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Effective and innovative procedures to use phosphogypsum waste in different application domains: review of the environmental, economic challenges and life cycle assessment

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Abstract

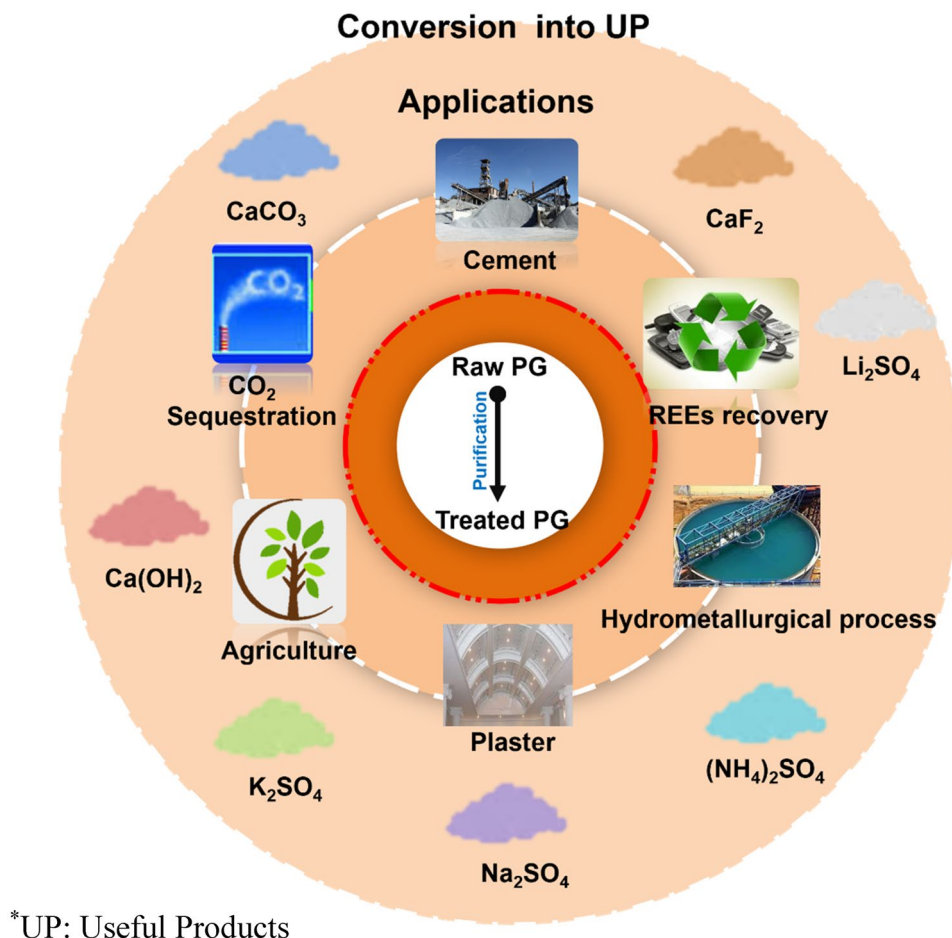
Phosphogypsum (PG) waste is a by-product generated from wet-process phosphoric acid (H_3PO_4) manufacturing during phosphate rock decomposition. Worldwide, the annual production of PG ranges between 100 and 300 million tons, with only a few quantities utilized in several application domains (about 15%), the unused PG is usually discharged into the sea or stocked in large stockpiles with potential serious human and environmental risks. Therefore, in this review article, we have studied and discussed the possible alternative ways for PG waste recycling and use. Indeed, this waste material could be considered as a mineral resource of secondary raw materials within the scope of a circular economy. An inclusive bibliographic search, dealing with our review's objectives, was performed according to the two famous-databases: Web of Sciences and Scopus. After different selecting processes, about 153 articles are found. PG is used in several sectors, including agriculture, as well as in the brick and cement industry, and road construction. Other applications are reported in this study such as PG conversion to valuable products and rare earths elements (REEs) extraction. In the same context and in the sense of reducing greenhouse gasses emissions (GHGs), PG is often used as a calcium source for CO_2 mineral sequestration. In addition, different methods of treatment and purification, techno-economic, life cycle and environmental assessment of the PG recycling, and valorization technologies are summarized and reported in this review. Finally, recent technologies used for extracting REEs from PG were investigated. The main results, conclusions, and recommendations reported here could be considered as a guide for future studies, and also should be of benefit to scientists, chemists and engineers interested in the utilization/ treatment of PG.

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Graphical Abstract



Keywords Phosphogypsum · Waste · Conversion · Purification · Solubility · REEs · Life cycle assessment

Introduction

Phosphorous is multivalent non-metal of the nitrogen group useful and well-established donor atoms in coordination chemistry [1]. It is one of the 19 elements strictly indispensable for the growth and development of living beings whether microbial, plant or animal, and the fifth element composing living matter [2]. This element is an essential component of nervous tissue, bone and cell protoplasm. No other element in the periodic table seems to be able to replace phosphorous in the three processes specific to life [3]: reproduction, energy transfer and respiratory mechanisms. Phosphorous is a strategic element for life on earth because of its low availability in most environments [4]. Generally, it originates from phosphate rocks that are chemically treated, while exploitable phosphate deposits are limited and concentrated in a few countries. The phosphate rocks, thus extracted from the mining and phosphates production sites, are converted into

marketable products, such as phosphoric acid H_3PO_4 (PA) and NPK fertilizers [5–8]. Worldwide, the most common process used for H_3PO_4 manufacture is the dihydrate process. This process consists of attacking the natural calcium phosphate ore (apatite) with sulfuric acid according to the simplified scheme shown in Fig. 1 [9–11]. It is formed of a high concentration of PA containing about 26–30% P_2O_5 and PG waste containing $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [12]. This wet-process is operated at a temperature of 70–80 °C [13]. The PG waste mainly contains gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (~95%), and numerous impurities (~5%) that are dependent to a large extent on the quality of phosphate rock (PR) used, its origin and the preparation process followed during the H_3PO_4 manufacture [14].

As shown in Table 1, the worldwide production of this waste is measured between 100 to 280 Mt/Year [15–17]. Only 45 Mt/Year (~15%) of the PG is recycled and used in agriculture, building, and construction materials [18]. This

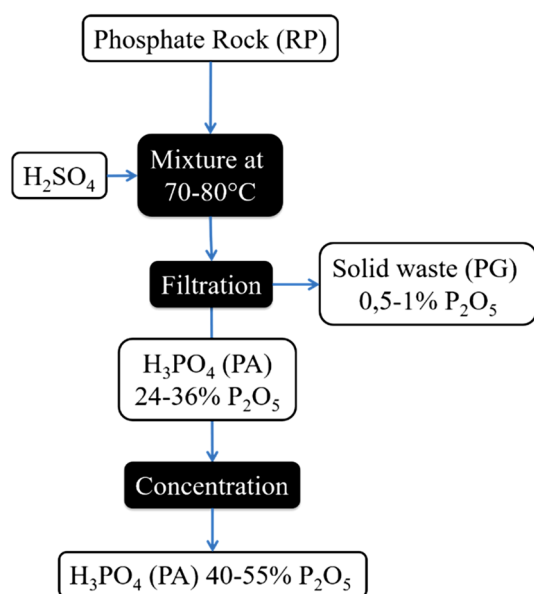


Fig. 1 Simplified schema of phosphoric acid manufacturing process

Table 1 Average of worldwide PG production

Countries	PG production Mt/Year	References
China	> 55	[33]
Egypt	0.2	[34]
Jordan	3	[35]
Morocco	15	[36]
Senegal ^(a)	~ 280/ stockpiles	[37]
Serbia	0.8	[38]
Spain	120/ stockpiles	[23]
Syria	0.4	[39]
Tunisia	10	[40]
Ukraine	10	[41]
USA	35	[42]
Worldwide production	Estimated at 280	[16, 17]

