Valorization of wastes from the fertilizer industry: current status and future trends.

Carlos Ruiz Cánovas*, Francisco Macías, Rafael Pérez-López, María Dolores Basallote, Ricardo Millán-Becerro.

Department of Earth Sciences, University of Huelva, Campus "El Carmen", 21071 Huelva, Spain.

Research Center on Natural Resources, Health and the Environment (RENSMA), University of Huelva, 21071 Huelva, Spain.

** Corresponding author:*

CR Cánovas (carlos.ruiz@dgeo.uhu.es; phone: +34 959219870)

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Abstract

Based on a systematic literature search (Number of initial publications = 1571; Number of in-depth publications = 97), this paper reviews the different potential applications for phosphogypsum, the main unwanted by-product of the fertilizer industry, providing some insights into the new valorization routes, and critically describing the advantages and drawbacks of each one. Industry and policy makers face the challenge to manage the increasing loads of phosphogypsum generated worldwide, especially on reasons of cost, safety and environmental impact. The recycling of this material could be an environmentally friendly, safe and cost-effective solution for this quandary. Different phosphogypsum valorization routes were developed in the last years in agriculture, building, and environmental and energy sectors, and these topics are described along this review. The first barrier to be overcome is the shift of paradigm needed to consider phosphogypsum not as a waste but as a raw material and the harmonization of classification rules of this material worldwide. Another issue to be faced is the heterogeneity of phosphogypsum reported worldwide, which could make unfeasible certain applications due to chemical and physical differences. On the one hand, while technical and economic constraints are increasingly lifted, many applications of phosphogypsum valorization consume low amounts of waste, and thus cannot satisfy the purpose of mass consumption. In addition, the different valorization routes may cause a secondary pollution which must be evaluated and compared with that caused by traditional disposal options. In order to provide a solution to this waste management, a better social and political awareness is needed. Economic and technical constraints must be lifted by a higher economic investment on research and development. However, site by site studies and assessment of secondary pollution using suitable tools (e.g. life cycle analysis) must be performed in order to assure the success of each valorization route.

Keywords: phosphogypsum; recycling; zero waste generation; raw materials; pollution prevention.

Introduction

The phosphate fertilizer industry is basic to maintain the levels of farming production worldwide. The main raw material used in the industrial process is the phosphoric acid, which is usually produced by two different approaches: by pyrometallurgy, applying thermal reduction of phosphate rock in an electric furnace to produce elemental phosphorus, or by a more common and cheaper hydrometallurgical method, from the chemical reaction of phosphate rock with sulfuric acid (Lottermoser, 2010). This latter process, known as "*wet digestion*", accounts for around 90% of the worldwide phosphoric production (USGS, 2017) though also generates an unwanted by-product; a solid waste known as phosphogypsum (PG). Phosphogypsum is mainly composed of gypsum ($CaSO_4\cdot 2H_2O$) although may also contain other minor solid phases (e.g. alkali fluorosilicates, fluorides, quartz, and feldspars), traces of unreacted phosphate rock, and organic matter. In addition, PG also contains remains of process waters, which are used in the industrial process, trapped in the interstices of mineral particles. The term PG is, therefore, a collective term for a waste mixture comprising major solid and minor liquid waste components (Lottermoser, 2010). The amount of PG produced during phosphoric acid production exceeds the mass of the final product, i.e. 4.5-5.5 tonnes of PG are generated per tonne of phosphorus pentoxide produced (El-Didamony et al., 2012). The total amount of PG produced up to 2006 is estimated to have been about 6 billion tonnes, of which 2.2 billion tonnes (37%) were produced in United States (IAEA, 2013).

World resources of phosphate rocks are more than 300 billion tonnes, including the largest sedimentary deposits found in northern Africa, China, the Middle East, and United States, and significant igneous deposits found in Brazil, Canada, Finland, Russia, and South Africa (USGS, 2017). Although China is currently the main phosphate rock producer worldwide, Morocco and Western Sahara host the largest reserves (Table 1). World phosphate rock production capacity is expected to increase by 2% per year, with Africa and the Middle East as the leading areas of planned growth (USGS, 2017). Associated to such level of production, a proportional increase in the generation of unwanted by-products is therefore expected. Assuming that approximately 95% of phosphate rock production is allocated to phosphoric acid production (USGS, 2017) and around 5 tonnes of PG are produced per ton of phosphate rock, then around 1.1 and 1.2 billion tonnes of PG could have been generated worldwide during 2015 and 2016 (Table 1). These figures could increase concomitantly to the expected rise of phosphate rock production worldwide.

Several disposal options have been considered to deal with this problem; the discharge of PG directly into the sea, the filling of mined-out open pits and the stacking in large heaps in the vicinity of the factory, being the latter the most common practice applied (Lottermoser, 2010). The storage process begins with the filtering and washing of PG at the processing plant to remove any trace of soluble phosphate. Then, the PG is converted into a slurry with the process water, freshwater or seawater in origin, and pumped to the top of the stack. Finally, the water is indirectly removed, after seeping through the stack and collected by perimeter channels to avoid the release of contaminants to the environment, and subsequently treated (Lottermoser, 2010). However, the stacking is not completely watertight and the treatment of these polluted waters is not always carried out (e.g. Pérez-López et al., 2015 and 2016). These waters are highly acidic (pH 1-3) and contain elevated concentrations of fluoride, sulfate, phosphate, ammonia, radionuclide, trace metals, and metal(loid)s. In this sense, the wastes generated by the fertilizer industry are of environmental concern due to the high pollutant content (e.g. Bolívar et al., 2002; Tayibi et al., 2009; Pérez-López et al., 2015; El Zreli et al., 2016). Thus, the huge amount of PG produced causes a serious disposal quandary and expensive managing costs. This environmental issue has attracted the interest of the scientific community as evidenced by the growing number of publications about PG in the last years (Fig. 1A).

Indefinite stacking is now imposing a negative externality on the phosphate industry because it constitutes disproportionately costs; for example, the cost of remediating the unlined Piney Point Stack in Florida (US) is estimated to date to have been of the order of 300 million USD (Hilton et al., 2010). For this reason, the adoption of more sustainable solutions to the management of these wastes is required in order to reach the objective of developing cleaner production of fertilizer products worldwide. The attractive economic potential of PG has promoted the development of numerous investigations focused on the search of new recycling alternatives for PG, such as manufacturing of building materials, application in agriculture, obtaining of mineral resources or environmental applications (Fig. 1B). However, such practices are often limited by the high content of toxic impurities, and only around 15% of the worldwide production is estimated to be recycled (IFA, 1998), mainly as raw material in building.

There are different reviews and/or official publications focused on environmental impacts of wastes from the fertilizer industry (Rutherford et al., 1994) and their potential uses in specific fields of application (e.g. Alcordo and Rechcigl, 1993; EC, 2002; Tayibi et al., 2009; Binnemans et al., 2015; Rashad, 2017); however, to the authors' knowledge, there is not a compilation work that critically reviews all potential uses developed to date. To bridge this gap, this study reviews the different potential applications for these by-products, providing some insights in the new routes of PG valorization, and critically describing the advantages and drawbacks of each potential application.

2. Methods

An exhaustive search of works dealing with phosphogypsum was performed, considering all fields of interest such as waste characterization, management, environmental impact, and recycling. The literature retrieval was conducted using the world-famous indexed databases Web of Science (WoS; http://www.webofknowledge.com/) and SCOPUS (http://www.scopus.com/). The publications compiled by both databases have been peer reviewed and considered of high quality. In addition, a comprehensive search was also performed in international government agencies (e.g. EC, USEPA, and USGS), international agencies (e.g. International Atomic Energy Agency, International Commission on Radiological Protection), patent office records and organizations related to the phosphate industry (e.g. Florida Industrial and Phosphate Research Institute).

The procedure of literature retrieving was initiated in both databases introducing the term phosphogypsum with a time span from 01/01/1975 to 31/08/2017. As a result more than one thousand references were obtained with both databases (SCOPUS, 1571; WoS, 1413). This information was obtained to construct the Figure 1A, which shows the interest of the scientific community on phosphogypsum. Potential papers were identified by a filtering process including different keywords related to the research object (i.e. management, characterization, recycling, agriculture, building, environmental applications, pollution treatment, mineral resources, industrial applications, and CO_2 sequestration). This information was used to build the Figure 1B, which indicates the main field of interest concerning research on PG. After the collection of potential related papers, a comprehensive screening was performed in each category by scanning titles and abstracts. As the scope of this study is to show the last advances in PG valorization, we have preferentially used the most recent papers. Finally, a cross referencing examination was performed to ensure the inclusiveness of this research. In total, 97 papers were object to an in-depth analysis.

3. Properties of PG: the key role for its potential application

Knowledge of physico-chemical properties of PG is of paramount importance to develop technical solutions for the sustainable management and/or valorization of this waste. Phosphogypsum consists primarily of silt-sized gypsum crystals, which are softly aggregated and whose morphology depends on the source of the phosphate rock, and the reaction conditions in the acid attack (IAEA, 2013). The total specific surface area of PG particles is exceptionally large causing high reactivity to the PG and, hence, PG piles dissolve more rapidly than a natural gypsum mass of the same size (Lottermoser, 2010). Physical properties of PG such as density, permeability or strength are influenced not only by the characteristics of the source rock and the reaction process, but also by the method of deposition, age, location, and depth within the PG stack. In this sense, the density and strength of the material generally increase with the age and the depth within the stack, while the water content and permeability tend to decrease (IAEA, 2013).

Since gypsum is the main component of PG, sulfate and Ca can constitute more than 90% of the total content. The presence of other minor minerals originated by the wet process or inherited from the raw materials could explain the occurrence of other elements in PG (e.g. Si, Na, Mg, Al, K, P, and trace metals), which can reach significant concentrations in PG (Rutherford, 1994). For instance, silica and fluoride contents of PG are highly variable around 0.5–18 wt.% and 0.1-1.8 wt.% respectively, depending upon the rock source and the efficiency of the wet process (IAEA, 2013). The presence of process waters trapped in the interstices of mineral particles confers to PG its acidic nature due to its high content in phosphoric, sulfuric, and hydrofluosilicic acids. In addition, this residual water contains high levels of nitrate, trace metals, metal(loid)s, and radionuclides (Luther et al., 1993). Moreover, the anomalously high concentrations of some toxic metal(loid)s (e.g. As) in PG could be also explained by the low quality of the sulfuric acid often used in the wet process (Macías et al., 2017).

During the acid process, elements contained in the phosphate rock are released from their host phases into solution. Thus, elements are partitioned into the phosphoric acid or the PG, according to their solubility and chemical affinity (Rutherford, 1994). The transference of radionuclides originally present in the phosphate rock to PG has been focus of much research (e.g. Rutherford, 1994; Mazzilli et al., 2000; Santos et al., 2006; Rentería-Villalobos et al., 2010). Uranium, Th, and Pb-210 concentrate in the phosphoric acid whereas most of Ra-226 and Po-210 are finally transferred into PG (Lottermoser, 2010). However, different results were reported by Santos et al. (2006) in Brazilian PG; these authors found a preferential accumulation of Th and Pb-210 in PG. This enrichment in Pb-210 was also observed by Rentería-Villalobos et al. (2010) in Spanish PG stacks.

