

Extraction of critical technology elements and radionuclides from phosphogypsum tailings

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Abstract. Phosphogypsum (PG) tailings from phosphate processing (fertilizer production) are an underestimated resource of remaining phosphate and critical metals (such as heavy REE and Y). The main mineral constituent of phosphate, apatite, contains significant amounts of REE (commonly 0.5-1.0%) and common phosphate processing tends to partition most REE (and other critical metals) into PG tailings (75-90%), and little into phosphoric acid (10-20%). The production of 1t of phosphoric acid typically generates 4-5t of PG tailings (annual world PG production is 160-170 million tons, and growing due to growing world population and increasing demand in fertilizer). Therefore, PG tailings form a growing resource of phosphorous, REE and other critical metals which could be extracted at relatively low cost from PG tailings in many PG processing countries, including Greece, Serbia and Bulgaria, but also northern Africa (e.g. Morocco, Algeria) where the phosphate industry forms a backbone of the national economy and where PG tailings are landscape-forming. However, PG tailings also contain heavy metals (a.o. Cd, Ba, Cr, Pb, As) and radionuclides (U, Th, Ra). PG are currently classified as TENORM which prevents PG recycling for the construction industry. Therefore, innovative PG processing requires both, a resource-efficient extraction of valuable critical metals to secure the supply for Europe's industry, and PG neutralization for recycling as construction material and sustainable land management. PG reprocessing technologies include physical, chemical (hydrometallurgical), and thermal treatment for extraction of critical technology elements and radionuclide removal, and further refining enables production of marketable products (e.g. REE, Y, P and Ra concentrate). This will not only enable zero-waste recycling and sustainable land management, with multiplier potential for many PG countries worldwide, but also eases the major worldwide concern of phosphorous depletion and its extreme impact on food supply including reduction of oversupply in K to oceans and N to the atmosphere.

1. Introduction

Phosphogypsum (PG) is a waste by-product from the processing of phosphate rock by the wet acid method of fertilizer production, which currently accounts for over 90% of phosphoric acid production (Figure 1).



Figure 1. Examples of PG tailings and fertilizer plant in Nea Karvali in Greece (left-middle), and in Serbia (right). Serbia generates about 8 million tons of PG per year.

The world PG production is variously estimated to be around 160-170 million tons per year (Parreira et al., 2003; Yang et al., 2009); the main producers of phosphate rock and phosphate fertilizers being located in the USA, the former USSR, China, Africa and the Middle East but also in the Eastern and Southeastern Europe region (ESEE).

In northern African states, such as Morocco where PG tailings are landscape-forming, the phosphate industry is an important contributor to the national economy, but also a growing environmental hazard due to serious contamination by heavy metals, fluorine and radionuclide content. Particularly the radionuclide content (mainly Radium ^{226}Ra) has led to classification of PG tailings as *Technologically Enhanced Naturally Occurring Radioactive Material* (TENORM, USEPA, 2002), which has prevented PG recycling as gypsum-based construction and building materials, as well as land re-use and land management (e.g. for income-generating agriculture and coastal tourism) over the last decades. Morocco is the world's third largest producer of phosphate and generates about 12 million tons of PG per year and. The ESEE region (e.g. Kosovo), Moroccan and South African PG tailings play a key role for recovery of REE and other critical metals as they contain about 85% of the world's estimated phosphate reserves. More than 22 million tons of phosphoric acid are produced annually worldwide (USEPA, 2002).

In the Middle East, Jordan is among the major producers of phosphate fertilizers with a mine production of over 7 million tons in 2014 and the 7th largest reserves by country. With an anticipated shift of global phosphate rock processing from North America and China to North Africa and the Middle East, phosphate rock processing is expected to further increase in Jordan. Similar to Morocco, the phosphate industry in Jordan is a main contributor to Jordan's national economy. In the coming years, new disposal facilities are planned and constructed and existing facilities are retrofitted to meet stricter environmental standards that enable on-land PG disposal to be achieved in an environmentally sound manner. However, already disposed PG in these extensive land areas prevents an environmentally sustainable land use.