^a166 million m³/stockpiles

low use is particularly due to the existence of undesirable contaminants, such as organic matter, metals, and trace elements like heavy metals and natural radionuclides [19–21]. The unused PG (~ 85%) is often deposited near the fertilizer plants in vast stockpiles or discharged into the sea, landfills, rivers, and ponds [22–26]. As many countries (including Morocco) have huge production of PG, the discharge of this quantities into the sea could be a practical alternative in terms of economy.

Relatively high levels of radionuclides and heavy metals in PG could have an impact on the environment which makes its commercial use impossible [27]. Remarkably, the

PG's massive production, inadequate storage, and high toxicity play a fundamental role in soil and water contamination [28–30]. From a toxicological point of view, an increase in the concentration of these elements in the marine environment could disturb this environment as well as its living beings, without sparing the highest level of the trophic chain, which is human [31]. This reflects significant and real environmental challenges [32] for the manufacturing units of H₃PO₄ worldwide. To address this issue, many researchers and laboratories have been exploring effective and innovative methods to use PG as a valuable resource for the preparation of useful compounds. This valorization provides added value to many existing industries such as fertilizers, cement and detergents. In addition, many hydrometallurgical process technologies used for leaching and extracting both rare earth elements and heavy metals from PG were investigated. It is very important to treat, purify, and identify the different applications of PG.

In summary, based on literature researches, this review attempts to outline different types of PG pretreatments, uses and chemical transformations. Advantages and disadvantages of these processes are discussed aiming large scale management and recycling methods of the large amount of PG produced annually. To the best of our knowledge, the study of PG use in several domains of applications has been presented largely in many review articles [35, 41, 100], however, there is no detailed report describe and discuss on the same time: the use, transformation, environmental, social and economic challenges, and life cycle assessment (LCA) study related to the PG field. The results of this study provide a guide and reference for future research in the field of PG application and treatment.

Materials and methods: methodology for the literature review

The continuous growth of the world population raises the need for food supply, that leads to a further increase in the phosphate fertilizer (PF), phosphoric acid (PA) production and, consequently, the annual release of large quantities of PG waste. The method used to carry out this review study consists of identifying first of all scientific publications related to the "phosphogypsum" by using search key as: phosphogypsum. This study was realized according to the two famous-databases: Web of Sciences and Scopus. The results from these two databases were used to construct the Fig. 2. In this figure, the results have been represented as follows:

- In Fig. 2a: the number of publications related to the key search "phosphogypsum" as function of the selected

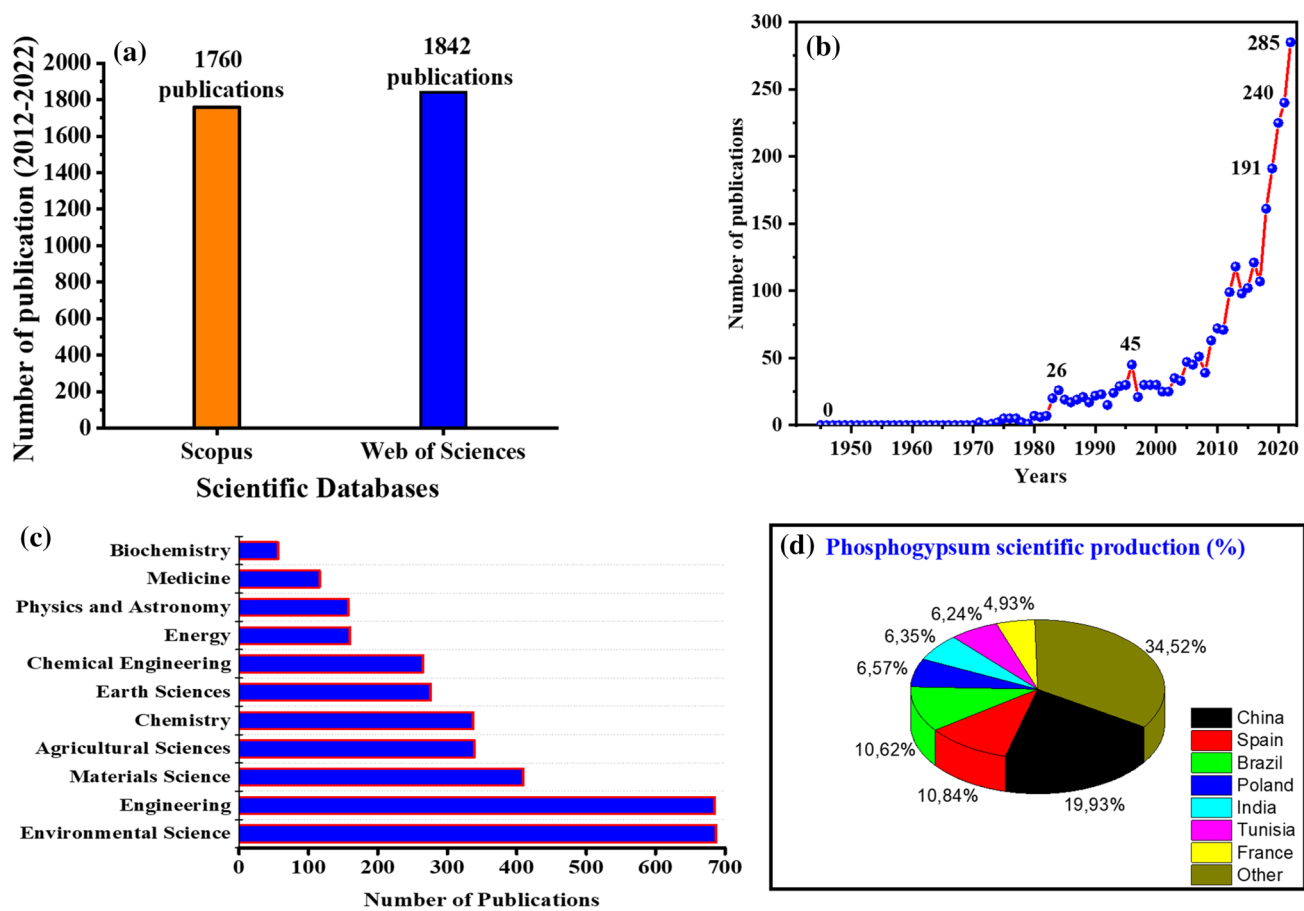


Fig. 2 “Phosphogypsum” scientific production as function of: scientific databases (a), years (between 1941 and 2022 results from Scopus Database available at: <http://www.scopus.com>) (b), scientific areas (c) and countries (d)

databases (between 2012 and 2022). In this period about 3602 publications are found;

- In Fig. 2b: the number of publications related to the key search “phosphogypsum” between 1941 and 2022 for the Scopus database. This figure shows a noticeable lack of scientific publications in the period of 1941 to 1970, despite the fact that superphosphates industry has significantly increased since the Second World War. The first publications related to PG start to appear only after 1975. After this period, an exponential increase in the number of articles published from 1975 till today, especially from 2000 to 2022 is clearly noticed.
- In Fig. 2c: the results are given also as function of the scientific areas. Globally, a high proportion of scientific publications are common to many scientific areas;
- In Fig. 2d: finally, the results are given by countries. It is remarkably that about five countries contribute to ~50% of the scientific production: China, Spain, Poland, Brazil, and India.