According to different authors (e.g. Rutherford et al., 1994; Al-Masri et al., 2004; Pérez-López et al., 2011), metals (e.g. Cd, Cu and Zn) are preferentially transferred into phosphoric acid. Some authors (i.e. Rutherford et al., 1994; Arocena et al., 1995) reported a heterogeneous distribution of impurities in PG with small and/or very large particles containing relatively more impurities than medium-sized gypsum particles.

Phosphate rocks can also host significant quantities of rare earth elements (REE) that can be transferred to PG during the phosphoric acid production. Igneous phosphate rocks are much richer in REE than sedimentary phosphate rocks (1-2 wt.%) and contain only trace amounts of U (Binnemans et al., 2015). It is interesting to note that U and Th are commonly present in REE phosphate ores and are a cause of major environmental concern that penalizes the extraction. Cerium, lanthanum, and neodymium account for 80% of the total REE content of phosphate rock (Habashi, 1985). During the production of phosphoric acid, around 70-85% of REE originally present in phosphate rocks are concentrated in PG and the REE pattern observed in the phosphate rock is preserved.

4. Routes for PG valorization

4.1. Application in building

One of the most explored valorization routes of PG is the manufacturing of building materials such as bricks, cement, plasterboard or tiles (Fig. 1B). The potential uses of PG in building have been recently reviewed by Rashad (2017). Phosphates and fluorides contained in PG may cause pernicious effects on the final properties of raw materials, such as delay in the setting time and reduction of strength of cement (Tayibi et al., 2009). For this reason, different methods have been proposed to obtain PG harmless and suitable to secondary uses (i.e. washing, wet sieving, alkaline neutralization, and addition of extractant solutions). The different pre-treatments of PG as raw material in the building sector have been reviewed by Tayibi et al. (2009). Among the studies mentioned by Tayibi et al. (2009), that of Ölmez and Yilmaz (1988) reported that all water-soluble impurities can be removed by simple washing treatment with water or lime milk, but the P_2O_5 and other impurities are enclosed to the crystal lattice and can be only removed by thermal treatment (from 130 to 150 °C). This latter process not only causes impurities immobilization but also the production of anhydrite which has a wide application in the manufacturing of building materials and cement industry. However, it also constitutes a high cost that may become technologically sub-economic. Valkov et al. (2014) proposed a method with sulfuric acid to process PG when heating to temperatures of 70-100 °C for 1-2 hours at a

S:L ratio of 1:(1-3) and bubbling air into the pulp. The resulting PG does not contain harmful impurities and can be used in road construction, as additives in the production of cement, and for the production of various building materials.

Another limitation in the use of PG as building material is the content of natural radionuclides if compared with those found in common building materials (Table 2). This natural radioactivity is of environmental concern taking into account that individuals spend 80% of their daily time indoors, and PG-manufactured building materials can be a source of interior radiation (Kovler, 2009). In this sense, chronic exposure of human beings to low doses of ionizing radiation can cause health damages which may appear 5–30 years after the exposure (ICRP, 1991). Kovler (2009) reported radiation exposure by building materials differentiating external and internal exposure, being the external exposure caused by direct gamma radiation while internal exposure is mainly caused by the inhalation of radon (^{222}Rn), and its short-lived decay products. The monitoring of radon gas in the environment is of critical importance in terms of radiological protection because radon is an inert gas that easily moves through porous media such as building materials. This subject was approached by Campos et al. (2017) by measuring the radon exhalation rate from plates and bricks manufactured with Brazilian PG. These authors concluded that the recycling of PG as building material is a safe practice from a radiological point of view. However, this work does not describe the PG content added to these building materials. In addition, these findings cannot be extended to each PG deposit, since radionuclide content varies widely among sites. According to the studies reported by the IAEA (2013), the use of PG in structural panels for house construction could, in extreme circumstances, result in the occupant receiving an annual effective dose exceeding 1 mSv. For all other uses of PG in home construction, including its use in cement, bricks, plasterboard and tiles, the annual effective dose received by the occupant is unlikely to exceed 1 mSv and restrictions on such use would appear to be unnecessary (IAEA, 2013). On the other hand, there is no information on the metal and metal(loid)s released from these products and thus, this issue should be addressed.

Another limiting factor in PG recycling relies on that most applications consume low amount of PG and do not meet the condition of high-consumption required to valorize the huge amount of PG generated by the fertilizer industry. Thus, low-cost and highly-consuming PG technologies are required. In this way, another possibility would be the use of PG in road base applications which could consume up to 25,000 tonnes per lane kilometer (IAEA, 2013). The use of PG in road construction may constitute a reduction of costs and the use of virgin raw materials of up to two thirds compared to using conventional materials (IAEA, 2013). In this sense, Cuadri et al. (2014) evaluated the potential utilization of PG as a bitumen modifier for paving industry. They found that after activation with a small quantity of sulfuric acid (0.5 wt. %), the addition of 10 wt. % PG leads to a notable improvement in the rheological response of the resulting material at high temperatures. However, no information on the release of impurities (i.e. radionuclides, metals.) of the resulting material under weathering conditions in the long term is available. Beretka et al. (1996) explored much earlier the use of PG in the manufacturing of calcium sulfoaluminate cements. These authors reported that these cements require, compared to ordinary Portland cements, lower energy in the manufacturing process and give higher mechanical strength at early ages due to the rapid formation of non-expansive ettringite. On the other hand, Yang et al. (2016) studied the possibility of recycling PG as raw material for the manufacture of self-leveling mortar. They obtained a final product which met the requirements of Chinese standards with PG contents of up to 55%, decreasing the production costs 5 to 7 times in respect of those for cement-based self-leveling mortar. In the same way, Tian et al. (2016) used non-pretreated PG to manufacture foam concrete with a high content in PG (up to 45-55%). However, these authors reported that the compressive strength of the formed concrete decreased dramatically with the increase in the PG percentage between the range of 40-70%. The addition of quick lime in the foam formulation may immobilize the acidic impurities present in PG, thus decreasing the secondary pollution and the costs required (i.e. energy, reagents) to pretreat the PG.

4.2. Application in agriculture

Due to its high content in some elements such as Ca, P and S, PG has been traditionally considered as an amendment in order to improve the physico-chemical properties of soils. This valorization route is not recent; Alcordo and Rechcigl (1993) reviewed the potential use of this by-product in agriculture. Since then, much research has been devoted to the agricultural uses of PG (Table 3), mainly to improve soil structure and crop yield (e.g. Tang et al., 2006), reduce soil erosion (e.g. Zhang et al., 1998), treat acidic or metal-rich soils (e.g. Takahashi et al., 2006; Rodriguez-Jordá et al., 2010) or increase available soil concentrations of S and P (Delgado et al., 2002). In order to assure a safe long-term application in agriculture, the characterization of PG impurities as well as their mobility and bioavailability is of critical relevance. Some authors have addressed this issue by applying different extractants to PG in order to simulate the migration of pollutants from PG-amended soils to agricultural products. Saueia et al. (2013) studied the leaching of radionuclides and metals from Brazilian PG using EDTA solutions, and compared the results with those obtained using different phosphate fertilizers. These authors concluded that the use of PG is safe for agriculture given that all metals remained below the limits established by the Brazilian Regulatory Agency, with values even lower than those obtained by applying phosphate fertilizers. The bioavailability of metals and radionuclides from PG has been addressed by other researchers using *aqua regia* digestion and sequential extractions (e.g. Santos et al., 2006; Al-Hwaiti et al., 2010). These studies concluded that the toxic metals in PG are not likely to be leached and thus, PG could be considered to be used as an amendment to agricultural soils. However, the real transfer of metals to soils and the effects on the living organisms should be properly addressed. Nisti et al. (2015) reported a low release of radionuclides and metals (i.e. As, Cd, Ni, Cr, Se, Pb, and Hg) from Brazilian PG amended soils in doses 10 times higher than those needed to achieve 50% of the soil base saturation (around 15 g PG/kg soil). On the other hand, Abril et al. (2008) and Enamorado et al. (2014) studied the trace-elements uptake by plant in soils amended with different doses of PG in SW Spain. After three decades of PG amendments in agricultural soils, these authors reported Cd levels in shoots and tomato fruits below, but close to, the limit values for food safety. In fact, these authors estimated that accumulated PG amendments greater than 16 g PG/kg soil would be enough to exceed such a limit. Similar conclusions were obtained from Al-Hwaiti (2015), who reported contamination in soils and vegetables (i.e. tomatoes and green peppers) in amended soils with Jordanian PG. Thus, these authors obtained contradictory conclusions to those reported by Nisti et al. (2015) applying similar PG doses to soils, which could be attributed to the higher metal content in PG used by Enamorado et al (2014) and Al-Hwaity (2015). This high variability in trace element content of PG worldwide has been recently reported by Macías et al. (2017) and evidences that the assessment of the metal/loid content of this by-product, and their release capacity before its use as soil amendment is of critical in agriculture to avoid the transference of these elements to the chain food.

In addition, any change in the soil properties may have a significant impact on its habitat. In this sense, the impact of PG soil amendments on bacterial biota, plants and invertebrates has not been evaluated until recently. Hence, Hentati et al. (2015) provided evidences of remarkable ecotoxicological effects on invertebrates, attributed mainly to Ca, due to metabolism disruption with consequences in the reproduction and even in the survival. Metals, Ca, and P provided to soils by PG may be easily mobilized to the aqueous solutions, affecting the aquatic life, in particular invertebrates like cladocerans, which have a critical role on the equilibrium of aquatic food chains.

The use of PG as an additive during composting has also been examined. During composting, a loss of N is commonly observed by ammonia volatilization in the early stage when decomposable organic N is abundant and pH increases with protonation of amine (Eghball et al., 1997). The addition of PG during composting may avoid ammonia volatilization due to the formation of ammonium salts ($(NH_4)_2SO_4$) retaining N and avoiding nutrient imbalance by reduction of the N:P ratio. Prochnow et al. (1995) investigated the effectiveness of PG and simple superphosphate in controlling ammonia losses by volatilization during the process of manure composting. These authors revealed that the amount of ammonia lost by volatilization from the samples decreased with the addition of both products, although PG was more efficient, and the reduction in volatilization increased with the rate of PG application. Lim et al. (2017) studied the N loss and changes in C content and dry matter losses using PG amendments, and different bulking agents (i.e. rice hulls and sawdust) during cattle manure composting. These authors reported a lower N loss using a mixture of sawdust and PG (2:1 mass ratio), although these results were obtained in mesophilic conditions due to the inability to achieve thermophilic conditions. However, these authors did not study the content of metals and radionuclides of the final compost neither the transfer to soils after addition.

4.3. Source of raw materials

Phosphogypsum could also be a source of raw materials after developing suitable recovery schemes. For instance, the potential of phosphate rock as a source of REE has been already recognized in the 1960s (Anon, 1966). During the manufacturing of phosphoric acid, elements are unevenly transferred from the phosphate rock to the phosphoric acid and PG (see section 2). The possibility of recovering elements of economic interest (e.g. REE, Sc, U, V, Cr, Ga, Ge, Be, and B) contained in these unwanted by-products must be explored. Although the concentration of these elements is one or several orders of magnitude lower in PG than those reported in conventional mineral deposits commonly mined, the huge volume of PG stacks could convert these repositories into secondary sources of these elements (Cánovas et al., 2017). However, most research has been focused on REE and to a lesser extent Sc and U. The first stage in the recovery process is the extraction of valuable metals from metal-bearing materials, which is frequently performed by the use of aqueous extractants. Once dissolved, further steps are needed to concentrate and separate elements of interest. The final goal is to obtain the highest purity by refining and purifying the element to achieve a marketable product.

