produced from phosphogypsum autoclaved in lower temperatures, in relation to the bricks obtained from the combination of phosphogypsum autoclaved in high temperature, were characterized by improved compressive strength, temperature variations or weight loss²².

In China, using waste phosphogypsum for preparation of adobe bricks were proposed. The “green bricks” were composed of phosphogypsum (75%), river sand (19.5%), Portland cement (4.0%) and slaked lime (1.5%). Proposed process of “hydration-recrystallization” consist of the following steps: formation of the bricks at a pressure of 20–40 MPa, wet curing, drying at 180°C for dehydration of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$, immersion in water for recrystallization of CaSO_4 and drying. Very good results on compressive strength, water-saturated compressive strength and bending strength were observed in prepared bricks³¹.

In Turkey, where the annual production of phosphogypsum reaches 3,000,000 Mg the use of waste as an additive for stabilization of the dried bricks was proposed. Such operation positively affects the resistance to softening, when exposed to water and reduces the shrinkage during drying. The best results were observed with the addition of 25% of phosphogypsum. Additionally produced material does not negatively affect the environment³⁰.

In the technology of Portland cement production, phosphogypsum was used as a retarder, as well as a factor lowering the firing temperature: the addition of 10% of phosphogypsum helped to reduce the process temperature from 1470°C to 1200°C, which significantly affects the growth of plant productivity^{32, 33}.

Russian patent also propose using purified phosphogypsum in the production of building materials. After treatment of phosphogypsum with sulfuric acid, rare earth metals are precipitated from the resulting solution by the introduction of oxalic acid. After neutralization with sulfuric acid solution to a pH value of 1.0–2.5, the oxalate residue is separated from the mother-liquor solution, and is rinsed, dried and calcined. After separation from the sulfuric acid solution, the solid phosphogypsum phase is also rinsed with water⁴⁵.

The use of waste phosphogypsum in agriculture is also reported. As a mineral additive to feed products, phosphogypsum increase the phosphorus content in bones of hens and in egg shells. It is preferred to use 1% addition of phosphogypsum. These studies were carried out on the waste from the production of wet phosphoric acid, but with the Tunisian phosphate³⁵. In the Chinese patent, 5–15% addition of phosphogypsum to mineral fertilizer production was proposed. Other components of the fertilizer were as followed: active medical stone (10–30%) subjected to activating treatment, active phosphorus slag (15–60%) subjected to activating treatment and raw materials such as phosphogypsum, amino acid (5–10%), diatomite, citric acid (5–10%) and asparaginic acid. The mineral fertilizer is reported to have multifunctional properties like: complete in nutrition, good rapid/sustained-release effects, improved fertilizer utilization rate, low consumption of fertilizer and water and improving saline alkali soil⁴⁶.

REVIEW OF METHODS APPLIED TO RECOVER RARE EARTHS

In nature, lanthanides occurred in the form of numerous minerals, but their concentration in the ore is low. Resources in Poland consist of 1.55% REO (Rare Earth Oxides) and are located in Bogatynia, while less rich deposits are located near Szklarska Poręba in which content of REO is up to 0.55%. The most important minerals include Monazite (Ce, La)PO₄, Bastnaesite (La, Ce)CO₃F and Xenotime (Y)PO₄. Pretreatment of Monazite is carried out by the gravitational, electromagnetic or electrostatic separation of Monazite concentrate from sand and other impurities. The obtained concentrate is treated in an alkaline or acidic process, that involves heating with 70% NaOH or 93% H₂SO₄ respectively, followed by leaching with water. The precipitated hydroxides or dissolved sulfates of lanthanides and thorium are separated by filtration. In order to concentrate Bastnaesite ore, flotation method is used. The concentrate is then treated with 10% HCl. Insoluble material, where content of REO is around 70%, may be used as a commercial product, or can be subjected to further thermal processing and dissolving in 10% HCl⁴⁰⁻⁴².