This increase in the PG publication is to find friendly routes for PG management, purification, and valorization in different application domains.

In continuation, the literature review procedure is as follow:

- (1) Filtration process: an important number of publications were identified by selecting the different keywords related to the review objective such as valorization, management, application, waste, characterization, recycling, solubility, agriculture, building, environment, pollution, treatment, carbon dioxide, carbonation, life cycle assessment, economic challenge.
- (2) Scanning process: after the filtration process, a scanning process was performed basing on the titles and abstracts of the above selected publications.
- (3) Papers selection process: as the subject of this work is “Effective and innovative procedures to use phosphogypsum waste in different application domains”, we

have favorably and globally used the recently published articles. This search is resulting in 153 analyzed publications.

This paper presents also a brief study on the application of Life Cycle Assessment (LCA) methodology, to assess environmental impacts of PG use and management. Generally, the application of LCA in this field is not largely reported. For that, this review attempts to discuss and analyze the most important decisions taken in recent LCA studies. We describe here (See Sect. “Techno-economical and life cycle assessment”) several LCA methods, by reporting their procedures (Software, data-base, indicators, parameters, etc.) and giving the final results for each method.

Solubility studies of phosphogypsum

The solubility measurement of PG and synthetic gypsum (SG) is the widely used information to describe the behavior and the optimal parameters influencing the dissolution of this waste in different solutions [43]. It is also of particular importance in chloride hydrometallurgy and numerous conversion processes, such as the manufacture of sodium, potassium and ammonium sulfate from PG by

simple dissolution in chloride solutions [44, 45]. Numerous investigations considered the solubility of SG and PG in aqueous solutions as described in Table 2. The procedure used in these investigations is shown in Fig. 3.

The study of PG solubility in multicomponent electrolyte aqueous solutions is of significant importance in many disciplines in science and engineering. Basing in the literature, it can be seen, that PG solubility was studied in different aqueous solutions such as: deionized water, sea water, sodium, potassium and ammonium chloride solutions. The maximum concentrations of sulfate (SO_4^{2-}) that can be extracted from PG are around 1600 and 1900 mg L^{-1} using respectively deionized and sea water [46]. While, the highest value of solubility (about 2600 mg L^{-1} of SO_4^{2-}) was obtained in a salt solution containing 25 g L^{-1} of NaCl [51]. Thus, using water with a high salt content (sea water or treated brine water) has the advantages of improving PG solubility and exerting lesser pressure on water resources [47]. In diluted acidic medium (nitric, hydrochloric and sulfuric) the solubility constant of PG reaches 3.14×10^{-5} [48]. For this purpose, the leaching of PG in acidic solutions is of great interest in order to extract add-value REEs elements. Generally, there is a strong correlation between PG solubility and acid leaching efficiency [49].

Table 2 Investigations related to solubility measurements of PG

Source	Reagent	Conc. mol L^{-1}	T ($^{\circ}\text{C}$)	Solubility g L^{-1}	Comments	References
SG ^a	Acetic acid	0.25	30	13.5 ^b	Solubility increases with increasing acid for a concentration less than 0.25 M and decreases again at higher concentration	[51]
	Oxalic acid			14.5 ^b		
	Tartaric acid			9 ^b		
	Succinic acid			6.5 ^b		
SG	Nitric acid	0 to 30 ^c	60	4.5	Variation of gypsum solubility in nitric acid passes through a maximum in the range 22–25 wt.% HNO_3	[52]
SG	HCl- CaCl_2 mixture	1	10 to 80	1	Parameters investigated are: HCl concentration up to 5 M, CaCl_2 concentration up to 2 M and temperature	[53]
SG	HCl	3	80	47	Parameters investigated are: HCl concentration up to 6 M, and KCl concentration up to 180 g L^{-1}	[45]
	HCl	3	25	24		
	KCl	130 ^d	25	9		
SG	NaCl	1	70	0.1 ^b	High solubility of PG in chloride solutions basically attributed to ionic strength effects but temperature changes have relatively minor effect	[50]
PG		25	25	5.3	Optimal concentration is 25 g L^{-1} of NaCl	[54]
PG and NG ^e	Pure water and lime solution	Saturated solution	35	2	Solubility of PG is different to that of NG due to the presence of some impurities such as heavy metals and radionuclides	[55]

^aSynthetic gypsum, ^bhere given as $[\text{SO}_4^{2-}]$, ^c(wt%), ^d(g L^{-1}), ^enatural gypsum