4.3.1. Metal recovery by acid leaching

The most common approach to separate REE contained in PG is performed by leaching with dilute acids (i.e. H_2SO_4, HNO_3) and subsequent recovery by solvent extraction or by precipitation with oxalic acid (e.g. Leveque et al., 1981; Jarosiński et al., 1993; Preston et al., 1996; Germeau et al., 2013). The type of acid and concentration, the solid to liquid ratio, temperature, and reaction time may have a significant influence on the extraction efficiency. Jarosiński et al. (1993) performed REE extraction in PG with nonylphenilphosphoric acid (NPPA) in kerosene and then re-extraction with 8M H_2SO_4, which allowed breaking the NPPA-REE complexes, and the precipitation of REE complexes (Fig. 2A). Optimal conditions were reached at temperature lower than ambient (0-10 °C) and acid concentration lower than 10% of H_2SO_4. As a result, these authors achieved a water-soluble concentrate with around 40% of REE_2O_3.

Preston et al. (1996) reported higher leaching efficiencies with HNO_3 instead of H_2SO_4, and maximum recovery of REE observed for 3M HNO_3. These authors also studied the leaching efficiency after successive additions of fresh portions of nitric acid (2M) at a fixed solid-to-liquid ratio (1:1), reporting a high cumulative recovery (80% after four interactions), but with a high acid consumption. After leaching, a solvent extraction with tri-n-butylphosphate (TBP) and di-n-butyl n-butylphosphonate (DBBP) allowed reaching a mixed REE oxide product of high purity (94-98%) (Fig. 2B). These authors also reported an increase in recovery with increasing temperatures, although the effect of temperature on the leaching recovery was reversible.

Lokshin et al. (2002) also found HNO_3 to be a more efficient extractant than H_2SO_4 for the recovery of REE from hemihydrate PG (different from the dihydrate obtained during the common wet process). Leaching with fresh portions of HNO_3 led to a 96% recovery of REE, while only 7.8% of the calcium content went into solution. Walawalkar et al. (2016) also investigated the optimal extraction of REE using different acids (i.e. HCl, H_2SO_4, and HNO_3). These authors reported optimal operation conditions at acid concentration of 1.5 M, 80 °C, solid-to-liquid ratio

(S/L) of 1:8 and 20 min of residence time for all three acids, but the leaching efficiency using nitric and hydrochloric acids was higher than using sulfuric acid.

The addition of some reactants can improve the leaching efficiency of REE. In this sense, Preston et al. (1996) reported an improvement in recovery rates by adding $Ca(NO_3)_2$ to HNO_3 solutions (from 35 to 76%). These authors attributed this improvement to the high calcium concentration in solution which tends to displace the REE from the gypsum, in which they are heterovalently substituted by calcium ions. However, these authors also consider the possibility of REE solubility that could be controlled by fluorides. The addition of Ca would complex F ions, allowing the REE to remain in solution. On the contrary, Lokshin et al. (2002) did not observe enhanced leaching of REE in PG upon addition of $Ca(NO_3)_2$ to the HNO_3 solution. In fact, based on the high percentage of REE extraction compared to the low rate of gypsum dissolution, these authors concluded that REE are not incorporated into the gypsum lattice, but rather exist as separate phases. The same conclusion was obtained by Shivaramaiah et al. (2016) and Cánovas et al. (2018) in studies performed under laboratory and field conditions, pointing out at metastable amorphous precipitates of phosphate and fluoride as minerals hosting REE in PG.

The existence of suitable technologies to extract REE from PG would justify the exploitation of these wastes; however, as pointed out by Cánovas et al. (2017), economic and market constraints may put in risk the development of these technologies at industrial scale. For instance, some initiatives become sub-economic due to the poor quality of the final product that does not meet the market specifications. Thus, improved refining processes are required to increase the purity of the final product which may control its market value. In addition, although the developed recovery technologies are cost-effective, they require significant financial investment and are subject to a relatively high degree of risk such as fluctuations of REE prices and feasibility to scale up the technological process (Kulczycka et al., 2016).

4.3.2 Metal recovery by organic solvents

The use of organic solvents instead of acidic solutions for metal recovery from PG could provide some advantages: the largely reduced consumption of acids, a major reduction in the volumes of the leaching solutions, and the possibility of achieving a much higher selectivity for metal recovery compared to conventional hydrometallurgical leaching methods. This route was explored by El-Didamony et al. (2012; 2013) who investigated the possibility of releasing metals from PG with organic extraction agents dissolved in kerosene. They initially tested the usage of tributylphosphate (TBP) dissolved in kerosene, recovering a 69.8% of REE present in the solid material. The method was improved by using mixtures of TBP and TOPO (TOPO 1/4 trioctylphosphine oxide) in kerosene with a recovery rate of around 80% (Fig. 2C), however, the authors did not quantify this improvement.

Uranium is also extracted by TBP. Selectivity can be pH-controlled: U is extracted at very low pH values (0.6-0.7) whereas the maximum recovery of REE can be achieved at a pH of 1.0 where a precipitate starts to form (Habashi and Awadalla, 1986). Al-Masri et al. (2004) reported U recoveries of around 60% using 1M H_2SO_4. The same authors performed a sequential extraction in PG to study U (and other metals) partitioning among different solvents. Around 20% U was released by distilled water reaction. Slightly higher amounts of U were released from the gypsum crystal lattice (ammonium oxalate) and the acid-soluble fraction (HNO_3+HCl+H_2O_2). Much lower amounts of U were reported linked to organic matter and the residual fraction.

4.3.3 Chemical transformation of PG

Another promising valorization route could be the chemical transformation of PG to obtain raw materials of economic interest. The recycling of PG can be approached by a process known as the Merseberg ammonocarbonation process (Fig. 3A) which yields ammonium sulfate, an excellent fertilizer, and calcium carbonate, a useful product for neutralization of acidic water (IAEA, 2013). This process has been used on a commercial scale in China, India and Indonesia. Almost all the radionuclides within the PG migrate to the calcium carbonate, leaving the ammonium sulfate fertilizer product lower in radioactivity than most natural materials (IAEA, 2013). Nevertheless, the process has found only limited use in practice because of abundant supplies of inexpensive ammonium sulfate from other industries. To overcome this barrier, the recovery of other elements of economic interest may be explored. So, Habashi (1985) followed the Merseberg ammonocarbonation route to recover REE from PG. The acidic leaching of REE-rich calcite with HNO_3 would yield REE in solution and the precipitation of $CaNO_3$, also a by-product of agricultural interest. Another way to recover REE would be the calcination of calcite to obtain CaO, which would be leached afterwards with ammonium carbonate.

Kolokolnikov and Shatov (2008) induced chemical transformation of PG using washing soda (Na_2CO_3) into calcium carbonate and sodium sulfate (Fig. 3B). This reaction was investigated within the temperature range of 40–90 ˚C and the Na_2CO_3 concentration of 240–260 g/L. These authors reported an increase in transformation rate with increasing temperature; 80–90 ˚C and 20–30 min yielded a 96–98 % conversion. However, these authors did not study in this paper the REE partitioning between different by-products of the reaction. A similar paper of Kolokolnikov and Kovalev (2009) reported an accumulation of REE in calcium carbonate (0.8% REE_2O_3) (Fig. 3B). These authors forced the transformation of $CaCO_3$ into CaO by heating at 950ºC, increasing the concentration of REE_2O_3 up to 1.2%. Afterwards, ammonium chloride (NH_4Cl) was added to CaO, giving rise to an increase of Sr and REE in the solid residue that can be used as a potential resource. Kolokolnikov and Kovalev (2009) performed the acidic attack of this residue using HCl, H_2SO_4, and HNO_3. They obtained a high efficiency recovery (> 90%) using 15-20% of HCl at 80ºC during 60 min. In turn, the same conditions using HNO_3 and H_2SO_4 did not get efficiencies higher than 60%.

The induction of such mineral transformations could be a hopeful route for the recycling of PG. However, some obstacles must be overcome. For instance, the secondary raw materials obtained during the mineral transformation (i.e. calcite, ammonium sulfate, or sodium sulfate) must usually compete with abundant and inexpensive supplies from other industries. As commented before, this could be solved encouraging the recovery of elements of economic interest contained in these by-products. In this sense, another problem to be solved is the preferential transference of target elements (i.e. REE) and impurities (i.e. metals and radionuclides) in Ca minerals during transformation. In addition, some of these processes require the consumption of energy and chemicals that can turn these schemes into sub-economic at industrial scale.

4.4. Applications in pollution prevention and remediation

Industrial activity is the main source of metals to the hydrosphere. For this reason, industries have tried to mitigate the metal release by different approaches such as chemical precipitation, adsorption, ion-exchange, reverse osmosis or electrochemical reduction (Fu and Wang, 2011). Although, there are available technologies to successfully reduce the metal concentration from industrial effluents, they are usually expensive, especially for developing countries, the reason why much research has been devoted in the search of low-cost technologies based on cheap materials or wastes. Among them, the use of PG as a potential raw material in the production of substances to mitigate pollution has received recent attention. Kadirova et al. (2014) reported the joint application of PG and kaolin to produce a low-cost inorganic sorbent material. This mineral assemblage was thermally activated (500-1000 ºC for 2h) and the resulting material turned to be a good sorbent for ammonium, dihydrophosphate and nickel ions. On the other hand, based on the high content of Fe and Al oxy-hydroxides in red mud, which are reported as great As scavengers in nature (e.g. Carrero et al., 2015), Lopes et al. (2013) studied the enhancement of As retention by the addition of PG to red mud at different rates (from 1 to 25%). These authors observed that As adsorption increased upon increasing the proportion of PG in the mixtures due to the presence of Ca^{2+} which alters the charge balance of the adsorbent, leading to the formation of ternary complexes. Zhang et al. (2012) used PG as raw material to prepare hydroxyapatite nanoparticles via microwave irradiation technology with the aim of studying the removal of fluoride from aqueous solution. This mineral has been previously recognized by its retention potential of metals and anions in surface and groundwater (e.g. Smičiklas et al., 2006; Sundaram et al., 2008). These latter authors found that fluoride adsorption by hydroxyapatite nanoparticle can be explained by electrostatic interaction and hydrogen bonds. A similar approach was followed by Balkaya and Cesur (2008) to study the adsorption of Cd on pre-conditioned PG. The PG was mixed with a 0.4% of lime milk to neutralize the water insoluble impurities and then, batch experiments were performed using a dosage of 10 g/L of sorbent. These authors obtained a high Cd removal rate, around 99%, using lime pre-conditioned PG, although this process is strongly pH-dependent; removal is driven by adsorption at pH values of about 9.0 but it could be slightly enhanced by cadmium hydroxide precipitation at pH > 9.0.