This publication focuses above all on phosphogypsum resulting from the processing of apatite as a phosphorus bearing compound, since it contains considerable amounts of lanthanides due to its magma origin. The method of phosphoric acid production is also an important aspect, as in the hemihydrate method almost 100 per cent of rare earth elements are transferred to phosphogypsum waste, whereas in the dihydrate method – only 75 per cent².

The available literature provides information on the possibilities of lanthanides recovery only from phosphogypsum or sediments formed during phosphoric acid production³⁶. The method for extracting lanthanides with 0.14 mol/dm³ HNO₃ directly from apatite ore or granite rocks is also known. However, the process appears to be economically disadvantageous due to the ore pollution, and significant quantities of phosphorus compounds important for phosphoric acid industry³⁷. An alternative source of rare earth metals are also electro-waste, however, the technologies of their recovery are still under investigation^{38-39, 43}.

In Poland the research works on apatite phosphogypsum were initiated at the end of the 1980s at Wrocław University of Technology and Cracow University of Technology. The possibility of isolating impurities from calcium sulphate was analysed, its subsequent application as a secondary raw material as well as the recovery of rare earths. A few attempts were carried out with the intention of extracting lanthanides from phosphogypsum, among others by applying concentrated sulphuric acid, nitric acid or a mixture of both. The effect of leaching is based on the phase transition of hemihydrate to hydrate through the process of calcium sulphate dissolution and its subsequent crystallization. Phosphogypsum free from impurities was then subjected to filtration, and the filtrate was directed for further purification. The following methods of isolating rare earths have been identified:

– precipitation methods, which make use of the fact that in spite of their low concentration lanthanides can

precipitate as sparingly soluble compounds, primarily hydroxides, oxalates or double sodium-lanthanum sulphates (Fig. 1);

– extraction methods in liquid-liquid systems with the participation of an organic phase, e.g. Rukanol PIO (approximately equimolar mixture of mono-2-ethylhexylphosphoric and di-/2-ethylhexyl-/phosphoric acids), NPPA acid (equimolar mixture of mono- and di- esters of nonyl phenyl phosphoric acid) (Fig. 2);

– crystallization methods of calcium sulphate with a simultaneous inclusion of rare earths into calcium sulphate crystal through concentration^{1, 21}. The conducted research confirmed a better efficiency of leaching lanthanides from phosphogypsum with the application of nitric acid (even as much as 90 per cent) than in the case of sulphuric acid (~ 60 per cent). However, the other analyzed process involved the generation of additional waste in the form of calcium nitrate solution, for which no application was found. The method of concentration by removing water turned out to exert a beneficial influence on the isolation of rare earths from phosphogypsum pulp. However the incurred costs related to heating of the solution dominated among production costs, which rendered the process unprofitable. As far as the applied extractants were concerned, the best effects were observed for Rukanol PIO diluted with kerosene.

Extraction of phosphogypsum with nitric acid was also proposed by Szczecin University of Technology. Phosphogypsum was dissolved until a saturated solu-

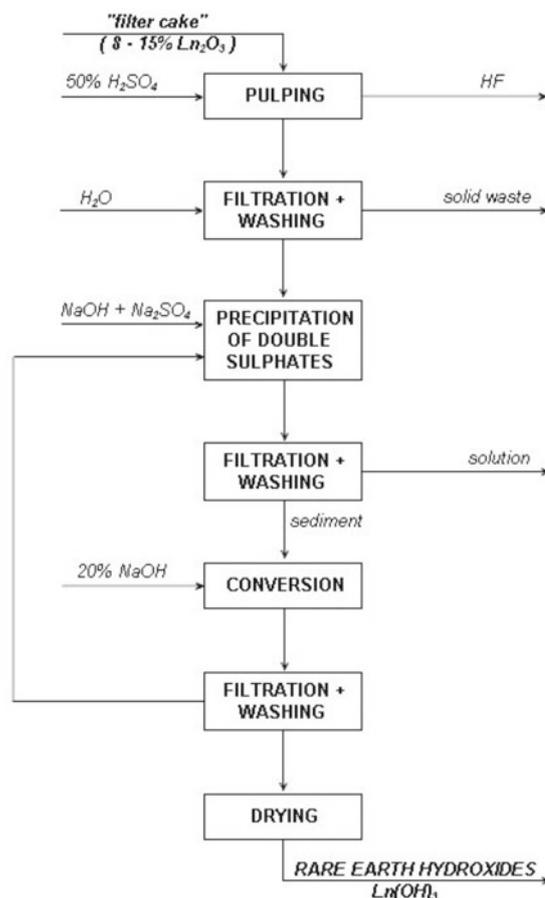


Figure 1. Precipitation method of isolating rare earths in the form of hydroxides²¹