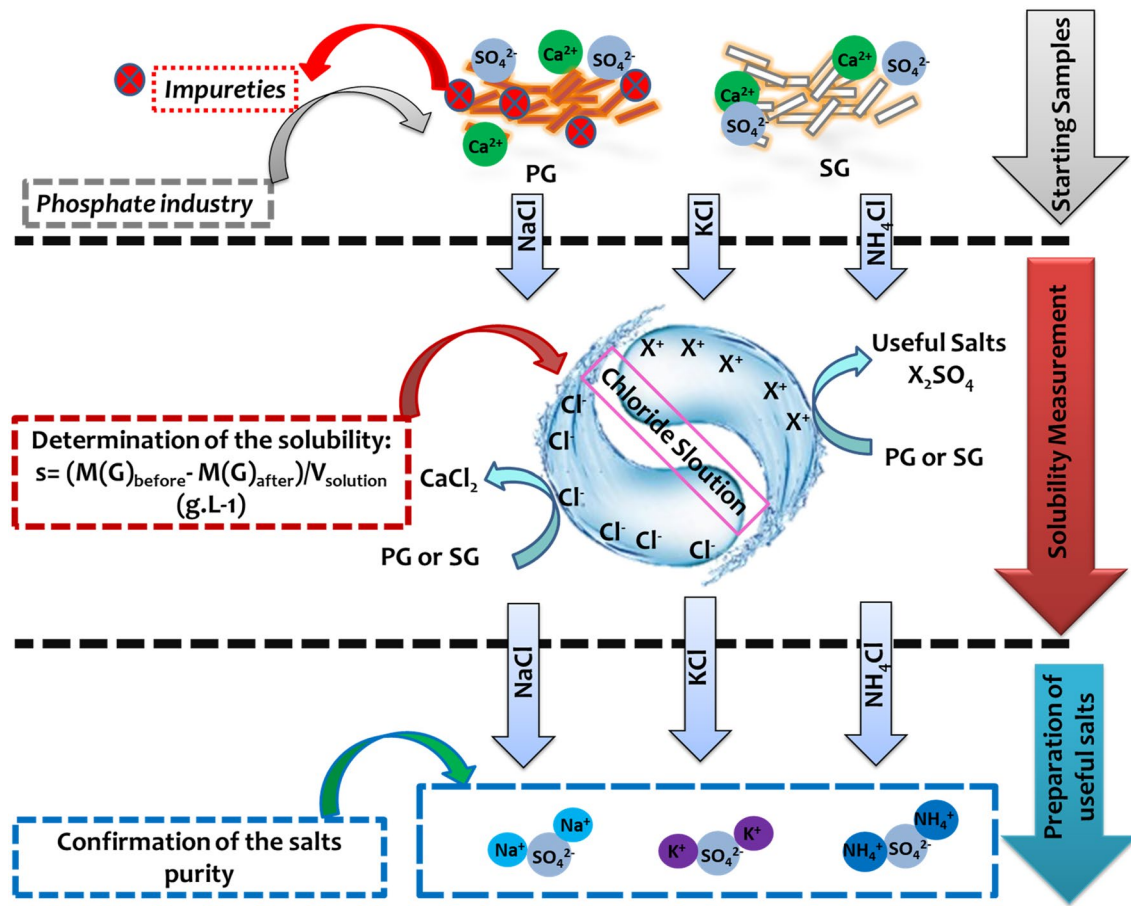


Fig. 3 PG solubility measurements, where: SG (Synthetic gypsum), M(G)_{before} (Gypsum mass before dissolution), M(G)_{after} (Gypsum mass after dissolution), V_{solution} (Volume of the chloride solution) and X₂SO₄ (corresponding salt)

In order to better understand the impact of the PG storage parameters (in stacks or stockpiles), it is necessary to study separately the impact of each parameter (e.g., ionic strength, Temperature, pH, and conductivity) on the PG stability and solubility. The most influential parameters are the ionic strength and pH, while the temperature changes have relatively less impact [50].

Treatment and purification of PG waste

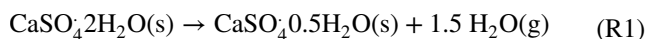
The most common PG process involves chemical (pyrometallurgical/hydrometallurgical), physical, and thermal treatment for separation and extraction of critical elements such rare earth elements (REEs), heavy metals and radionuclides. The PG treatment methods are very useful in extracting all relevant impurities and toxic elements in this by-product [56]. It is possible to use PG in agriculture and clinker [57, 58] instead of natural gypsum by applying appropriate pre-treatment such as flotation, calcination, and wash with acidic

solutions [59]. In all cases, there are two essential treatment categories of PG: thermal and wet treatment.

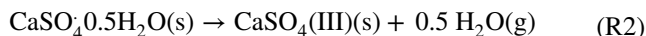
Several studies have been conducted to purify the PG waste, improve its quality, and enhance its efficiency to accommodate it in many industries: the manufacture of composite plaster and Portland cement slag for example [60]. Taher et al. have studied the thermal behavior of Egyptian PG at different temperatures [61]. The treated Egyptian PG was found to contain fewer impurities in P₂O₅, fluorides, and organic matter than raw PG. Likewise, El Issiouy et al. 2013 tested the Moroccan PG, recommending an efficient approach to maximize the elimination of undesirable gases and volatile impurities. The thermally treated PG was recommended to be used in the production of sulfuric acid [62]. The thermally purified Tunisian PG presents some strong characteristics that encourage and facilitate its use as a replacement for natural gypsum in the plastering industry [63]. Generally, drying PG at 60 °C removes free water from the sample without losing structural water in gypsum [23, 64].

Generally, all PG dehydration studies using differential thermal and thermogravimetric analysis (DTA-TGA) indicate the presence of two anhydrite and hemihydrate associated endothermic peaks. However, the reported values of the corresponding temperatures are remarkably different as peaks were obtained at 130–180, 180–215, and 149–169 °C [62, 65]. The dehydration of pure gypsum takes place in several stages. El Issiouy et al., 2013 find peaks relating to gypsum dehydration separately and precisely, 2 endothermic peaks at 125 °C and 140 °C corresponding to the dehydration of dihydrated calcium sulfate to hemihydrate (plaster) and then to anhydrite III, reflecting a change in the crystal structure (Gypsum: Monoclinic → Anhydrite II: Hexagonal):

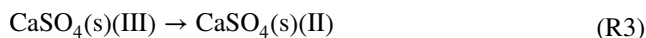
1st peak (endothermic) at 125 °C:



2nd peak (endothermic) at 140 °C:



3rd peak (exothermic) between 320 and 450 °C corresponds to crystallographic transformation (anhydrite III: orthorhombic → anhydrite II: hexagonal):



On the other hand, the impurities existing in PG could be removed by simple techniques such as washing with distilled, tap or seawater [40]. A significant amount of soluble impurities have been successfully reduced by three to five water washes at a liquid /solid ratio (v/w) of 2:1 (ratio of the water volume per g of PG: 2 ml/g) [66–68]. Similar findings have been reported by Liu et al., which confirm that all undesirable impurities can be considerably eliminated by a simple washing technique with deionized water for the possible use of PG in cemented paste backfill (CPB) [69]. The less extensive cleaning of PG by rinsing with water, or add a little amount of calcium oxide helps to obtain high-quality gypsum for several industries such as agriculture, cement and plaster sectors. An efficacy, cheap and useful treatment method was proposed by Valkov et al. that claims using ~0.5 M sulfuric acid [70], to extract the rare earth elements (REE). The purified PG showed negligible concentrations of impurities <0.02 wt. % [71, 72]. Treating PG with a mixture of sulfuric acid, silica or hot ammonium sulfate solution is also necessary to reduce the content of P_2O_5 and F in the PG samples before application [73]. A recent study revealed that the content of soluble phosphorus and fluorine in PG can be reduced by adding lime, and flotation [74].

Seawater seems to be most effective in eliminating the traces of cadmium in PG. But, as it salinizes, it can accumulate large quantities of salts in the purified PG material. However, under these circumstances, the prospect of using it in plaster industries occurs with less cadmium and

phosphorous [75]. A mixture of $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2:\text{H}_2\text{O}$ (zeolite hydrosodalite) was added to PG, to neutralize its acidic impurities. This mechanical activation was suggested to stabilize the properties of the PG and improve its strength characteristics [76]. The use of Margin (an industrial by-product less polluting than PG) in the treatment of PG has also found its place in the new pre-treatment methods. The purified PG should be able to be used directly in agricultural activities because of the presence of water and organic matter only [75].

Applications and environmental risks of PG

The general recommendations for managing PG indicate its valorization as the main way for minimizing storage costs and for reducing the negative environmental effects caused by this waste [77]. In agriculture, natural gypsum has long been used as a fertilizer for many crops. Some authors have shown that for many crops, PG is as effective as natural gypsum. However, the quantities to be used are limited by certain standards [78]. This waste is also used as a soil improver, when deficient in calcium and sulfur, but also for sodic soil permutation, which has been amended by replacing excess sodium with calcium on the soil exchange complexes (due to the high content in some elements such as Ca, P and S existing in PG). For this purpose, PG is used by peanut growers in various countries. Saline soils, once treated with PG, regain suitable physical and chemical characteristics [57, 79]. Other advantages of PG utilization in this area are listed in Table 3.