The use of PG has also been focus of research to mitigate air pollution. Mineral sequestration is a promising approach to the problem of managing and capturing carbon dioxide permanently and safely, and thus to mitigate the global warming. The mineral sequestration process involves a chemical reaction where aqueous cations (e.g. Ca or Mg) react with CO_2 to form stable carbonate minerals. This route was explored by Zhao et al. (2015), following a similar procedure after Habashi (1985), using ammonia and carbonation under pressurized conditions in a one-step process. As a result, an almost complete carbonation ratio (around 97%) was achieved in 5 minutes, yielding calcite and ammonium sulfate which can be reused as raw materials (see point 3.3.3 and Fig. 3A). However, these authors did not report the transference of impurities from PG to the resulting final products. This issue was in contrast addressed by Cárdenas-Escudero et al. (2011) by dissolving PG with NaOH to yield Na_2SO_4 and portlandite ($Ca(OH)_2$) (Fig. 4A). This latter mineral proved to be very efficient CO_2 sequester under carbonation even in environmental weathering conditions and CO_2 was permanently captured in the form of calcite (Fig. 4A). However, these authors also reported the total transference of metals and metal(loid)s from PG to portlandite and finally to calcite. In that case, the purity of Na_2SO_4 would allow its use by detergent or paper industries, while $CaCO_3$ could be used for acid mine drainage (AMD) remediation due to the amount of metal(loid)s transferred from PG to calcite is total but negligible compared to the content existing in AMD. On the other hand, Contreras et al. (2015) traced the transfer of radionuclides through PG carbonation. As occurred for metal(loid)s, a complete transference of radionuclides from PG to the final product was observed. In the case of ^{226}Ra, the most important radionuclide in PG, it is not surprising its behavior through the process due to their chemical affinity with Ca. These authors highlighted the hazardousness of these products (i.e. portlandite and calcite); according to the EU regulations both are NORM materials and their commercialization must be controlled. On the other hand, the described processes rely on the consumption of pure reagents (i.e. ammonia, soda) whose costs and energy consumption of their production may put in risk the economic viability of the process. This problem can be overcome by the use of by-products and wastes generated in industrial processes. In this sense, Romero-Hermida et al. (2017) studied the PG carbonation using liquid wastes of the aluminum anodizing industry (Fig. 4B).

The use of PG to mitigate other greenhouse agents have also been explored. Hao et al. (2005) studied the effect of PG on greenhouse gas emissions during cattle manure composting. These authors added PG at target rates of 10, 20, and 30% of manure dry weight and monitored the composting process during 134 days, when the windrow temperature dropped below 40ºC. During the composting process, the emission of N_2O was not affected by PG addition. On the other hand, PG addition reduced the emissions of CH_4, attributed to the increased content of sulfate that may enhance the interaction between sulfate-reducing bacteria and methane-producing bacteria. Luo et al. (2013) came to the same conclusions after adding PG during composting of mixtures of pig manure and cornstalks. These authors reported a significant decrease in CH_4 emissions with PG addition rate at 5% and 10% of mixture dry matter, but no significant effect on the emission of N_2O was detected. The addition of PG has also been tested to reduce gas emissions during kitchen waste composting, which physical and chemical properties vary widely from those of animal manure. Yang et al. (2015) reported that the addition of 10% of PG drastically reduced CH_4 and NH_3 emissions by around 86% and 24%, respectively, while increased around 3.2% the N_2O emissions. In total, a reduction of around 17% of greenhouse gas emissions was obtained by adding PG during kitchen waste composting.

The use of PG has also been tested in applications aimed at prevention of pollution. For instance, Li et al. (2017) studied the manufacturing of cemented paste backfill (CPB) for underground disposal of tailings and industrial by-products using PG and an artificial cementitious agent (CA) composed of ordinary Portland cement, fly ash, yellow phosphorus waste, and lime. These authors reported the suitability of PG (a ratio PG:CA of 4:1) to produce materials to prevent pollution in mining and industrial sites. However, the amount of binder agents required during the manufacturing of PG-based CPB (over 14%) was higher than that used in common CPB (3-7%) due to the high acid and sulfate contents in the PG. This problem could be solved if raw PG is washed previously to the PG-based CPB manufacturing. Unless other studies dealing with manufacturing of materials from PG, the leaching potential of the PG-based CPB was assessed, resulting in a low release of pollutants during the leaching tests due to the stabilization by cementation. In the same way, Çoruh and Ergun (2010) studied the application of PG as a liner material for the disposal of hazardous zinc leach residue waste. These authors reported a drastic reduction of trace metal content in the leachate when adding 10% of PG as liner. However, they recommend the use of other more efficient wastes (i.e. fly ash and red mud) which were also tested.

4.5. Applications in the industrial sector

The use of PG as raw material has been explored in a variety of industrial processes. For instance, PG has been tested as oxygen carrier during syngas generation. Yang et al. (2017) reported that PG has high reactivity and high oxygen transport capacity to contribute to syngas production in an environmentally and cost-effective manner. These authors also recommended, using a

PG:lignite ratio of 1:5, to reduce the size of PG particles for shortening the time of reaction equilibrium, and avoiding sintering. Another example of PG recycling as raw material is its use as fillers in paper making that can provide cost and energy savings, improved paper properties, increased productivities, and specifically desired paper functionalities. This route has been studied by Mechi et al. (2017) who used raw and pretreated PG samples (i.e. washing and calcination) to prepare PG fillers to be added to paper pulp in an amount of 5 to 15%. As a result, these authors concluded that the optical properties of the filled paper were strikingly enhanced, while the strength properties were practically negatively influenced. However, as in other applications involving PG, the transference of pollutants was not evaluated by these authors.

Other examples of PG recycling in the industrial sector as a raw material can be found in the metallurgical industry. Jena et al. (2016) studied the extraction of K from feldspars by roasting and leaching using NaCl and PG as a source of Cl and Ca, respectively. These authors reported an increase of extraction from 61% to 92.5% with the addition of PG during the process.

5. Legal, socio-economic and environmental considerations

The policy of stacking, regarding the indefinite restraint of PG as the best option, is now under pressure on reasons of cost, safety and environmental impact and because it erroneously considers a recyclable material as a waste, for which there are increasingly stringent controls on disposal (Hilton et al., 2010). In some cases, the reason for compulsory stacking is somewhat definitional, as in the United States, where PG is characterized by the US Environmental Protection Agency (USEPA) as a waste of no commercial value. In fact, there is no clear unanimity among different countries about the characterization of these wastes. This issue was highlighted by Macías et al. (2017), who reported the discrepancies observed between EU and US regulations dealing with hazardousness classification of these materials. Following contemporary definitional trends, however, PG must be reclassified as a potential resource. The valorization of PG may contribute to a reduction of environmental and social impacts, nevertheless industry and policy makers must face different political, technical, economic, and environmental challenges (Table 4). The first challenge to be overcome is the paradigm shift needed to consider a waste as a raw material. The use of secondary or recycled materials has traditionally met resistance in the industrial sector and only obtains acceptance after proved experience is attained.

As described above, the recycling of PG has attracted the interest of much research in recent years (Fig. 1), giving rise to several technologies to valorize this unwanted by-product. These technologies have been successfully tested at lab or pilot scale. However, some factors may limit its application at real scale. The valorization of PG may face legal requirements before application. For instance, since 1989 PG stacking in the US became a legal necessity when the USEPA banned its use. However, in 1992, this rule was modified to allow the use of PG with an average Ra-226 concentration below 10 pCi/g for agricultural application as a soil amendment (FIPR, 2016). This limit is based on the dose of radiation, calculated by the EPA that a person might receive under a series of scenarios in which PG could be used. This strict limit constitutes an absolute barrier to PG valorization in the US, which generate 37% of PG worldwide, due to the availability of large amounts of low-cost natural gypsum produced as a by-product of coal-fired power plants (FIPR, 2016). As a result, there is an oversupply of gypsum and the market for the PG generated by the fertilizer industry has been limited.

Another challenge to be faced by recycling technologies is to treat the increasing loads of PG generated worldwide. Many applications of PG valorization consume low amounts of PG, thus the demand of the resulting product is limited and cannot satisfy the purpose of mass consumption. In this sense, the most promising applications are found in agriculture and road construction, where large amounts of PG are used. However, there is still a lack of information about the potential release of metals and radionuclides during the life time of certain applications. For instance, one of the main environmental concerns of its use as building material is the radon exhalation, which must be considered of critical importance. For these reasons, case by case studies on metal and radionuclide release must be performed before application for safety purposes. This need is supported by the high variability of physical and chemical characteristics in worldwide PGs that could make certain PG unsuitable for the projected valorization route.

On the other hand, the application of technologies may suffer from technical and economic constraints: most of available technologies are quite expensive and its development is complex. Some technologies developed to valorize PG need a physical or chemical pretreatment which may consume much energy and reagents, increasing thus the costs. For this reason, the costs generated by implementing each technology must be estimated and compared to the rest of potential solutions in order to assure the return on investment and the cost efficiency of the valorization scheme.

In addition, the different valorization routes may cause a secondary pollution. In this sense, the environmental impact associated to each technology may be evaluated and compared with that caused by disposal conventionally performed close to fertilizer plants. This issue can be approached by Life Cycle Assessment (LCA), a cradle-to-grave approach to assess the cumulative environmental impacts resulting from all stages in the life of a product or a process. This approach was followed by Belboom et al. (2015) to determine the most environmentally-friendly route to produce phosphoric acid. This methodology also allows combining environmental and economic factors during the assessment of each process. For instance, Kulczycka et al. (2016) studied by applying a LCA methodology the most effective solution for the management of PG in the Wizôw plant (Poland) taking into account both aspects. These authors assessed the environmental impacts and economic feasibility of land disposal and the recovery of REE by leaching with sulfuric acid and subsequent crystallization of REE oxides. That study found that PG landfilling had much less impact on the environment than the proposed valorization technology even though this latter option took into account the potential beneficial environmental impacts associated with the acquisition of new materials: REE concentrates and anhydrite. In that case, the key factor affecting the impact of the proposed valorization technology was the excessive use of technological steam which required a large consumption of natural gas. Therefore, more sustainable technologies must be developed and compared to alternative options in order to address this technological and environmental quandary.

Another aspect to be considered is the social externality associated with the traditional production of goods compared to that related to recycled products. Teah and Onuki (2017) performed a social life cycle analysis (SLCA) to contrast the social impacts associated with mineral and recycled P fertilizers using the case study of Japan. These authors recommend including not only economic factors in the decision making of recycling policy but also social factors such as health and safety, resource security, human rights or equity. The health and safety aspects of PG stacking cannot be absolutely ignored. The impact of these waste containments on the human health and safety may be noteworthy (Zakharova et al., 2002) and the settling of these industrial repositories commonly find social rejection.

Conclusions

The phosphate fertilizer industry is witnessing double-digit growth in order to maintain the farming production worldwide, however produces huge amounts of an unwanted by-product known as phosphogypsum (PG) which is commonly stacked near the fertilizer plants. This study reviews the different potential applications for this by-product, providing some insights into the new valorization routes and critically describing the pros and cons of each approach. The policy of stacking is however under pressure by reasons of cost, safety and environmental impact and because it erroneously considers a potentially recyclable material as a waste. Much research on PG valorization has been done in the last years, mainly in agriculture, building and in industrial, environmental, and energy applications. However, the successful development of these technologies/applications met resistance due to social, political, technical, and economic constraints.