Until now, only 15% of world PG production is recycled as building materials, agricultural fertilizers or soil stabilization amendments and as set controller in the manufacture of Portland cement. The remaining 85% is disposed of without any treatment. The PG by-product is usually dumped in large landscape-forming stockpiles exposed to weathering processes, occupying considerable land areas and causing serious environmental damage (chemical and radioactive contamination), particularly in coastal regions which are ideal for land recovery and re-use as agricultural and recreational tourism areas. As long as PG reprocessing is not yet feasible, PG stacks have to be isolated from rainwater, in order to prevent dissolution, seepage of contaminants and pollution of the environment. PG waste is generally transported and disposed as aqueous slurry so that PG piles can be affected by tidal variations and dissolution/leaching of the elements naturally present in PG. Dissolved elements are typically being deposited in nearby soils or transferred to waters and finally to living organisms (Reijnders, 2007).

Since PG stack dimensions have substantially increased over the last decades, PG stack management is now a serious and top-priority land management challenge. The main issue is the removal of the heavy metals and radionuclide impurities in PG, or at least a reduction to environmentally tolerable concentrations as set by legal and environmental policies and guidelines.

Interestingly, PG also contains economically relevant concentrations of critical raw materials including phosphorous (depending on the phosphate resource up to 2.5%), sulfur (S), and also Rare Earth Elements (REE) and Yttrium (Y). Apatite as main phosphate mineral typically contains about 0.5-1% of REE and other critical metals (such as Te, but also V, F, Ag, Mo, Se), and its widespread occurrence has the potential to significantly reduce criticality of these elements for many high-technology applications in Europe. The amount of PG resources in the ESEE region is expected to increase considerably due to increasing global food and therefore fertilizer demand. The phosphate industry concentrates on production of fertilizer from phosphoric acid while neglecting to recover REE and other critical raw materials as important byproducts from otherwise uneconomic PG waste tailings.

Critical raw materials such as REE, Y, phosphate and other critical raw materials are a key to many high-technology applications, and Radium (Ra) is an important ingredient for medical cancer treatment applications (e.g. Xofigo). Governmental organizations such as the European Commission, the U.S. Department of Energy, and the British Geological Survey are constantly monitoring the demand and supply market for critical raw materials as well as for the technological shifts that drive them, especially for the REE being the most critical materials (Figure 2). Economic content of critical raw materials in secondary resources such as PG is relevant to policy makers as these elements are an integral part of the European mineral resource policy on securing critical raw materials for sustainable green technology industries.

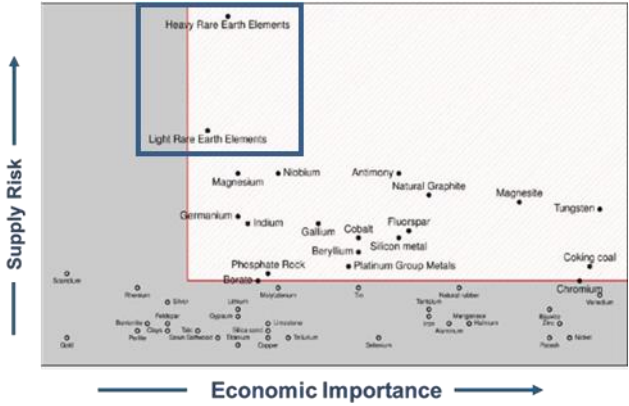


Figure 2. Graph showing the criticality (i.e. supply risk vs. economic importance) of critical raw materials, such as light and heavy REE (highlighted box), but also phosphate, relative to other critical raw materials in the EU (Report on Critical Raw Materials for the EU 2014).

The REE, such as neodymium (Nd), dysprosium (Dy), europium (Eu) and terbium (Tb), are particularly rare in supply and in high and fast growing demand as they are indispensable to the production of Fe-B-Nd (Dy) permanent magnets used in renewable energy wind generators, and to the production of phosphors essential to the production of fluorescent compact, energy saving, light bulbs and displays. At the current 10% compound annual growth rate of the demand for these REE, the question arises of their future availability.