The plaster manufacturing industry is one of the most explored avenues for the development of PG. As noted above, PG can replace natural gypsum in several industries, but it is necessary to remove soluble impurities (phosphate, fluoride and organic matter), since the presence of a small amount of these impurities affects the setting time and strength of the plaster. It is known that PG can traditionally be used to slow down the hydration of tri-calcium aluminates ($\text{Ca}_3\text{Al}_2\text{O}_6$), by temporarily forming a double sulfate of calcium and aluminum, ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$. This practice avoids the phenomenon of stiffening. In the plaster industry, there are two manufacturing processes: (1) Route α : the plaster (called plaster α) is obtained from PG autoclaved in water at a temperature of 128 °C and a pressure of 2 bars. (2) Route β : the PG is heated to 190 °C at normal pressure where it transforms into basanite (plaster β). This way is used to produce plasters to be mounted [80]. The two routes are done according to the following reaction:

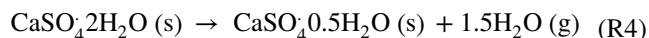


Table 3 Main benefits and environmental risks associated with the PG applications

Application domains	Benefits	References	Environmental risks	References
Agriculture	Decreasing the soil organic carbon (SOC) and the total nitrogen loss (TNL)	[82, 83]	PG is enriched by ^{226}Ra , ^{210}Pb , ^{232}Th , REE, Ba and Cd allowing uptake of these toxic trace elements and heavy metals (some radioactive) by	[84]
	Reclamation of the saline-sodic soils	[85]	Contamination of groundwaters	[86]
	Amendment of the soil habitat and retention functions;	[77]	Negative impact on soil organisms	[77, 87]
	Treatment of acidic or metal-rich soils	[82]		
Plaster manufacturing industry	Slow down the hydration of tri-calcium aluminates ($\text{Ca}_3\text{Al}_2\text{O}_6$), by temporarily forming a double sulphate of calcium and surface aluminates, ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$]	[80]	PG high acidity	[88]
Cement industry	Reduce the clinkerization temperature (from 1470 to 1200 °C),	[89]		
	Adjusts the retarder in portland cement	[81]	The use of PG in this sector required special treatments and neutralizing methods (high energy demand)	[90]
	High compression strength compared to the natural gypsum	[91]		
	It improves the hydration rate as well as the mechanical resistance, especially at the 90-day hardness of the cement	[92]		

Currently, only Japan considers the recovery of PG for the manufacture of plaster as profitable because the volcanic soil is naturally devoid of gypsum. It thus recovers 3 million tons of PG per year [79]. However, the treatment of PG has proven to be too expensive in most circumstances, and most plaster fabrication plants have gradually stopped their production. The use of PG in this area faces other environmental and economic benefits and risks (Table 3). These problems can, however, be considered differently if (i) there are limited resources of natural gypsum in the immediate proximity and (ii) the quality of the PG by-product is suitable in some cases. The PG has also been used in the manufacture of cemented materials. It is added to clinkers to reduce the clinkerization temperature, and adjusts the retarder in Portland cement. Clinker is partially replaced by materials such as ash, blast furnace slag and fly limestone during the production of composite cement (Table 4) [81]. Finally, and as authors point of view, using treated PG in building materials production (cement, bricks, ...) can be safe.

Recent procedures for the recovery of REEs from PG

It is well-known that PG contains significant amounts of rare earth elements (REEs), especially, radium and other radionuclides [88]. In general, these elements may be further grouped, based on atomic mass, into-light rare earth elements (LREE) and heavy rare earth elements (HREE) [95]. These elements co-crystallized with PG due to their isomorphs substitution for Ca^{2+} ions [96]. The increasing demand, especially for green energy technology, has enhanced the need to develop processes for extracting REEs from PG and other mine wastes as REEs secondary sources [97]. Moreover, PG samples contain an overall amount of REE in the range of 0.34–0.64% by mass [98, 99]. The decomposition of phosphates by sulfuric acid causes the selective separation and concentration of naturally occurring Ra, U and Th: about 80% of Ra is migrated in PG, replacing calcium in the chemical structure. While about 86% of uranium and 70% of thorium is found in the phosphoric acid product. Cerium, lanthanum, and neodymium account for 80% of the total REE content of phosphate rock [100]. In the last few decades, effort has been focused towards the REE extraction and separation from PG, which has various advantages over traditional REE mining. The main advantage is the absence of costs for exploration, mining, ore handling, and comminution [101].

Several researchers have reviewed various methods used for REE recovery from PG. Extraction of rare earths from PG minerals had been realized by using sulfuric, nitric, and hydrochloric acids, although nitric acid leaching (nitrophosphate process) is incredibly beneficial, however H_2SO_4 is

Table 4 Use of PG in the cement industry

Treatment type	Notes and advantages	References
Raw PG	Compared to the cements elaborated with natural gypsum, the compression strength is similar at short times but higher at long times	[91]
Raw PG	PG can be used directly in the production of Ordinary Portland Cement (OPC). It improves the hydration rate as well as the mechanical resistance, especially at the 90-day hardness of the cement	[92]
Water-washing and neutralization	The removal of soluble impurities or at least reduce these impurities from PG by washing and neutralization at pH 6–7 makes the use of PG as an additive for cement grinding possible. In the case of high-quality cement, the PG used as a setting regulator is conditioned by the presence of syncrystallized P_2O_5	[93]
Treatment with ammonium hydroxide solution (NH_4OH)	Purified PG using a 10 to 20% of ammonium hydroxide solution is suitable for use in the cement industry (its mechanical properties are almost similar to those of cement produced from natural gypsum)	[90]
Weathered PG	The highest 28-day compressive strength was found in the sample with 3 wt.% PG	[22]
Lime milk-washing	The 90-day strength of the cement prepared with PG is higher than that prepared with natural gypsum	[94]

economical in the extraction process and it is evident that HNO_3 leaching doesn't produce PG [102]. Using a sulfuric acid solution (15%) to leach pre-treated PG, at 100 °C for 2 h with a liquid/solid weight ratio 3:1, allowed obtaining a final leach liquor with a total REEs content of 4309 mg L^{-1} . In all cases, pre-treating the PG, by washing with saline water (25 g L^{-1} of NaCl) and treatment with a carbonated solution (60 g L^{-1} of Na_2CO_3), allowed the solubilization of water-soluble impurities and the production of a calcite phase easily attacked in an acid medium [103]. In case of nitric and phosphoric acid mixture the REEs take the form of $REEH_2PO_4^{2+}$, $REENO_3^{2+}$, and REE^{3+} .

In addition to acid leaching methods, there are a few works that used organic solvents as leaching agents. For example, the experimental results obtained from [104] show that about 70% of ^{226}Ra , ^{210}Pb , ^{238}U and ^{40}K were successfully removed from the PG by applying this method. Table 5

and Fig. 4 summarizes some other REE leaching procedures from the recent published works.