The first challenge to be overcome is the paradigm shift needed to consider a waste as a raw material. The use of secondary or recycled materials in the industrial sector has gained attention but only after proved experience is achieved. Many valorization routes consume low amounts of phosphogypsum, thus the demand of the product is limited and cannot satisfy the purpose of mass consumption. In this sense, the most promising applications are found in agriculture and road construction, where larger amounts of this material are used. However, there is still a gap of information about the potential release of metals and radionuclides during the life-time of certain applications, mainly in building. For this reason, case by case studies on metal and radionuclide release must be performed before application for safety purposes. The application of technologies may suffer from technical and economic constraints; some available technologies are quite expensive and its development is complex or the material needs a physical or chemical pretreatment which may consume much energy and reagents, increasing thus the costs. Therefore, costs generated by each technology must be estimated and compared to the rest of potential solutions to assure the return on investment and the cost efficiency of the valorization scheme. Valorization routes may also cause secondary pollution which must be evaluated and compared with that produced by other options, including in this assessment the social externalities that are not commonly considered.

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References

Abril, J.-M., García-Tenorio, R., Enamorado, S.M., Hurtado, M.D., Andreu, L., Delgado, A., 2008. The cumulative effect of three decades of phosphogypsum amendments in reclaimed marsh soils from SW Spain: 226Ra, 238U and Cd contents in soils and tomato fruit. Science of the Total Environment 403(1), 80-88. https://doi.org/10.1016/j.scitotenv.2008.1005.1013.

Al-Hwaiti, M., Al-Khashman, O., 2015. Health risk assessment of heavy metals contamination in tomato and green pepper plants grown in soils amended with phosphogypsum waste materials. Environmental Geochemistry and Health 37(2), 287-304. http://dx.doi.org/210.1007/s10653-10014-19646-z.

Al-Hwaiti, M., Ranville, J., Ross, P., 2010. Bioavailability and mobility of trace metals in phosphogypsum from Aqaba and Eshidiya, Jordan. Chemie Der Erde-Geochemistry 70(3), 283-291. https://doi.org/210.1016/j.chemer.2010.1003.1001.

Al-Masri, M., Amin, Y., Ibrahim, S., Al-Bich, F., 2004. Distribution of some trace metals in Syrian phosphogypsum. Applied Geochemistry 19(5), 747-753. https://doi.org/710.1016/j.apgeochem.2003.1009.1014.

Alcordo, I.S., Rechcigl, J.E., 1993. Phosphogypsum in agriculture: a review. Advances in Agronomy 49, 55-118.

Anon, 1966. Phosphate rock may be new rare-earth source. Chem. Eng. News 44, 52-53.

Arocena, J., Rutherford, P., Dudas, M., 1995. Heterogeneous distribution of trace elements and fluorine in phosphogypsum by-product. Science of the Total Environment 162(2), 149-160. https://doi.org/110.1016/0048-9697(1095)04446-04448.

Balkaya, N., Cesur, H., 2008. Adsorption of cadmium from aqueous solution by phosphogypsum. Chemical Engineering Journal 140(1), 247-254. https://doi.org/210.1016/j.cej.2007.1010.1002.

Belboom, S., Szöcs, C., Léonard, A., 2015. Environmental impacts of phosphoric acid production using di-hemihydrate process: a Belgian case study. Journal of Cleaner Production 108, 978-986. https://doi.org/910.1016/j.jclepro.2015.1006.1141.

Beretka, J., Cioffi, R., Marroccoli, M., Valenti, G., 1996. Energy-saving cements obtained from chemical gypsum and other industrial wastes. Waste Management 16(1), 231-235. https://doi.org/210.1016/S0956-1053X(1096)00046-00043.

Binnemans, K., Jones, P.T., Blanpain, B., Van Gerven, T., Pontikes, Y., 2015. Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review. Journal of Cleaner Production 99, 17-38. http://dx.doi.org/10.1016/j.jclepro.2015.1002.1089.

Bolívar, J.P.,García-Tenorio, R., Mas, J.L., Vaca, F., 2002. Radioactive impact in sediments from an estuarine system affected by industrial wastes releases. Environment International 27(8), 639-645. https://doi.org/610.1016/S0160-4120(1001)00123-00124.

Campos, M., Costa, L., Nisti, M., Mazzilli, B., 2017. Phosphogypsum recycling in the building materials industry: assessment of the radon exhalation rate. Journal of Environmental Radioactivity 172, 232-236. http://dx.doi.org/210.1016/j.jenvrad.2017.1004.1002.

Cánovas, C., Pérez-López, R., Macías, F., Chapron, S., Nieto, J., Pellet-Rostaing, S., 2017. Exploration of fertilizer industry wastes as potential source of critical raw materials. Journal of Cleaner Production 143, 497-505. https://doi.org/410.1016/j.jclepro.2016.1012.1083.

Cánovas, C.R., Macías, F., Pérez-López, R., 2018. Mobility of rare earth elements, yttrium and scandium from a phosphogypsum stack: Environmental and economic implications. Science of the Total Environment (in press). https://doi.org/10.1016/j.scitotenv.2017.08.220.

Cárdenas-Escudero, C., Morales-Flórez, V., Pérez-López, R., Santos, A., Esquivias, L., 2011. Procedure to use phosphogypsum industrial waste for mineral CO_2 sequestration. Journal of Hazardous Materials 196, 431-435. https://doi.org/410.1016/j.jhazmat.2011.1009.1039.

Carrero, S., Pérez-López, R., Fernandez-Martinez, A., Cruz-Hernández, P., Ayora, C., Poulain, A., 2015. The potential role of aluminium hydroxysulphates in the removal of contaminants in acid mine drainage. Chemical Geology 417, 414-423. https://doi.org/410.1016/j.chemgeo.2015.1010.1020.

Contreras, M., Pérez-López, R., Gázquez, M., Morales-Flórez, V., Santos, A., Esquivias, L., Bolívar, J., 2015. Fractionation and fluxes of metals and radionuclides during the recycling process of phosphogypsum wastes applied to mineral CO_2 sequestration. Waste Management 45, 412-419. http://dx.doi.org/410.1016/j.wasman.2015.1006.1046.

Çoruh, S., Ergun, O.N., 2010. Use of fly ash, phosphogypsum and red mud as a liner material for the disposal of hazardous zinc leach residue waste. Journal of Hazardous Materials 173(1), 468-473. https://doi.org/410.1016/j.jhazmat.2009.1008.1108.

Cuadri, A., Navarro, F., García-Morales, M., Bolívar, J., 2014. Valorization of phosphogypsum waste as asphaltic bitumen modifier. Journal of Hazardous Materials 279, 11-16. http://dx.doi.org/10.1016/j.jhazmat.2014.1006.1058.

Delgado, A., Uceda, I., Andreu, L., Kassem, S., Del Campillo, M., 2002. Fertilizer phosphorus recovery from gypsum-amended, reclaimed calcareous marsh soils. Arid Land Research and Management 16(4), 319-334. http://dx.doi.org/310.1080/15324980290000421.

EC, 2002. Design Guide — Road Construction Based on Phosphogypsum and Fly Ash, Disposal Management System For Utilization of Industrial Phosphogypsum and Fly Ash, EU Rep. Project No.: LIFE98ENV/FIN/000566, Office for Official Publications of the European Communities, Luxembourg.

Eghball, B., Power, J.F., Gilley, J.E., Doran, J.W., 1997. Nutrient, carbon, and mass loss during composting of beef cattle feedlot manure. Journal of Environmental Quality 26(1), 189-193. http://dx.doi.org/110.2134/jeq1997.00472425002600010027x.

El-Didamony, H., Ali, M.M., Awwad, N.S., Fawzy, M.M., Attallah, M.F., 2012. Treatment of phosphogypsum waste using suitable organic extractants. Journal of Radioanalytical and Nuclear Chemistry 291(3), 907-914. https://doi.org/910.1007/s10967-10011-11547-10963.

El-Didamony, H., Gado, H., Awwad, N., Fawzy, M., Attallah, M., 2013. Treatment of phosphogypsum waste produced from phosphate ore processing. Journal of Hazardous Materials 244, 596-602. . http://dx.doi.org/510.1016/j.jhazmat.2012.1010.1053.

El Zrelli, R., Courjault-Radé, P., Rabaoui, L., Castet, S., Michel, S., Bejaoui, N., 2015. Heavy metal contamination and ecological risk assessment in the surface sediments of the coastal area surrounding the industrial complex of Gabes city, Gulf of Gabes, SE Tunisia. Marine Pollution Bulletin 101(2), 922-929. https://doi.org/910.1016/j.marpolbul.2015.1010.1047.

Enamorado, S., Abril, J.M., Delgado, A., Más, J.L., Polvillo, O., Quintero, J.M., 2014. Implications for food safety of the uptake by tomato of 25 trace-elements from a phosphogypsum amended soil from SW Spain. Journal of Hazardous Materials 266, 122-131. http://dx.doi.org/110.1016/j.jhazmat.2013.1012.1019.

FIPR, 2016. Phosphogypsum and the EPA ban. Florida Industrial and Phosphate Research Institute, http://www.fipr.state.fl.us/about-us/phosphate-primer/phosphogypsum-and-the-epa-ban/. Last accessed: July 28th 2016.

Fu, F., Wang, Q., 2011. Removal of heavy metal ions from wastewaters: a review. Journal of Environmental Management 92(3), 407-418. https://doi.org/410.1016/j.jenvman.2010.1011.1011.

Germeau, A., Guidi, T., Fati, D., 2013. Method for treating phosphate rock. Patent WO 2013060689, A1.

Habashi, F., 1985. The recovery of the lanthanides from phosphate rock. Journal of Chemical Technology and Biotechnology 35(1), 5-14. http://dx.doi.org/10.1002/jctb.5040350103.

Habashi, F., Awadalla, F.T., 1986. The recovery of uranium and lanthanides during the production of nitrophosphate fertilisers using tertiary amyl alcohol. Journal of Chemical Technology and Biotechnology 36(1), 1-6. http://dx.doi.org/10.1002/jctb.280360102.

Hao, X., Larney, F.J., Chang, C., Travis, G.R., Nichol, C.K., Bremer, E., 2005. The effect of phosphogypsum on greenhouse gas emissions during cattle manure composting. Journal of Environmental Quality 34(3), 774-781. http://dx.doi.org/710.2134/jeq2004.0388.

Hentati, O., Abrantes, N., Caetano, A.L., Bouguerra, S., Gonçalves, F., Römbke, J., Pereira, R., 2015. Phosphogypsum as a soil fertilizer: Ecotoxicity of amended soil and elutriates to bacteria, invertebrates, algae and plants. Journal of Hazardous Materials 294, 80-89. http://dx.doi.org/10.1016/j.jhazmat.2015.1003.1034.

Hilton, J., Birky, B., Johnston, A., 2010. The “constructive regulation” of phosphates and phosphogypsum A new, evidence-based approach to regulating a NORM industry vital to the global community, Proceedings of IRPA12: 12. Congress of the International Radiation Protection Association: Strengthening Radiation Protection Worldwide-Highlights, Global Perspective and Future Trends.

IAEA, 2013. Radiation protection and management of norm residues in the phosphate industry. SAFETY REPORTS SERIES No. 78 — Vienna: International Atomic Energy Agency, 308 pp.

ICRP, 1991. Recommendations of the International Commission on Radiological Protection, Annals of the ICRP 21(1–3), ICRP Publication 60, Pergamon Press, Oxford, UK.