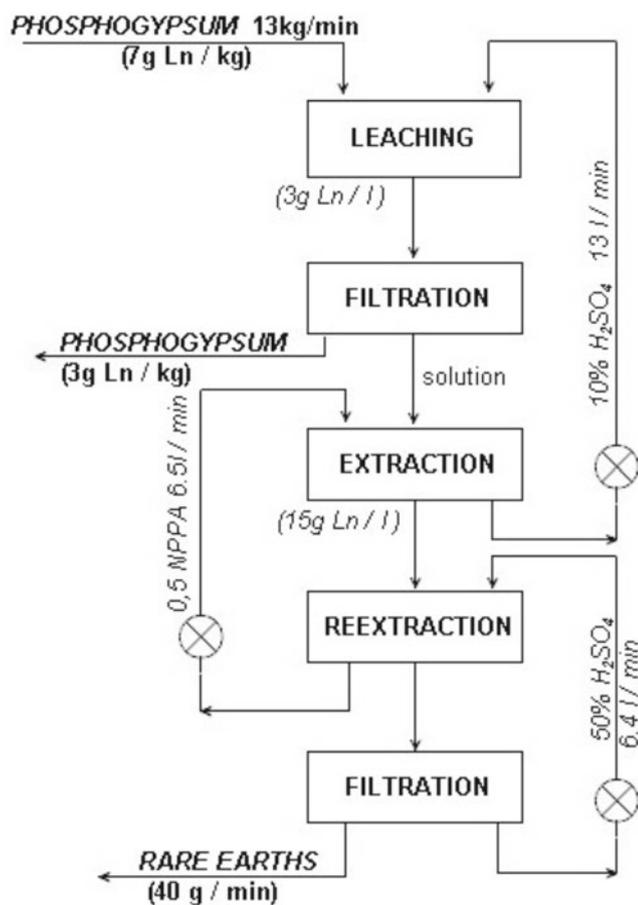


Figure 2. Extraction method of isolating rare earths with the application of NPPA extractant²¹

tion of calcium sulfate in dissolution temperature was obtained. Then α -hydroxy acid was added, which results in the formation of complexes of rare earth elements. After lowering the temperature to 20–25°C, calcium sulphate crystallizes from the solution. The calcium sulfate crystals were separated from the solution by filtration. The remaining solution of nitric acid containing rare earth complexes, were concentrated by recycling it into multiple phosphogypsum dissolving⁴⁴.

The worldwide research focused also on the possibility of applying solvent extraction with the use of organic solvents, including a D₂EHPA extractant (diethyl hexyl phosphoric acid) dissolved in kerosene. This compound may be applied in an extremely acidic environment, and the best effects of the separation were observed with a higher concentration of the extractant (max 2 mol/l), larger coefficient of the liquid/solid body phase distribution (ratio 4:1), stoichiometric coefficient of H₂SO₄ to CaO equal to 1.05, lower temperatures (max 343 K) – exothermic reaction and a higher concentration of present phosphoric acid. Leaching efficiency increased from 32 per cent to 75 per cent, whereas by analogy the P₂O₅ content changed from 5 per cent to 25 per cent, which resulted in lower energy costs²³. Literature on the subject also mentions possible applications of a D₂EHPA solvent together with HNO₃ for the formation of a liquid membrane in which the inner phase is composed of the following solutions: HCl, HNO₃ and NaOH. These research works helped to determine the optimal conditions to conduct the process of neodymium extraction in 4.0 mol/l HNO₃, the voluminal ratio of the

solution in the membrane to the expelled liquid equal to 1.0, the concentration of the D₂EHPA extractant equal to 0.100 mol/l in the recirculated phase, and pH 4.60 in the feeding phase. Under such optimal conditions for the process one achieved the recovery of 92.9 per cent neodymium within 75 min.