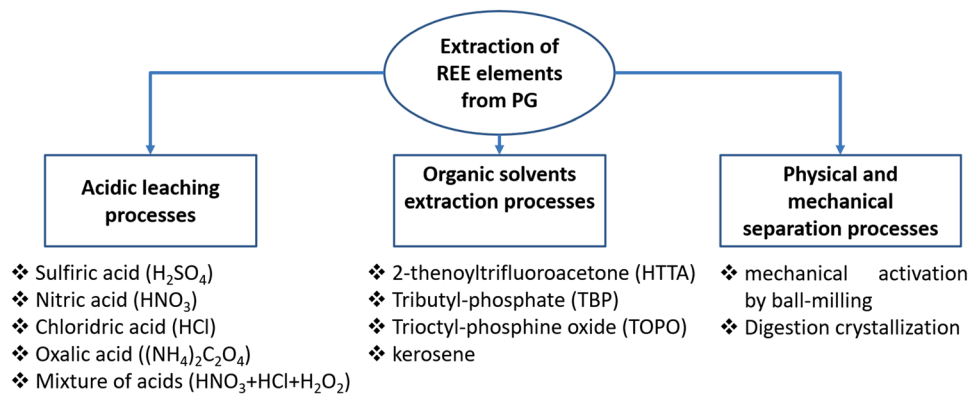
As reported in many reviews, the use of organic methods compared to the conventional hydrometallurgical acidic leaching methods for REE recovery from PG could provide some benefits: the largely reduction of acids consummation, the major reduction in the leaching solutions volumes, and the possibility of achieving a much higher selectivity for REE recovery [100]. To purify REE elements additional separation and purification methods such as: precipitation, solvent extraction, ion exchange and solid phase extraction are needed. These methods are highly selective and lead to obtain extremely high-quality materials [105].

As conclusion, the recovery of REEs from PG (considered as secondary source) through hydrometallurgical processes is becoming a sustainable and viable approach due to the low energy consumption, low waste generation, few

Table 5 A summary of application of acidic and organic reagents in the REE leaching and recovery from PG. Modified from [105]

Leaching type	Reagent	Experimental conditions				Recovery efficiency (%)	References
		Reagent concentration (mol L^{-1})	t (min)	T (°C)	L:S ratio (mL g^{-1})		
Acidic leaching	HNO_3	1.5	19.8	80	8	57	[106]
	HNO_3	7.1	60	72	4	58	[96]
	HNO_3	3	480	25	30	72	[107]
	HCl	1.5	19.8	80	8	51	[106]
	H_2SO_4	1.5	19.8	80	8.0	23.0	[106]
	H_2SO_4	0.8	120.0	50	7.0	52.0	[108]
	H_2SO_4	1.6	90.0	60	1.3	50.0	[109]
Organic leaching	TBP–TOPO in kerosene	0.7–0.9	120.0	55	1.0	69.8	[104]
	TBP–TOPO in Na_2CO_3	0.7–0.9	120.0	55	1.0	80.0	[104]

TBP and TOPO are respectively tributyl phosphate and trioctylphosphine oxide

Fig. 4 REEs leaching techniques

emissions, environmentally friendliness, and economically feasibility.

PG chemical conversion into valuable products

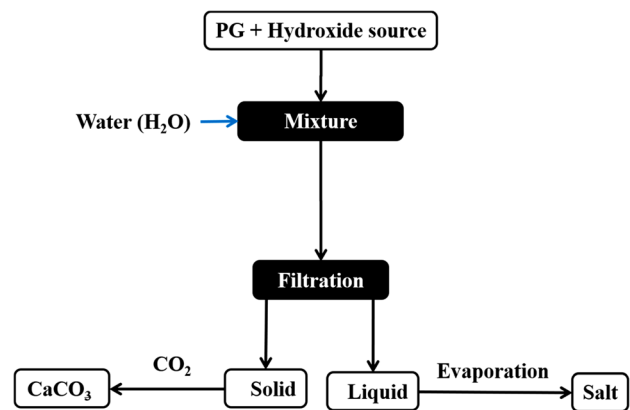
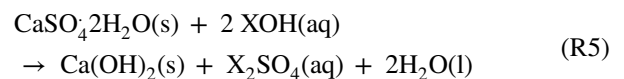
The transformation of PG into certain value-added products using hydrometallurgical routes is extremely interesting for its economic and environmental advantages in general frameworks of sustainability and waste management policies. These methods were used to selectively recover the calcium and sulfate ions. Recently, researchers have focused on the development of new wet processes for the transformation of PG. Compared with other techniques, the wet process is the simplest and cheapest one. The conversion of PG comprises three main steps:

- Pre-treatment and identification of the starting sample (see the pre-treatment methods previously shown in Sect. “Applications and environmental risks of PG”5);
- Extraction of calcium and sulfates using different aqueous solutions (hydroxide, carbonate, chloride, and fluoride);
- Characterization of the final products.

Conversion using hydroxide mediums

The alkaline conversion of PG in aqueous hydroxide solutions under ambient pressure and temperature has been studied by a number of researchers. The procedure consists of two essential steps (Fig. 5):

- Alkaline PG dissolution, the chemical reaction of this first step can be written as follow (R₅) with X = Na, K or NH₄:

**Fig. 5** PG conversion procedure using hydroxide solution

- The carbonation process carried out by injecting a CO₂ flow in a Portlandite solution (Ca(OH)₂ formed in precedent):



So there are two aims for this method, the first is the use of PG as a calcium source for CO₂ mineral sequestration in the framework of the mitigation of greenhouse gasses emissions, approximatively 30 Mt of CO₂ were utilized in this process [23]. The second is the production of add-values materials for direct application in several areas with good conversion efficiency and high purity. For a better understanding of the dissolution mechanism of PG in the hydroxide aqueous solutions, the authors have studied the evolution of the pH and conductivity during the conversion

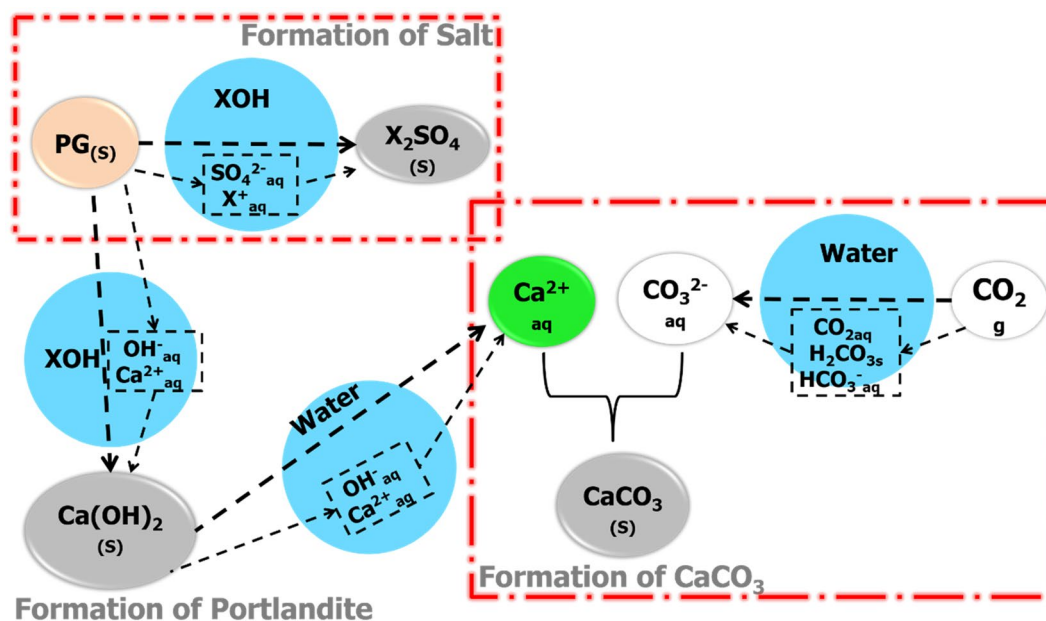
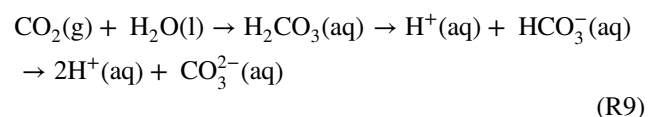
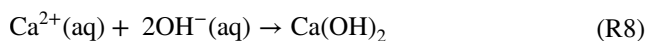
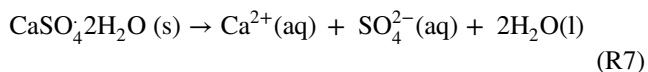