IFA, 1998. Recommendations of the International Commission on Radiological Protection, Annals of the ICRP 21(1–3), ICRP Publication 60, Pergamon Press, Oxford, UK.

Jarosiński, A., Kowalczyk, J., Mazanek, C., 1993. Development of the Polish wasteless technology of apatite phosphogypsum utilization with recovery of rare earths. Journal of Alloys and Compounds 200(1-2), 147-150. https://doi.org/110.1016/0925-8388(1093)90485-90486.

Jena, S., Misra, P., Das, B., 2016. Studies on extraction of potassium from feldspar by roast-leach method using phosphogypsum and sodium chloride. Mineral Processing and Extractive Metallurgy Review 37(5), 323-332. http://dx.doi.org/310.1080/08827508.08822016.01218869.

Kadirova, Z.C., Hojamberdiev, M., Bo, L., Hojiyev, R., Okada, K., 2014. Ion uptake properties of low-cost inorganic sorption materials in the CaO–Al_2 O 3–SiO_2 system prepared from phosphogypsum and kaolin. Journal of Cleaner Production 83, 483-490. http://dx.doi.org/410.1016/j.jclepro.2014.1006.1084.

Kolokolnikov, VA, Shatov, A., 2008. Phosphogypsum Processing into Sodium Sulphate and Technical Grade Calcium Carbonate. Chemistry for Sustainable Development 16, 401–405.

Kolokolnikov, V.A., Kovalev, M.I., 2009. Technology for Processing Technical Calcium Carbonate Obtained from Phosphogypsum into Pure Calcium Carbonate and Rare-Earth Element Concentrate. Chemistry for Sustainable Development 17, 387-393.

Kovler, K., 2009. Radiological constraints of using building materials and industrial by-products in construction. Construction and Building Materials 23(1), 246-253. https://doi.org/210.1016/j.conbuildmat.2007.1012.1010.

Kulczycka, J., Kowalski, Z., Smol, M., Wirth, H., 2016. Evaluation of the recovery of Rare Earth Elements (REE) from phosphogypsum waste–case study of the WIZÓW Chemical Plant

(Poland). Journal of Cleaner Production 113, 345-354. http://dx.doi.org/310.1016/j.jclepro.2015.1011.1039.

Leveque, A., Foraison, D., Sabot, J.L., 1981. Procédé permettant la récupération globale de l'uranium, des terres rares, du thorium et de l'yttrium contenus dans une solution acide. Google Patents. https://www.google.ch/patents/EP0026132A1?cl=fr.

Li, X., Du, J., Gao, L., He, S., Gan, L., Sun, C., Shi, Y., 2017. Immobilization of phosphogypsum for cemented paste backfill and its environmental effect. Journal of Cleaner Production 156, 137-146. http://dx.doi.org/110.1016/j.jclepro.2017.1004.1046.

Lim, S.-S., Park, H.-J., Hao, X., Lee, S.-I., Jeon, B.-J., Kwak, J.-H., Choi, W.-J., 2017. Nitrogen, carbon, and dry matter losses during composting of livestock manure with two bulking agents as affected by co-amendments of phosphogypsum and zeolite. Ecological Engineering 102, 280-290. http://dx.doi.org/210.1016/j.ecoleng.2017.1002.1031.

Lokshin, E., Vershkova, Y.A., Vershkov, A., Tareeva, O., 2002. Leaching of lanthanides from phosphohemihydrate with nitric acid. Russian Journal of Applied Chemistry 75(11), 1753-1759.

Lopes, G., Guilherme, L., Costa, E., Curi, N., Penha, H., 2013. Increasing arsenic sorption on red mud by phosphogypsum addition. Journal of Hazardous Materials 262, 1196-1203. http://dx.doi.org/1110.1016/j.jhazmat.2012.1106.1051.

Lottermoser, B., 2010. Mine Wastes: Characterization, Treatment and Environmental Impacts. Springer-Verlag Berlin Heidelberg.

Luo, Y., Li, G., Luo, W., Schuchardt, F., Jiang, T., Xu, D., 2013. Effect of phosphogypsum and dicyandiamide as additives on NH3, N2O and CH4 emissions during composting. Journal of Environmental Sciences 25(7), 1338-1345. https://doi.org/1310.1016/S1001-0742(1312)60126-60120.

Luther, S., Dudas, M., Rutherford, P., 1993. Radioactivity and chemical characteristics of Alberta phosphogypsum. Water, Air, and Soil Pollution 69(3-4), 277-290.

Macías, F., Cánovas, C.R., Cruz-Hernández, P., Carrero, S., Asta, M.P., Nieto, J.M., Pérez-López, R., 2017. An anomalous metal-rich phosphogypsum: Characterization and classification according to international regulations. Journal of Hazardous Materials 331, 99-108. http://dx.doi.org/110.1016/j.jenvman.2009.1003.1007.

Mazzilli, B., Palmiro, V., Saueia, C., Nisti, M., 2000. Radiochemical characterization of Brazilian phosphogypsum. Journal of Environmental Radioactivity 49(1), 113-122.

Mechi, N., Khiari, R., Ammar, M., Elaloui, E., Belgacem, M.N., 2017. Preparation and application of Tunisian phosphogypsum as fillers in papermaking made from Prunus amygdalus and Tamarisk sp. Powder Technology 312, 287-293. http://dx.doi.org/210.1016/j.powtec.2017.1002.1055.

Nisti, M., Saueia, C., Malheiro, L., Groppo, G., Mazzilli, B., 2015. Lixiviation of natural radionuclides and heavy metals in tropical soils amended with phosphogypsum. Journal of Environmental Radioactivity 144, 120-126. https://doi.org/110.1016/j.jenvrad.2015.1003.1013.

Ölmez, H., Yilmaz, V., 1988. Infrared study on the refinement of phosphogypsum for cements. Cement and Concrete research 18(3), 449-454. https://doi.org/410.1016/0008-8846(1088)90079-90078.

Pérez-López, R., Castillo, J., Sarmiento, A.M., Nieto, J.M., 2011. Assessment of phosphogypsum impact on the salt-marshes of the Tinto river (SW Spain): Role of natural attenuation processes. Marine Pollution Bulletin 62(12), 2787-2796. https://doi.org/2710.1016/j.marpolbul.2011.2709.2008.

Pérez-López, R., Macías, F., Cánovas, C.R., Sarmiento, A.M., Pérez-Moreno, S.M., 2016. Pollutant flows from a phosphogypsum disposal area to an estuarine environment: An insight from geochemical signatures. Science of the Total Environment 553, 42-51. http://dx.doi.org/10.1016/j.scitotenv.2016.1002.1070.

Pérez-López, R., Nieto, J.M., Jesús, D., Bolívar, J.P., 2015. Environmental tracers for elucidating the weathering process in a phosphogypsum disposal site: Implications for restoration. Journal of Hydrology 529, 1313-1323. http://dx.doi.org/1310.1016/.

Preston, J., Cole, P., Craig, W., Feather, A., 1996. The recovery of rare earth oxides from a phosphoric acid by-product. Part 1: Leaching of rare earth values and recovery of a mixed rare earth oxide by solvent extraction. Hydrometallurgy 41(1), 1-19. https://doi.org/10.1016/0304-1386X(1095)00051-H.

Prochnow, L., Kiehl, J., Pismel, F., Corrente, J., 1995. Controlling ammonia losses during manure composting with the addition of phosphogypsum and simple superphosphate. Scientia Agricola 52(2), 346-349. http://dx.doi.org/310.1590/S0103-90161995000200024

Rashad, A.M., 2017. Phosphogypsum as a construction material. Journal of Cleaner Production 166, 732-743. http://dx.doi.org/10.1016/j.jclepro.2017.08.049.

Rentería-Villalobos, M., Vioque, I., Mantero, J., Manjón, G., 2010. Radiological, chemical and morphological characterizations of phosphate rock and phosphogypsum from phosphoric acid factories in SW Spain. Journal of Hazardous Materials 181(1), 193-203.

Rodríguez-Jordá, M., Garrido, F., García-González, M., 2010. Potential use of gypsum and lime rich industrial by-products for induced reduction of Pb, Zn and Ni leachability in an acid soil. Journal of Hazardous Materials 175(1), 762-769. https://doi.org/710.1016/j.jhazmat.2009.1010.1074.

Romero-Hermida, I., Santos, A., Pérez-López, R., García-Tenorio, R., Esquivias, L., Morales-Flórez, V., 2017. New method for carbon dioxide mineralization based on phosphogypsum and aluminium-rich industrial wastes resulting in valuable carbonated by-products. Journal of CO2 Utilization 18, 15-22. http://dx.doi.org/10.1016/j.jcou.2017.1001.1002.

Rutherford, P., Dudas, M., Samek, R., 1994. Environmental impacts of phosphogypsum. Science of the Total Environment 149(1-2), 1-38.

Santos, A., Mazzilli, B., Fávaro, D., Silva, P., 2006. Partitioning of radionuclides and trace elements in phosphogypsum and its source materials based on sequential extraction methods. Journal of Environmental Radioactivity 87(1), 52-61. http://dx.doi.org/10.1016/j.jenvrad.2005.1010.1008.

Saueia, C.H.R., Le Bourlegat, F.M., Mazzilli, B.P., Fávaro, D.I.T., 2013. Availability of metals and radionuclides present in phosphogypsum and phosphate fertilizers used in Brazil. Journal of Radioanalytical and Nuclear Chemistry 297(2), 189-195.

Shivaramaiah, R., Lee, W., Navrotsky, A., Yu, D., Kim, P., Wu, H., Hu, Z., Riman, R., Anderko, A., 2016. Location and stability of europium in calcium sulfate and its relevance to rare earth recovery from phosphogypsum waste. American Mineralogist 101(8), 1854-1861. https://doi.org/1810.2138/am-2016-5684.

Smičiklas, I., Dimović, S., Plećaš, I., Mitrić, M., 2006. Removal of Co2+ from aqueous solutions by hydroxyapatite. Water research 40(12), 2267-2274. https://doi.org/2210.1016/j.watres.2006.2204.2031.

Sundaram, C.S., Viswanathan, N., Meenakshi, S., 2008. Defluoridation chemistry of synthetic hydroxyapatite at nano scale: equilibrium and kinetic studies. Journal of Hazardous Materials 155(1), 206-215. https://doi.org/210.1016/j.jhazmat.2007.1011.1048.

Takahashi, T., Ikeda, Y., Nakamura, H., Nanzyo, M., 2006. Efficiency of gypsum application to acid Andosols estimated using aluminum release rates and plant root growth. Soil Science & Plant Nutrition 52(5), 584-592. http://dx.doi.org/510.1111/j.1747-0765.2006.00071.x.

Tang, Z., Lei, T., Yu, J., Shainberg, I., Mamedov, A., Ben-Hur, M., Levy, G., 2006. Runoff and interrill erosion in sodic soils treated with dry PAM and phosphogypsum. Soil Science Society of America Journal 70(2), 679-690. http://dx.doi.org/610.2136/sssaj2004.0395.

Tayibi, H., Choura, M., López, F.A., Alguacil, F.J., López-Delgado, A., 2009. Environmental impact and management of phosphogypsum. Journal of Environmental Management 90(8), 2377-2386. http://dx.doi.org/2310.1016/j.jenvman.2009.2303.2007.