Sedimentary phosphate deposits, and particularly its processing waste product PG, are an important non-Chinese resource of critical raw materials as PG contains relatively low concentrations (e.g. REE

generally <2%; Zhang, 2014). PG occurs worldwide in very large – and successively growing – volumes forming a secondary resource of REE, Y, P, and Ra and other critical technology elements which are currently unexploited. By generating a smart zero-waste extraction processing chain of critical raw materials from PG, Europe would be able to significantly reduce dependency on critical raw materials from non-European states. The resulting optimized processing chains and marketable products would help to build up processing capacities, capital stocks and add wealth and independence to present and future generations. The key lies in combining PG reprocessing and extraction technologies for critical raw materials, heavy metals and radionuclides from PG in an optimized processing chain, so that REE, P, heavy metals and radionuclides can be extracted or disposed of, and PG can be recycled for construction and/or building material, so that former tailings sites can be re-used (e.g. for income-generating agricultural or tourism purposes).

A review and further development of physical and chemical properties of PG and existing lab-tested technologies and processes for PG treatment and neutralization allows potential upscaling to industry-scale. PG reprocessing (i.e. treatment and neutralization) consists of effective numerous physical, chemical, potentially biological, and thermal processing methods for reducing the heavy metal and radionuclide content, which may potentially be combined with existing state-of-the-art processing technologies for critical raw material extraction (P, REE).

Properties of Phosphogypsum (PG)

The nature and characteristics of the resulting PG are controlled by the phosphate ore composition and quality (Arman and Seals, 1990). In order to produce phosphoric acid, phosphate ore is processed either by dry thermal or wet acid methods. The dry thermal method produces elemental phosphorus using an electric arc furnace. The wet chemical phosphoric acid treatment process, or wet process, is widely used to produce phosphoric acid and calcium sulphate - mainly as dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; eq. 1):



The wet process is economic but generates 5 tons of PG per ton of phosphoric acid produced (USEPA, 2002). Wet processing also causes the selective separation and concentration of REE and Y, and naturally occurring radium (^{226}Ra), uranium (U) and thorium (Th). The wet process tends to concentrate 80-90% of the naturally occurring U and 70% of Th into the phosphoric acid (fertilizer), and the remaining 10-20% U and about 30% of Th into PG (Bolivar et al., 2000). In contrast, wet processing tends to concentrate 80-90% of the REE content and Y, and 80% of ^{226}Ra into PG tailings (Kremer and Chokshi, 1989; Zhang, 2014). The REE concentrations vary among different phosphate deposits (between 0.14 and 1.0%; Zhang, 2014) and consequently among the different PG tailings. Some phosphate ore or processing streams contain even much higher REE concentrations. For instance, a Canadian phosphate deposit near Quebec contains 1,800 ppm of REE (Zhang, 2014) and a Canadian phosphate deposit in Ontario has an estimated content of 1.59% of $\text{La}_2\text{O}_3 + \text{Ce}_2\text{O}_3$ (PhosCan, 2011). Some recently discovered deposits in northern China (Xia, 2011) shows REE contents (total R_2O_3) ranging from 1.5% to ~ 6.41%. At least one phosphate sample from Morocco shows a TREO content with 900 ppm and one sample from the Boucraa deposit shows 415 ppm TREO (Christmann, 2014). The REE content of Moroccan PG tailings alone may hold a key to significantly reduce EU dependency of REE imports from China (Haschke et al., 2016).

PG tends to be a powdery material with a predominant particle size ranging from 0.250-0.045 mm in diameter with little or no plasticity (May and Sweeney, 1984), depending on the source of the phosphate rock (Becker, 1989). Milos and Dragan (2003) showed that PG has a marked crystal structure, mostly of orthorhombic and hexagonal forms. The mineralogical composition of phosphate ore is dominated by fluorapatite [$\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6 \cdot \text{CaCO}_3$], goethite and quartz, with minor amounts of Al-phosphate, anatase, magnetite, monazite and barite (Oliveira and Imbernon, 1998; Carbonell-Barrachina et al., 2002). PG is mainly composed of calcium sulfate di-hydrate (ca. 90% gypsum) and sodium fluorosilicate

(Na_2SiF_6 , Berish, 1990; Kacimi et al., 2006) with impurities of H_3PO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_3(\text{PO}_4)_2$, residual acids, fluorides (NaF , Na_3AlF_6 , Na_3FeF_6 and CaF_2), sulfate ions, trace metals (Cr, Cu, Zn and Cd), and organic matter as aliphatic compounds of carbonic acids, amines and ketones, adhered to the surface of the gypsum crystals (Rutherford et al., 1996). Determining the types of impurities present is critical when defining waste management processes and environmental policies.