Fig. 6 PG conversion mechanism in hydroxide aqueous solution

process. Then they characterized the solid phases to confirm the obtaining of the desired products. The reaction mechanisms proposed can be represented in Fig. 6 [67, 110–113]. Looking more specifically at the dissolution of PG and the carbonation process, the initial reactions involve these two processes:

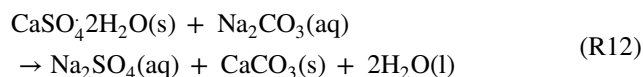
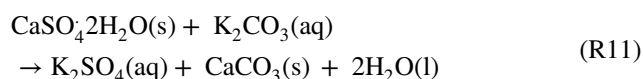
1. the dissolution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to give Ca^{2+} ions (R_7), and the decrease in OH^- ions that will combine with Ca^{2+} to precipitate as $\text{Ca}(\text{OH})_2$ (R_8)
2. The dissolution of CO_2 into the water to form carbonic acid, which dissociates to form finally CO_3^{2-} ions (R_9).

The carbonate species are then able to form via reaction with the divalent cation (Ca^{2+}) resultant in the dissolution of $\text{Ca}(\text{OH})_2$ (R_{10}) [114, 115]:



Conversion using carbonate mediums

The results of fundamental researches were realized in some fields of industry; corresponding to the conversion of the PG to CaCO_3 and K_2SO_4 or Na_2SO_4 by using carbonate aqueous solutions [116], this procedure has many advantages such as the fact that it is reproducible, ecological and inexpensive. The calcium carbonate is recovered after filtration and drying at 100 °C, then the sulfate obtained after evaporation of the supernatant liquid. The chemical reactions are given in the following [117, 118]:



The production of ammonium sulfate has significant applications, especially in agriculture. It is used as a source of nitrogen and sulfur for plant nutrition. Burnett, from the Florida Institute Oceanography, suggests a practical solution to the PG problem [119]. The authors propose converting this waste into ammonium sulfate by the process called Merseburg (Ammonia-carbonation) [120, 121]. Recently, based on this process, a study has been conducted on the transformation of Egyptian PG into ammonium sulfate and calcium carbonate. In this case, the treatment of PG with sulfuric acid is very effective in

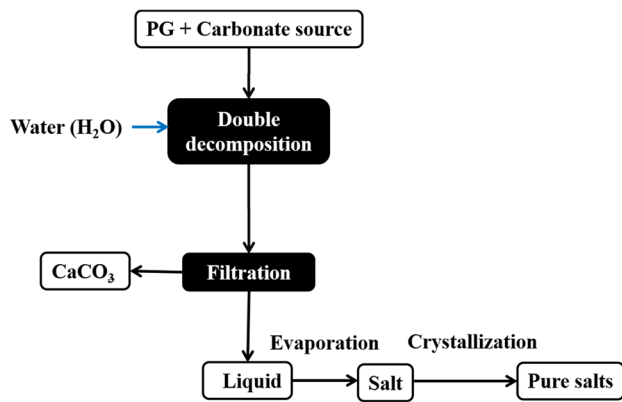
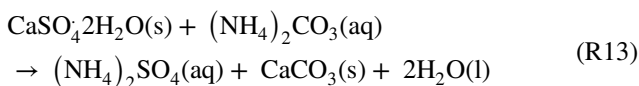


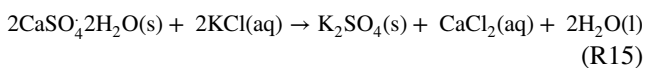
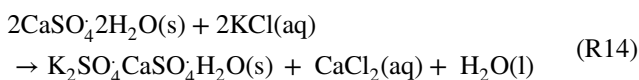
Fig. 7 PG conversion procedure using carbonate solution

removing the impurities associated with PG and which contaminate the synthesized products. This procedure is presented in Fig. 7 [56]. The Merseburg process is based on the reaction between gypsum and ammonium carbonate as shown in the following reaction (R13) [122]:



Conversion using chloride mediums

It is also possible to produce some sulfates from PG using chloride aqueous solution (R₁₄). The presence of some additives (like ammonia or isopropanol) has an efficient role to move in the desired direction and to selectively crystallize the salt formed, for example potassium sulfate K_2SO_4 , as shown in the reaction R15 [68].



Several disadvantages intercept the production of K_2SO_4 by this process. The difficulty of separating the salt from the other salts can be, to some extent, inconvenient [123]. For that, many researchers have succeeded in converting the filtrate solution of PG, into calcium carbonate and ammonium sulfate (Fig. 8), by simple treatment with ammonium carbonate and sulfuric acid [54].

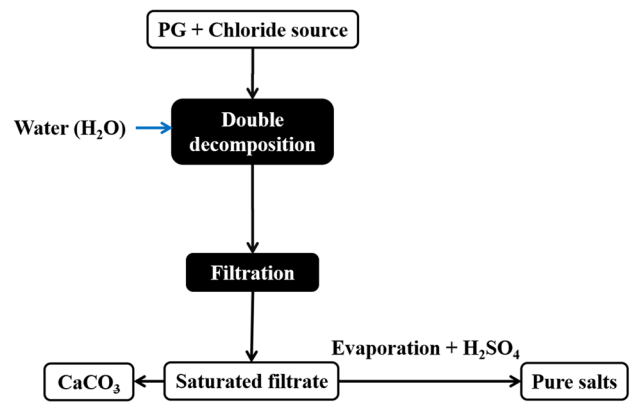


Fig. 8 PG conversion procedure using chloride solution

Conversion using fluoride mediums

CaF_2 formation has its place in the global PG transformations; this reaction is possible within 30 min [124]. The conversion yield is about 96%, more details are listed in Table 6 and Fig. 9.