A significant benefit for such a process is the possibility of conducting leaching on both concentrates and purified substances²⁴. Also the application of the mixture of D₂EHPA (di-(2-ethylhexyl)phosphoric acid) with TBP (tributylphosphate) in kerosene results in the recovery of 89.9 per cent of lanthanides with the purity of 96 per cent. The reaction consists in filtering off a residual phosphoric acid, separating radioactive compounds through their precipitation with oxalic acid and removing fluorine compounds (Fig. 3). Rare earths should be removed from the solution before the subsequent crystallization of gypsum through filtering and washing with water, and precipitation with the use of oxalic acid applied in excess. One confirmed the dependence between ionic radius and the possibility of inclusion of various elements in the structure of calcium sulphate – the closer the ionic radius to the ionic radius of calcium the greater the possibility of inclusion in the structure of sulphate²⁵.

Combination of tri-butyl phosphate (TBP) and tri-octyl phosphine oxide (TOPO) in kerosene was also used for leaching of ²²⁶Ra, ²¹⁰Pb, ²³⁸U and ⁴⁰K from phosphogypsum⁵³. As a result of process optimization 92.1, 88.9, 83.4, 94.6% of ²²⁶Ra, ²¹⁰Pb, ²³⁸U and ⁴⁰K respectively were successfully removed from the phosphogypsum. Using organic extractant under optimum conditions for treatment of the phosphogypsum waste, decontaminated product that can be safely used in many industrial applications was received.

Other very commonly encountered organic compounds applied for the extraction of rare earths include the HEHPA solution (2-ethylhexyl 2-ethylhexylphosphonic acid) in kerosene, where the compound functions as a liquid ion exchanger. The possibility of separation of middle rare earths thanks to the application of 1.0 mol/l HEHPA solution was confirmed, since the extraction process is based on ionic (proton) exchange. The highest coefficient of extraction was observed for Tb>Gd>Eu>Sm²⁶. Also the mixture of D₂EHPA and HEH/EHP (2-(ethylhexyl) phosphonic acid mono-2-ethylhexyl ester) demonstrates synergistic extraction of rare earths in sulphuric acid, similarly to the mixture of MEHPA and DEHPA, commonly known as Cyanex 272 for the separation of lanthanides, on the basis of the cationic ion exchange. The research works confirmed a better possibility of extraction of heavy metal rare earths, also from acidic solutions²⁷.

One also proposes a method consisting in ion-exchange extraction with the application of resin globules similar to the ones applied in water softeners. As a result, one obtains chemically pure calcium sulphate, and the applied globules may be subject to regeneration with a solution of hydrochloric acid. In these research works, one observed the dependence between the ionic radius of an appropriate lanthanide and a possibility of inhibiting the growth of other crystals in a solution with a similar ionic radius (Fig. 4)^{28–29}. Recent patents propose