Teah, H.Y., Onuki, M., 2017. Support Phosphorus Recycling Policy with Social Life Cycle Assessment: A Case of Japan. Sustainability 9(7), 1223. http://dx.doi.org/1210.3390/su9071223.

Tian, T., Yan, Y., Hu, Z., Xu, Y., Chen, Y., Shi, J., 2016. Utilization of original phosphogypsum for the preparation of foam concrete. Construction and Building Materials 115, 143-152. http://dx.doi.org/110.1016/j.conbuildmat.2016.1004.1028.

USGS, 2017. Geological Survey, 2017, Mineral commodity summaries 2017: U.S. Geological Survey, 202 p., https://doi.org/10.3133/70180197.

Valkov, A., Andreev, V., Anufrieva, A., Makaseev, Y., Bezrukova, S., Demyanenko, N., 2014. Phosphogypsum technology with the extraction of valuable components. Procedia Chemistry 11, 176-181. https://doi.org/110.1016/j.proche.2014.1011.1031.

Walawalkar, M., Nichol, C.K., Azimi, G., 2016. Process investigation of the acid leaching of rare earth elements from phosphogypsum using HCl, HNO 3, and H 2 SO 4. Hydrometallurgy 166, 195-204. http://dx.doi.org/110.1016/j.hydromet.2016.1006.1008.

Yang, F., Li, G., Shi, H., Wang, Y., 2015. Effects of phosphogypsum and superphosphate on compost maturity and gaseous emissions during kitchen waste composting. Waste Management 36, 70-76. http://dx.doi.org/10.1016/j.fuel.2016.1012.1077.

Yang, J., Ma, L., Dong, S., Liu, H., Zhao, S., Cui, X., Zheng, D., Yang, J., 2017. Theoretical and experimental demonstration of lignite chemical looping gasification of phosphogypsum oxygen carrier for syngas generation. Fuel 194, 448-459. http://dx.doi.org/410.1016/j.fuel.2016.1012.1077.

Yang, L., Zhang, Y., Yan, Y., 2016. Utilization of original phosphogypsum as raw material for the preparation of self-leveling mortar. Journal of Cleaner Production 127, 204-213. http://dx.doi.org/210.1016/j.jclepro.2016.1004.1054.

Zakharova, T., Tatano, F., Menshikov, V., 2002. Health cancer risk assessment for arsenic exposure in potentially contaminated areas by fertilizer plants: A possible regulatory approach applied to a case study in Moscow region–Russia. Regulatory Toxicology and Pharmacology 36(1), 22-33. https://doi.org/10.1006/rtph.2002.1561.

Zhang, D., Luo, H., Zheng, L., Wang, K., Li, H., Wang, Y., Feng, H., 2012. Utilization of waste phosphogypsum to prepare hydroxyapatite nanoparticles and its application towards removal of fluoride from aqueous solution. Journal of Hazardous Materials 241, 418-426. https://doi.org/410.1016/j.jhazmat.2012.1009.1066.

Zhang, X., Miller, W., Nearing, M., Norton, L., 1998. Effects of surface treatment on surface sealing, runoff, and interrill erosion. Transactions of the ASAE 41(4), 989.

Zhao, H., Li, H., Bao, W., Wang, C., Li, S., Lin, W., 2015. Experimental study of enhanced phosphogypsum carbonation with ammonia under increased CO_2 pressure. Journal of CO_2 Utilization 11, 10-19. https://doi.org/10.1016/j.jcou.2014.1011.1004.

Figure captions

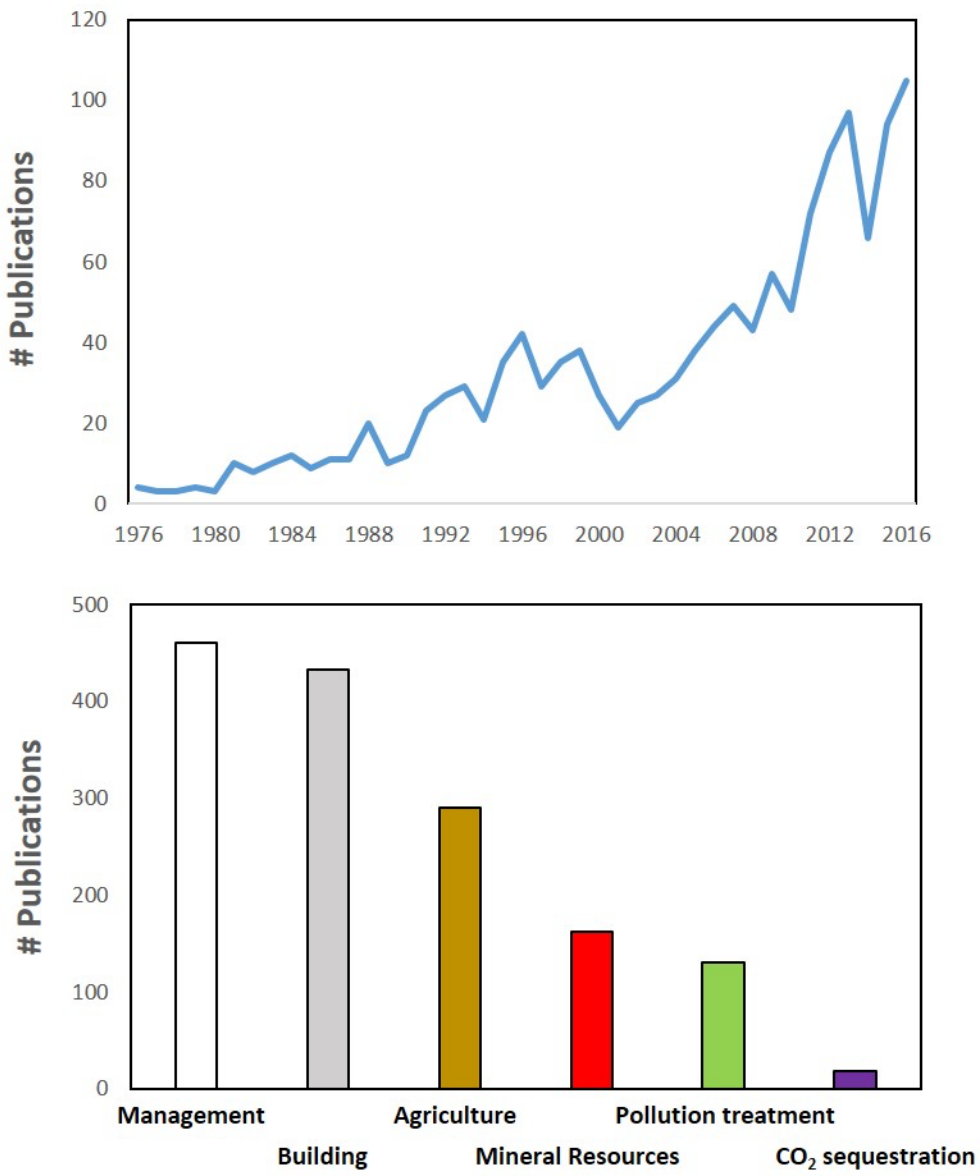


Figure 1. A) Number of publications dealing with PG in the last 40 years; B) main subjects of interest on PG research.

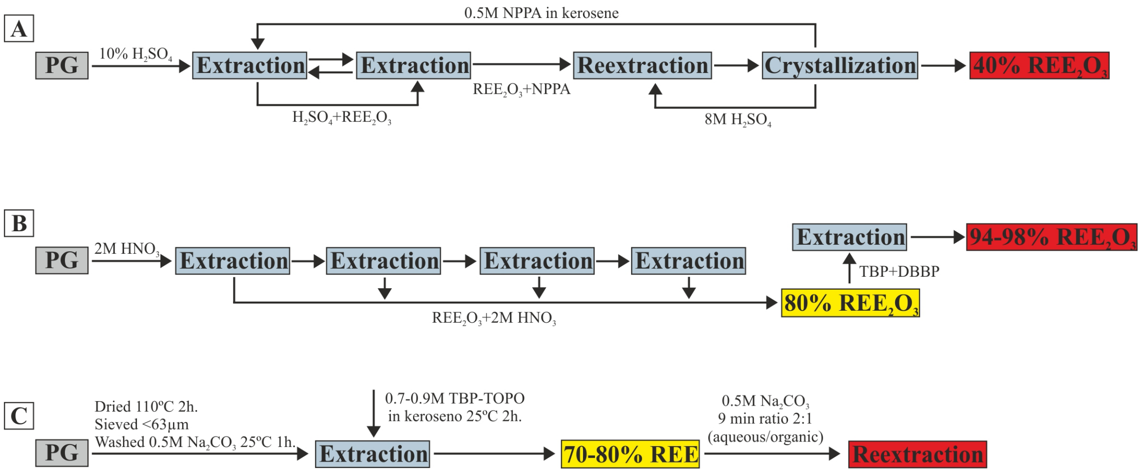


Figure 2. Some examples of REE recovery schemes developed at lab scale.

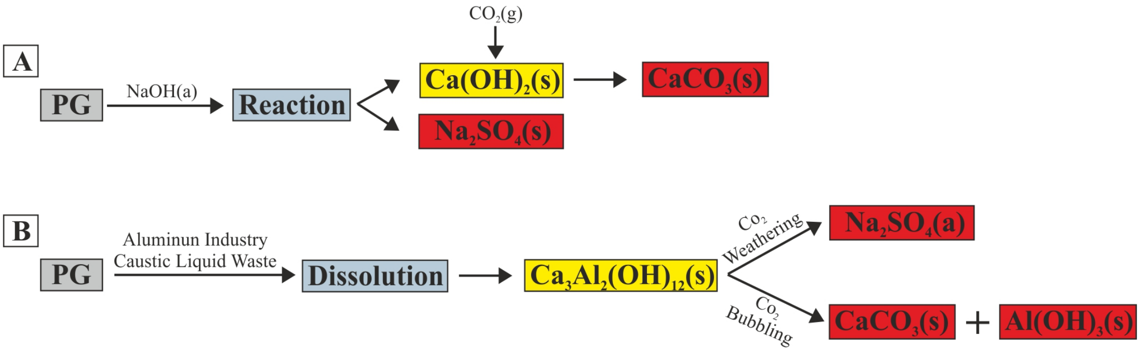


Figure 3. Some examples of PG transformation into raw materials of commercial interest.