PG from filter cake usually has a free moisture content of 25-30% and a vertical hydraulic conductivity of $1 \cdot 10^{-3}$ to $2 \cdot 10^{-5}$ cm/s (Senes, 1987). The free water content may vary greatly, depending on how long the PG is allowed to drain after stacking and on local weather conditions. PG solubility is dependent upon its pH but generally highly soluble in saltwater (ca. 4.1 g/l; Guo et al., 2001). Its particle density ranges between 2.27 and 2.40 g/cm³ (Senes, 1987) and its bulk density between 0.9 and 1.7 g/cm³ (Vick, 1977; Keren and Shainberg, 1981; May and Sweeney, 1984).

Water and Soil Contamination

Depending on the reaction temperature used to produce phosphoric acid, either the di-hydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or the hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) form is generated as a by-product filter cake. The free water content in gypsum cake is about 25% and due to the residual phosphoric, sulfuric and hydrofluoric acids highly acidic ($\text{pH} \ll 3$). PG contains impurities such as silica, usually as quartz, and unreacted phosphate rock. The main trace metal contents of PG include arsenic (As), barium (Ba), cadmium (Cd), nickel (Ni), chromium (Cr), lead (Pb), mercury (Hg) and selenium (Se) in mg/kg in some PG sources. These elements are on the Environmental Protection Agency (EPA) list of potentially toxic elements. Environmental concerns have developed in the last ten years because of the presence of the trace toxic metals and radionuclides in PG and its pore water. The PG by-product is usually dumped in large landscape-forming stockpiles exposed to weathering processes, occupying considerable land areas and causing serious environmental damage (chemical and radioactive contamination), particularly in coastal regions.

The most important source of PG radioactivity is reported to be ^{226}Ra (Rutherford et al., 1994) which tends to show a wide variation of ^{226}Ra activity concentrations from 15 to 1,140 Bq/kg for Sweden and Florida USA, respectively. This is attributed to the nature of the phosphate rock, the depth of sampling, and some ^{226}Ra migration (Dueñas et al., 2007). ^{226}Ra produces radon gas (^{222}Rn) which has a short half-life of 3.8 days, an intense radiation capacity, and causes significant damage to internal organs (USEPA, 2002). The potential problem of PG piles is the emanation of ^{222}Rn from the alpha-decay of ^{226}Ra , a radionuclide classified by the USEPA as a *Group A* human carcinogen. For this reason PG is classified as *Technologically Enhanced Naturally Occurring Radioactive Material* (TENORM, USEPA, 2002) so that PG exceeding 370 Bq/kg of ^{226}Ra has been banned from all uses (incl. agricultural soil) by the EPA since 1992. The maximum regulatory limit of ^{222}Rn exhalation (i.e. the flux density of ^{222}Rn gas entering the atmosphere from the surface of a ^{226}Ra -bearing material) established by the EPA (1998) is 0.74 Bq/m²/s.

Most PG is disposed of, either by discharging to water bodies, by backfilling of the phosphate mine after neutralizing with lime, by stacking of wet pulp, or by stacking of dry cake. The tailings dams are very soluble, prone to karst dissolution and readily leak contaminated sulfate-rich pore waters to underground water reservoirs and surface streams, and to dam failure (e.g. Spain, Florida). Industry and government tend to adopt environmental land management procedures that aim at the permanent isolation of PG tailings after stack closure. As a result, its usage, transportation and storage, as well as that of the associated ponds, are regulated by state environmental protection agencies. Since contaminants cannot be easily removed from PG without reprocessing, this hampers the processing of PG into structural filler, fertilizer or building material. There is a need for efficient and cost-effective PG processing and geochemical engineering methods. The only alternative presently available includes capping of these tailings by expensive geomembranes, plastic liner, clay and soil, after which they are to be vegetated.