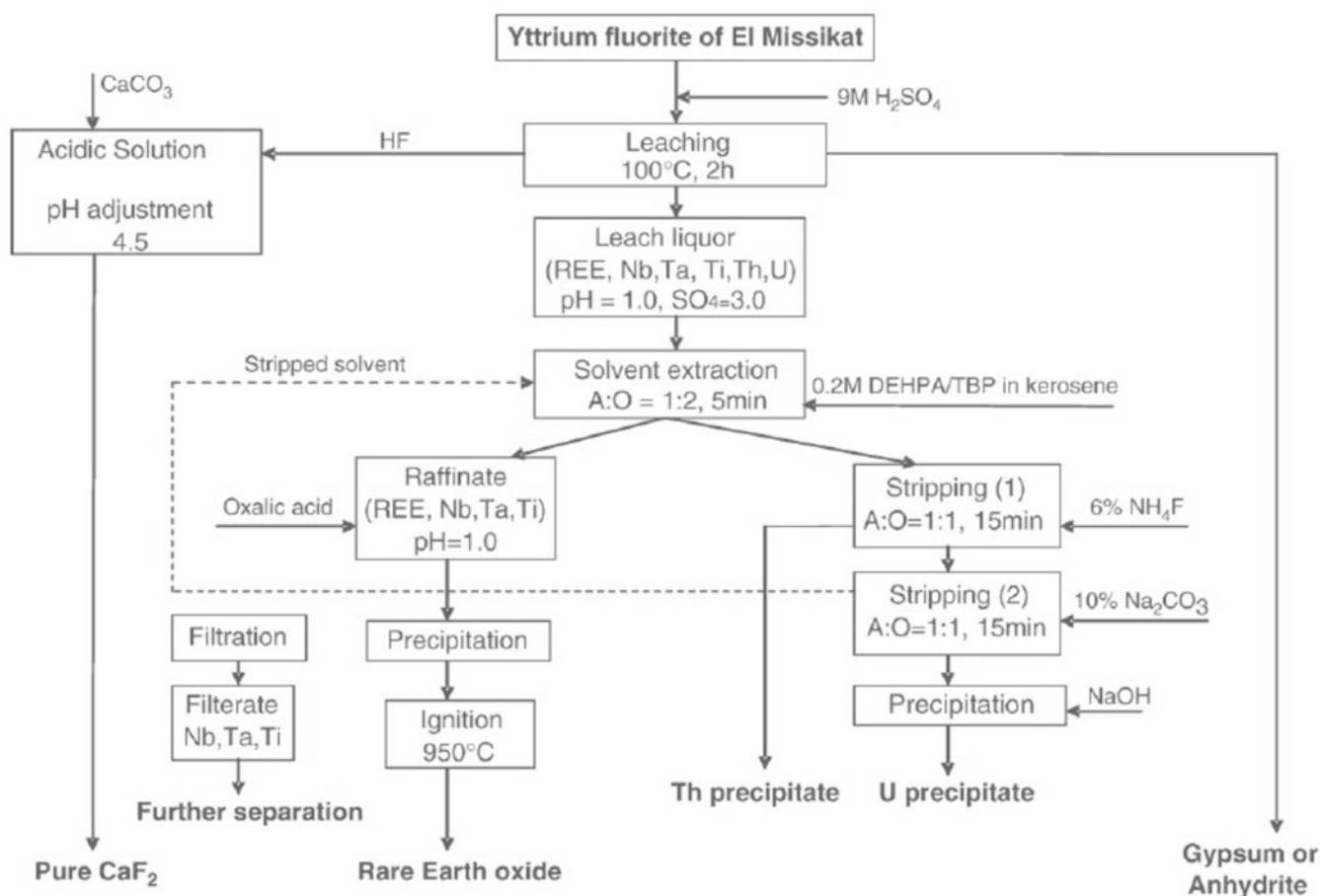


Figure 3. Scheme illustrating generation of rare earth oxides from phosphogypsum waste²⁵