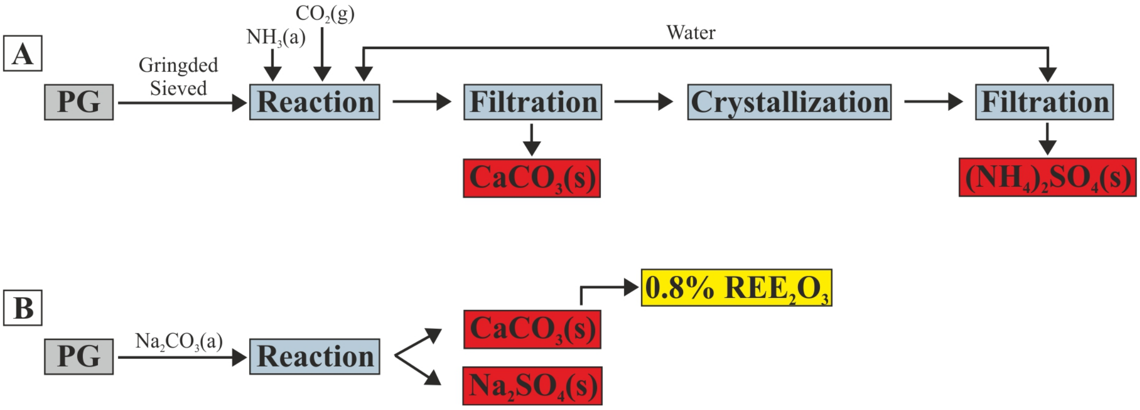
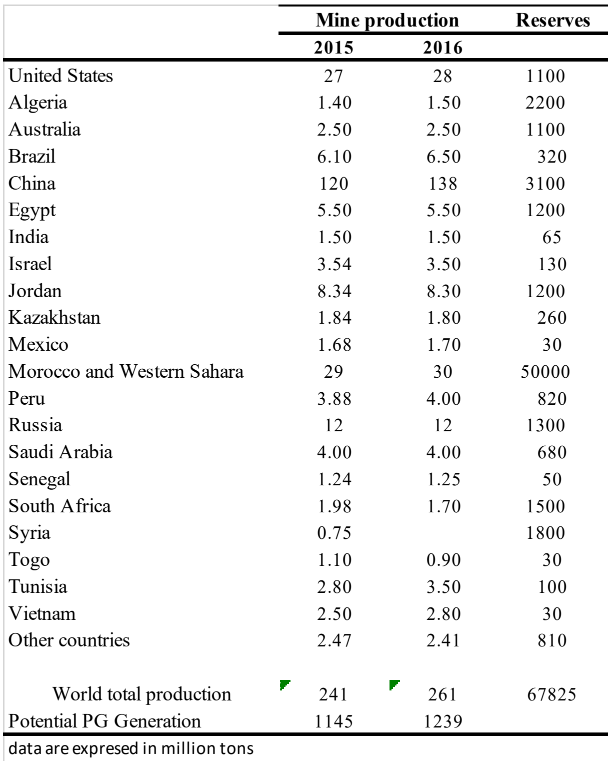


Figure 4. Some examples of CO_2 sequestration using PG and obtaining of raw materials of commercial interest.

Tables



	Mine production		Reserves
	2015	2016	
United States	27	28	1100
Algeria	1.40	1.50	2200
Australia	2.50	2.50	1100
Brazil	6.10	6.50	320
China	120	138	3100
Egypt	5.50	5.50	1200
India	1.50	1.50	65
Israel	3.54	3.50	130
Jordan	8.34	8.30	1200
Kazakhstan	1.84	1.80	260
Mexico	1.68	1.70	30
Morocco and Western Sahara	29	30	50000
Peru	3.88	4.00	820
Russia	12	12	1300
Saudi Arabia	4.00	4.00	680
Senegal	1.24	1.25	50
South Africa	1.98	1.70	1500
Syria	0.75		1800
Togo	1.10	0.90	30
Tunisia	2.80	3.50	100
Vietnam	2.50	2.80	30
Other countries	2.47	2.41	810
World total production	241	261	67825
Potential PG Generation	1145	1239	

data are expresed in million tons

Table 1. Worldwide production of phosphate rock in 2015 and 2016, potential reserves and PG generated (modified from USGS, 2017).

Material	Typical activity concentration (Bq kg-1)			Maximum activity concentration (Bq kg-1)		
	^{226}Ra	^{232}Th	^{40}K	^{226}Ra	^{232}Th	^{40}K
Concrete	40	30	400	240	190	1600
Aerated and light-weight	60	40	430	2600	190	1600
Clay (red) bricks	50	50	670	200	200	2000
Sand-lime bricks	10	10	330	25	30	700
Natural building stones	60	60	640	500	310	4000
Natural gypsum	10	10	80	70	100	200
Phosphogypsum	390	20	60	1100	160	300

Table 2. Typical and maximum activity concentrations in common building materials and phosphogypsum used for building materials in the EU (from EC, 1999).

Applications	Treatment		Results	References
	PG type/composition	Dose		
Improving soil structure and crop yield	PG (85% $CaSO_4$, and particle size, 2 mm)	PG alone (2 and 4 Mg ha^{-1}). PG mixed with dissolved polyacrylamide (PAM 20 Kg ha^{-1} and PG 2 Mg ha^{-1}; PAM 20 Kg ha^{-1} and PG 4 Mg ha^{-1})	Preventing the dispersion of the clay, and subsequently decreasing soil loss	Tang et al. (2006)
Controlling surface sealing and reducing runoff and soil erosion	Gypsum (chemical treatment, PG from Bortow, Florida: 95% $CaSO_4{\cdot}2H_2O$)	Gypsum powder at 5 Mt ha^{-1}. 1Kg m^{-3} PAM solution (prepared in 2.5 mol m^{-3} gypsum solution)	Reduction of seal-crust formation, runoff, and erosion	Zhang et al. (1998)
Acidic soils (non-allophanic Andosol)	Gypsum ($CaSO_4{\cdot}2H_2O$)	Gypsum + 4.3 g kg^{-1} soil samples; Gypsum + 8.6 g Kg^{-1} soil samples	Root growth in horizons poor in humus and decrease in Al release	Takahashi et al. (2006)
Reduction of the avaliability of Pb, Zn, and Ni in a metal-spiked acid soil	PG and RG (Fertiberia S.A., SW Spain)	Portions of 210 g of soils mixed with PG and RG alone, and with other industrial by-products (sugar foam and ashes from burnt biomass ACB)	Decrease of metal (Pb, Zn, and Ni) leachability by formation of non-cristalline Al-hydroxy polymers	Rodriguez-Jordá et al. (2010)
Phosphorus fertilizer recovery from marsh soils	Gypsum (Fertiberia S.A., SW Spain)	Gypsum at 6, 20, 100 g Kg^{-1} added to marsh soils with 200 or 2000 mg PKg^{-1} applied as $NH_4H_2PO_4$	Increase the efficiency of fertilizer P, contributing to enhanced productivity of freshly reclaimed saline and sodic marsh soils	Delgado et al. (2002)
Evaluation of the bioavailability of metals (As, Cd, Cr, Co, Cu, Hg, Ni, Pb, Se, Zn) and radionuclides (^{226}Ra, ^{228}Ra and ^{210}Pb) present in PG	PG and phosphate fertilizers from Copebras S.A., Ultrafertil S.A., and Fosfertil (Brazil)	NI	PG presented metals concentration lower than the phosphate fertilizers. The radionuclides present in PG and fertilizer were not available to the environment	Saueia et al. (2013)
Evaluation of the bioavailability of REE, Ba and radionuclides to the surrounding aquatic system	Phosphate rocks from Catalão I carbonatite complex (Brazil); PG from two Brazilian producers of phosphoric acid	PG as water-soluble phase	PG is enriched by ^{226}Ra, ^{210}Pb, ^{232}Th, ^{228}Ra, REE and Ba during the treatment of phosphate rock with sulphuric acid but without representing a threat to the surrounding aquatic environment	Santos et al. (2006)
Estimation of the lixiviation of the radionuclides (^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th and ^{228}Ra) and metals (As, Cd, Cr, Ni, Se, Hg and Pb) present in PG	PG from Vale Fertilizantes Industry (Uberaba, Minas Gerais State), Installation (PG UBE) and in the unit of Cubatão (PG CUB, São Paulo State) (Brazil)	Sandy and Clay Brazilian soils mixed with PG (percolated with water): 5 kg of soil + two types of PG; mixture of soil + recommended dose and mixture of soil + 10 times the recommended dose + distilled water (sandy soil 1400 mL; clay soil 2400 mL)	No enhancement of the radionuclides and metals content in water was observed	Nisti et al. (2015)
Soil amendment to reduce Na saturation in soils	PG from a non-active PG stack in Huelva (Fertiberia, SW Spain)	Cotton and sugar beet crops; 25 Mg ha^{-1} PG in April 2003 and September 2004, applied in triplicate in 0.5 ha (250×20 m) plots	Significant increment in ^{226}Ra-concentration in three-decade application of PG soils. Cd concentrations in tomato fruits one order of magnitude higher than those found in tomatoes from a market survey but within the European-Union acceptance levels	Abril et al. (2008)
Ca-amendment to reclaim sodic soils	PG from a non-active PG stack in Huelva (Fertiberia, SW Spain)	Industrial tomato crop; four PG treatments equivalent to 0, 20, 60, and 200 Mg ha^{-1}	Decreased concentrations of Mn, Co, and Cu in shoots; and B, Cu, Sb, Cs, Ba, Tl, and Th in fruits. Enhanced accumulation of Se in fruits. Cd concentrations in tomato below the maximum allowed levels in control pots (0 Mg PG ha^{-1})	Enamorado et al. (2014)
Assessing the impact of PG amendments on the soil habitat and retention functions, before recommending the use of Sfax PG as a soil fertilizer	PG from Tunisian industrial plant (Sfax, Tunisia)	OECD artificial soil mixed with PG percentages (0.0, 4.9, 7.4, 11.1, 16.6, and 25) and elutriates obtained from OECD soil batch amended with PG percentages (0.0, 6.25, 12.5, and 25)	Acute and chronic effects on invertebrates exposed to amended soils and elutriates related mainly to the extremely high levels of Ca. Terrestrial and aquatic plants were the most tolerant species. No stimulatory effects on growth were observed for any of the species tested	Hentati et al. (2015)
Additive during composting	NI	NI	Addition of PG during composting may avoid ammonia volatilization due to the formation of ammonium salts ($(NH_4)_2SO_4$) retaining N and avoiding nutrient imbalance by reduction of the N:P ratio	Eghball et al. (1997)
Effectiveness of PG and superphosphate in controlling ammonia losses	PG (17.93% S) and ground simple superphosphate (19.31% total P_2O_5 and 12.93% S)	PG and superphosphate applied at the rates equivalent to 50, 100, 150, and 200 kg.t^{-1} of prepared substrate	Ammonia lost decreased by volatilization due to the presence of gypsum or sulfate	Prochnow et al. (1995)
The effects of PG and zeolite amendments on reducing N loss and concurrent changes in carbon (C) and dry matter losses	PG sample from a P fertilizer manufacturing company (Namhae Chemical, Yeosu-city, Chonnam province, Republic of Korea)	A ratio of cattle manure, bulking agents (i.e. rice hull, sawdust) and amendment (i.e. zeolite, PG) of 2:2:1	Decreased total N loss; reduced N, C, and dry matter loss in mesophilic composting. Reduction in N loss in mesophilic composting	Lim et al. (2017)

NI, non indicated; PG, phosphogypsum; RG, red gypsum

Table 3. Some examples of PG application in agriculture.

PG Valorization	Advantages	Drawbacks	Solutions/Tools
Building	Reduction of pollutants	Legal barriers	Social and political awareness
		Reluctance to consider PG as raw material	
Agriculture	Energy saving	Consumption requirements	Research and development
Source of raw material	Preservation of mineral resources	Technical constraints	
Industrial Sector	Reduction of landscape impacts	PG heterogeneity	Site by sites studies
Energy sector	Reduction of social impacts	Classification discrepancies	Harmonization of International rules
Pollution prevention and remediation	Reutilization of derelict industrial sites for other land uses	Secondary pollution	Social Life Cycle Analysis (SLCA)
		Social Impact	

Table 4. Potential application sectors of phosphogypsum, main advantages, drawbacks and associated solutions.