Atmospheric Contamination

Negative atmospheric impacts can be caused by the erosion of PG piles and the release of highly polluting substances, due to the presence of hazardous vapors containing heavy metals, sulfates, fluorosilicates, hydrogen fluorides (Szlauer et al., 1990) and phosphorus, Cd and ^{226}Ra (Marvic and Sencar, 1995). ^{226}Ra produces radon gas (^{222}Rn), which has a short half-life of 3.8 days, an intense radiation capacity, and causes significant damage to internal organs (USEPA, 2002). Atmospheric agents can transport the contamination to neighboring areas.

In Spain, PG stacks located on salt marshes in Huelva contain about 100 Mio t of PG (area of ca. 1,200 ha with average height of 5 m; Mas et al.; 2006), and are generally not completely watertight or even covered with any inert material, leading to a local gamma radiation level between 5 and 38 times the normal rate (0.74 Bq/m²/s). Measurements by CRIIRAD (Chayeyron, 2007) of the equivalent dose to 1 square meter of soil showed a result 2-7 times higher than the normal rate. In other words, 9 minutes exposure per day is equivalent to an accumulated dose of more than 10 mSv/year. This value is well above the recommended worldwide exposure limit of ca. 2.4 mSv/year (UNSCEAR Report, 2000), and may thus pose a health threat to workers on the site or people living nearby (EURATOM Council Directive, 1996).

In Cyprus, Lysandrou et al. (2007) measured the ^{222}Rn emanation rate of PG samples dumped in a coastal area of the island, placing them in a sealed plastic container and monitoring radon activity growth as a function of time for about 80 h. The ^{222}Rn emanation rate ranged from 0.35 to 1.1 Bq/h, which is higher than the geological background radon emanation rate in Cyprus. This is likely to cause an increase in radon levels and thereby generate excessive radiation exposure for humans, in extreme cases reaching values of up to 17 mSv/year.

Demand and Supply for neutralized PG

There is significant interest in using PG as an alternative raw material for many applications based on its chemical properties; more than 95% is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. PG was previously used in the cement building and construction industry as a setting regulator in place of natural gypsum (Akin and Yesim, 2004) and in the gypsum industry to produce PG based mortars and gypsum plaster. PG has been found to be suitable for making wallboard or plaster, building bricks and blocks as well as road base material (especially in US where almost 20,000 lane km of new roads every year are constructed). PG is also suitable for production of ammonium sulfate (used on a large scale in China for in-situ leaching of REE from ion-adsorption clays). Both uses are currently viable economically in some parts of the world, and feasible in many other places with some industry initiative and government support.

However, the presence of impurities has given rise to many restrictions on the potential applications of PG as studies have shown that phosphates and fluorides delay the setting time and reduce the early strength development of cement. The total use of PG in building materials is currently well below 15% of world PG production (Kelly et al., 2002). In the U.S. this use was banned in 1990 (Federal Register, 1990) and in the European Union it was discontinued in 1992. PG has also been used as agricultural fertilizers or soil stabilization amendments (Papastefanou et al., 2006; Degirmenci et al. 2007; Reijnders, 2007), and as a fly ash-lime reaction activator with wide application in the manufacturing of building materials (Weiguo et al., 2007). The key issue remains the lack of suitable, industry-scale processing technologies for PG treatment and neutralization.

Proposed Solution

Development and upscaling of lab-tested methods (incl. verification) for removal of impurities and pollutant concentrations in PG stockpiles would allow PG to be processed and neutralized effectively. A rigorous and consequent approach for PG impurity removal requires a prior volume, structural and chemical assessment and geotechnical knowledge of these stockpiles. It is essential to assess the proposed physical, chemical, biological and thermal treatment methods for potential upscaling to industry-scale and develop an advanced zero-waste flowsheet with treatment options for PG neutralization. PG treatment and neutralization consists of numerous physical, chemical, optionally biological, and thermal processing methods for reducing heavy metal and radionuclide content, which should be combined with existing state-of-the-art extraction technologies for critical raw material extraction (P, REE, S).