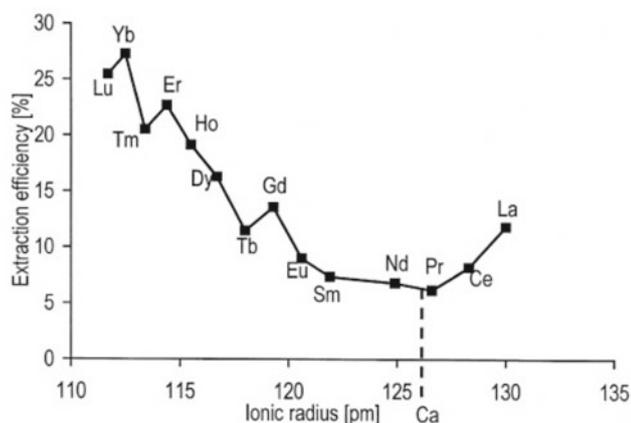


Figure 4. Extraction efficiency versus ionic radius of elements²⁸

preparation of pulp from phosphogypsum and sulphuric acid or water before sorption of REM (rare earth metals)^{51, 52}. Pulp from phosphogypsum and sulphuric acid solution with pH = 0.5–2.5 is prepared until achieving liquid to solid ratio of 4–7. Sorption of rare-earth elements is carried out directly from the phosphogypsum pulp on a sorbent with sulphuric acid functional groups, that effects in higher extraction of rare-earth elements, without a filtration step⁵¹. In the second solution prior to sorption, phosphogypsum is crushed in water so that pulp is obtained with the solid to liquid ratio 1:(5–10). Sorbent containing sulfate and phosphate functional groups is used at the solid to sorbent ratio 1:(5–10)⁵².

Rare earth metals recovery process can be also conducted by using chelating agents. A proposed method use

hydrothermal leaching of phosphogypsum with aqueous solution of chelating agents and separation of rare earth metals from such solution. Authors claim that presented solution does not require any special equipment and is less corrosive than separation of rare earth sulfates⁴⁷.

Another solutions use cation exchangers for rare earth metal separation^{48, 50, 54}. At the first step, phosphogypsum is leached with sulfuric acid. REM concentrate is extracted from the solution by crystallization and fed to REM and phosphorus leaching stage. Prior to leaching phosphogypsum is subjected to washing with water to obtain solution containing REM and phosphorus. Insoluble residue is washed before processing, by calcium compound, to produce pulp with pH not over that of REM phosphate precipitation. REM is sorbed on cation exchangers and after desorption is sent to REM concentrate production stage. Phosphorus and associated impurities are deposited from sorption mother pulp. Obtained pulp is separated as an residue for further recovery⁴⁸. In other patented solution for sorption of rare-earth elements sulfoxide cationite is used. Invention enables to remove phosphorus, fluorine and sodium impurities from phosphogypsum while ensuring a high degree of extraction of rare-earth elements, reduces consumption of sulfuric acid and calcium-containing reagent⁴⁹. Using sulfocationite in hydrogen or ammonia form with further desorption of rare-earth elements with ammonia sulphate solution, extraction of rare-earth elements of medium and yttrium groups to concentrates was 41–67% and 28–51.4% respectively⁵⁴.

Biotechnological methods of processing phosphogypsum are also reported for rare earth elements recovery^{55,56}. Acidophilic thionic bacteria in the active growth phase (bacterial population of 107 cells/ml) leached phosphorus and rare-earth elements under aerobic condition during 3–30 days, at temperature 15–45°C and solid-to-liquid ratio 1:5–1:9⁵⁵. Rare earth elements and phosphorus is transferred to the liquid phase. The resulting cake is treated with an aqueous solution, containing potassium carbonate as an alkali metal carbonate, heated followed by separation of calcium carbonates and strontium⁵⁶.

CONCLUSIONS

Phosphogypsum is undoubtedly a noxious industrial waste contributing to global environmental and economic problems. The possibilities of its waste-free processing are large, however they require the application of suitable technologies, frequently expensive ones, and allowing for the individual characteristics of the given waste.

Taking into consideration the lack of direct possibility of implementing global methods for recovering rare earths from domestic phosphogypsum, it is sensible to devise effective technologies permitting the management of newly created and already deposited waste. Among the currently applied methods, extractions with the application of organic compounds prevail, however the fact should be noted that the more selective solvent is chosen for a reaction, the higher its price will be. Therefore, regarding the so far discussed methods for the processing of phosphogypsum, the most promising ones include those based on initial purification of phosphogypsum through the precipitation of impurities, selective separation of rare earths with the application of liquid membranes, and subsequently the final purification of the material with the use of ionic liquids.

The research works conducted so far confirm the possibility of applying phosphogypsum for the recovery of lanthanides, and the process enhances the removal of remaining impurities, thanks to which the purified calcium sulphate (gypsum) may find application for the production of construction materials. These activities permit not only to reduce the phosphogypsum heaps deposited in Poland, but also to eliminate the need to import valuable concentrates of rare earths from other countries.

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