Physical and Chemical Treatment

The treatment options for PG impurity removal (and neutralization) should be distinguished into physical, chemical, biological and thermal treatment methods. Most of these methods are based on washing, wet sieving, neutralization with lime, biological leaching, and treatment with a mixture of sulfuric acid and silica or hot aqueous ammonium sulfate solutions, as well as heating. The paragraph below outlines some published lab-scale methods for PG treatment and neutralization potentially suitable for upscaling to industry-scale:

- (1) [Manjit et al. \(1993\)](#) successfully tested an aqueous ammonium hydroxide solution (5-20%) to reduce phosphate and fluoride contents in PG before its use in the cement industry. The method achieved a decrease in all types of impurities. In a follow-up study, [Manjit \(2002\)](#) used 2-5% aqueous citric acid solution instead of ammonium hydroxide. The impurities were removed as water-soluble compounds: H_3PO_4 , $Na_3(C_6H_5O_7)_2$, HF, H_3SiF_6 , H_3AlF_6 and H_3FeF_6 . In further work by [Manjit et al. \(1996\)](#), another purification process based on wet sieving and hydrocyclone trials was investigated. The results showed that impurity concentrations were lower in the fine fraction that passed through the sieve (85%) than in the coarse fraction retained in sieving (15%), dropping from 1.28 to 0.41% for P_2O_5 , from 1.80 to 0.57% for fluorides, and from 1.58 to 0.34% for organic matter.
- (2) The PG purification process used by [Al-Jabbari et al. \(1988\)](#) consists of washing PG with water, sieving it through a 100 μm sieve, and calcining it at different temperatures (low and high). In order to improve the setting time and the compressive strength of the resulting material, accelerators (such as calcium hydroxide) were added to the calcined PG. The purified PG was chemically analyzed and physically tested. The results indicated that the best and least expensive method of purifying PG was by washing with water, sieving through a 100 μm sieve, and then neutralizing with calcium hydroxide.
- (3) [Potgieter et al. \(2003\)](#) studied the effect of chemical and physical treatments of PG incorporated in clinker to obtain cement with a SO_3 content of 2.3%. Two PG samples (one dried directly at 50°C and the other washed with water for 10 min and then dried at 50°C) were subjected to different treatments using acidic and basic additions (HCl, H_2SO_4 and NH_4OH) during the washing stage. All treatments resulted in an increase in the final strength of the cement.
- (4) [Olmaz and Erdem \(1989\)](#) studied the removal of impurities using methods based on the neutralization of water-soluble impurities in PG with water and lime milk, the removal of P_2O_5 substituted in the gypsum crystal lattice, and a calcining process. Best results were obtained when PG was washed with lime milk, due to the inactivation of the all water-soluble impurities. In another study, [Olmaz and Yilmaz \(1988\)](#) washed PG in water or lime milk and then exposed it to thermal treatments at 140-150°C for 30 min and at 130-150°C for 60 min to improve its chemical and

physical properties. The results showed that all water-soluble impurities can be removed by simple washing treatment with water or lime milk, but the P_2O_5 , substituted in the PG crystal lattice, and other impurities cannot be removed by the washing process and require thermal treatment.

- (5) [Kovler and Somin \(2004\)](#) used a topochemical reaction with an unspecified agent, solubilizing phosphates and radioactive and other metal salts at temperatures between 140 and 350°C to reduce the levels of metal salts, phosphates and radioactive compounds. They showed that the ^{226}Ra content of PG can be decreased by a factor of 20-50% and the P_2O_5 content by a factor of 16-28%.
- (6) [Azouazi et al. \(2001\)](#) investigated ^{226}Ra solubility from Moroccan PG in aqueous solution. The leaching study involved mixing 20 g of PG with 50 ml of distilled water for 20 h at various pH values (2.10-8.84). The results showed an average ^{226}Ra leaching rate of 26.4%, which could be reduced to 6% when the leached PG was previously calcined at 800°C. When the calcined PG was leached with acidified aqueous solutions, HCl (4 N) or H_3PO_4 (22.1 N), no ^{226}Ra was detected. Analysis of a water sample from an area close to the phosphate mine revealed the presence of 0.2 Bq/l of ^{226}Ra , which is below the radium chemical safety limit for water (1 Bq/l).

Thermal Treatment

Thermal treatment of PG has been found to result in fewer impurities than untreated PG material which makes the heat-treated material ideal for construction, building and cement industry applications. Earlier results also show that heat treatment of PG allows an inertization of impurities and the production of anhydrite, which has wide application in the manufacturing of building materials and cement industry. Heat treatment of PG generally includes different temperatures at variable heating times; for instance, [Manjit and Garg \(2000\)](#) developed the production of stable, high strength stable anhydrite cement according to U.S. Standards from PG waste at 1,000°C. The data also showed that anhydrite cement produced from PG has lower energy requirements than other traditional building materials. The addition of chemical activators during thermal treatment, such as sodium sulfate, ferrous sulfate, ammonium sulfate, potassium sulfate, potassium dichromate, calcium chloride and calcium hydroxide, resulted in improved compressive strength so that anhydrate plaster from heated PG can be used to manufacture flooring tiles by mixing with catalyzed monomers, glass fiber, pigments, fly and ash/red mud.

Several researchers have tested the effect of PG as a mineralizer on burning temperature of clinker and as a set controller in Portland cement and its effect on the cement properties, and its effect on cement setting and mechanical properties. The data indicated that cement prepared with the PG which was mixed with the raw mix before clinkering required the lowest time of milling (55 min), while the ones made by incorporating PG directly to the clinker required 90 min. This confirmed the negative effect of the impurities on the grinding process.

Until now, only 15% of world PG production is recycled as building materials, agricultural fertilizers or soil stabilization amendments and as set controller in the manufacture of Portland cement. The remaining 85% is disposed of without any treatment. This by-product is usually dumped in large landscape-forming stockpiles exposed to weathering processes, occupying considerable land areas and causing serious environmental damage (chemical and radioactive contamination), particularly in coastal regions.

Discussion and Conclusion

PG processing and neutralization is an urgent problem worldwide, with the main issue being the heavy metal and radionuclide content of PG tailings. In spite of some earlier laboratory research on PG physical, chemical and thermal treatment options, there is a severe need in efficient processing options as well as upscaling work towards an advanced and environmentally sustainably zero-waste flowsheet for PG processing and neutralization at industry scale. The key lies in combining PG treatment (heavy

metal and radionuclide extraction) and contemporaneous extraction of critical raw materials (e.g. REE, P) because:

- PG tailings are easily accessible
- PG tailings form a worldwide abundant – and growing – secondary resource
- PG tailings removal is a priority problem and supported by government policies
- Many phosphate and PG processing chains are operational and could be modified at relatively low cost to accommodate heavy metal, radionuclide and critical raw materials extraction.

Critical raw materials such as REE and P, but also the heavy metals, may be extracted, concentrated and refined towards marketable products which would help significantly to reduce Europe's dependency from non-European mineral resources. The radionuclides, especially Ra, may be extracted, concentrated and processed for medical applications, such as an alpha particle radiation source and ingredient for cancer treatment medication (e.g. Xofigo/Alpharadin). One potential pilot implementation site in the East and Southeastern Europe region could be the 250,000 t PG tailings at the Mitrovica industrial park in Kosovo.

The additional costs for extracting REE (and other critical metals) from PG tailings are relatively low compared to costs incurring from mining and separating REE from conventional REE ores containing bastnaesite, monazite and xenotime, as REE could be recovered from existing PG tailings and waste phosphoric acid, or alternatively during the existing phosphate processing routine, with limited additional investment and operating costs. For instance, the value of REE in Moroccan phosphate is ca. 50 US\$/t of P₂O₅ treated vs. recovery cost of ca. 10 US\$/t, though this applies to currently inefficient processing methods. There is significant economic potential for more cost-effective recovery by development of more efficient processing options. For comparison, the costs for PG stockpiling are in the order of about 25 US\$/t.

PG recycling is not only an engineering or scientific problem, but also an economic and political concern. The only alternative, a reduction in fertilizer consumption, would help to avoid continuously mounting PG stockpiles, but it would also imply some hard-to-implement changes in farming methods in developed countries, and especially in developing countries who defend their right to the same quality of life as developed countries. The recycling of PG ponds under the umbrella of a zero waste strategy provides significant positive impact to the environment. It might just be the phosphate industry that turns environmental problems into sustainable development supportive, profitable, solutions and contemporaneously reduces criticality of REE to the global economy.

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