Trace and radioelements distribution

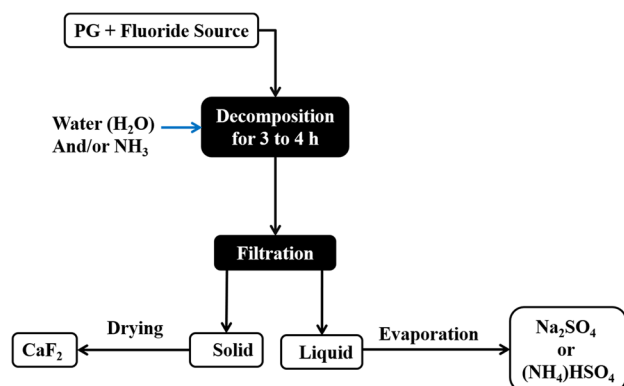
The most important step during the PG hydrometallurgical conversion was the measurement of the concentration of the toxic elements (i.e., trace and radioelements) existing in PG and their transfer into the synthesized compounds. In this context, several techniques can be used to calculate the concentration of these elements during the corresponding process:

- Inductively coupled plasma mass-spectrometry to the characterization of the trace elements: Sr, Cd, V, As, Pb, La, Cr, Cu, Y...[125, 128];
- Alpha-particle spectrometry to the characterization of the radioelements: uranium (^{235}U and ^{238}U), Thorium (^{228}Th , ^{229}Th , ^{230}Th and ^{232}Th) and lead (^{210}Pb) [38, 129, 130];
- Gamma spectrometry with Ge detectors to the characterization of the radioelements: radium (^{226}Ra), and potassium (^{40}K) [131].

An important number of works have confirmed that PG is highly rich in toxic elements [132]. And also most of these elements would be fixed in the final products: portlandite, and calcite [23]. They were almost incompletely transferred to the sulfate salts. Tables 7 and 8 represent the concentration and the transfer factor of some toxic elements during the transformation of PG into thenardite, portlandite and calcite [23, 64, 125]. The particular beneficial aspect of this process is the preferential accumulation

Table 6 PG's conversion into valuable compounds

Alkaline solution	Formed products		Experimental conditions					References
			T (°C)	T (min)	MR ^a	VCO ₂ (L min ⁻¹)	S (rpm)	
Hydroxide solutions	NaOH	Na ₂ SO ₄ and CaCO ₃	25	180	2	1.2	Constant speed	[88, 125]
	NaOH	Na ₂ SO ₄ and CaCO ₃	25	90	2.1	3	300	[126]
	NH ₄ OH	(NH ₄) ₂ SO ₄ and CaCO ₃	20 to 80	60	120 ^b	6.7	400	[127]
	NH ₄ OH	(NH ₄) ₂ SO ₄ and CaCO ₃	25	90				
	2.1	3	300		[126]			
	KOH	K ₂ SO ₄ and CaCO ₃	25	180	2 to 3	0.02	600	[67]
Carbonate solutions	Na ₂ CO ₃	Na ₂ SO ₄ and CaCO ₃	Ambient	180	1	–	Constant speed	[117]
	Na ₂ CO ₃	Na ₂ SO ₄ and CaCO ₃	80 to 100	120	2			
	–	500	[103]					
	NH ₄ CO ₃	(NH ₄) ₂ SO ₄ and CaCO ₃	55	240	1.1	–	150	[56]
	K ₂ CO ₃	K ₂ SO ₄ and CaCO ₃	Ambient	90	1	–	–	[118]
	Li ₂ CO ₃	Li ₂ SO ₄ ·H ₂ O and CaCO ₃	Ambient	90	1	–	Constant speed	[36]
Chloride solutions	NaCl	NaHSO ₄ ·H ₂ O and CaCO ₃	25	–				
	25 ^c	–	Constant speed	[54]				
	KCl	CaCl ₂ et K ₂ SO ₄	25	45	50 ^d	–	Constant speed	[68]
Fluoride solutions	NaF	CaF ₂ et Na ₂ SO ₄	25	30 to 120	1.5 to 2	–	600	[124]

^aMolar ratio alkaline solution/CaSO₄·2H₂O^b120 wt. % of NH₃ (c) g/L (d) 50% excess of PG**Fig. 9** PG conversion procedure using fluoride solution

of the different radionuclides ²³⁸U, ²²⁶Ra and ²¹⁰Pb in calcite with an important transfer factor (> 90%). Moreover, calcite is much more soluble than PG in acidic media, which favors the recovery of both rare earth elements (REEs) and radioelements.

Synthesized products applications

In all cases, these methods give high-purity sulfates, carbonates and fluorites. The researchers recommended applying these compounds directly in several domains. Table 9

presents the general application domains of the products formed from PG.

In summary, the procedures cited in this review represent an environmental proposal to jointly enable on-land PG disposal to be achieved in an environmentally sound manner [63, 143]. Besides, the results indicate that the lower aqueous solubility of PG is the major problem faced with the elaboration development of new chemical technology to convert PG to valuable compounds. Based on this literature review, we recommend that the appropriate selection of solubility enhancement technique should be considered as key to revolutionizing the industrial valorization of PG waste.

Techno-economical and life cycle assessment

It is well known that phosphate rock (PR) could be crude or upgraded as phosphate concentrates that are used for phosphoric acid and phosphates fertilizer manufacturing. PR production and consumption have increased significantly in different world regions, such as United States, China, Africa, Middle East, and Eastern Europe, and they are driven by phosphate fertilizers supply and demand, especially in Eastern Europe, the Middle East, and Africa. The largest phosphate rock producers are Yunnan Yuntianhua Co., Ltd (China), OCP (Morocco), Mosaic (United States), and Apatit OAO (Russia) whereas Africa, Eastern Europe, and the Middle East are the main phosphate rock exporters [144]. These

Table 7 Average concentrations of radioelements during the preparation of $\text{Ca}(\text{OH})_2$, Na_2SO_4 and CaCO_3 from PG and Soda, Data from previous work

Elements	PG	NaOH	$\text{Ca}(\text{OH})_2$		Na_2SO_4		CaCO_3	
	$C^{(a)}$	C	C	$F^{(b)}$	C	F	C	F
<i>Radioelements (Bq Kg⁻¹)</i>								
²¹⁰ Pb (± 51)	554.0	<0.2	1104.0	96.7	21.0	3.6	1124.0	104.7
²³⁴ Th (± 8)	63.5	<0.2	118.0	90.0	3.6	<0.1	114.0	99.5
²³² Th (± 1.5)	7.5	<0.2	16.0	92.5	<2.2	<0.1	16.0	100.8
²³² Th (± 32)	502.0	<0.2	946.0	88.1	12.0	2.2	853.0	92.8
²²⁶ Ra (± 80)	670.0	<0.2	1451.0	101.2	<9.2	<0.1	1420.0	100.7
²³⁸ U (± 6)	68.0	<0.2	143.0	102.4	1.5	2.1	128.0	91.9
⁴⁰ K	<18.0	<15.0	<20.0	—	<16.0	—	<15.0	—

^aConcentration of the radioelement/ Bq.Kg–1

^bTransfer factors is calculated using the following equation: $F = (C_i \cdot m_i / \sum C_f \cdot m_f) \cdot 100$, with: C_i and C_f are respectively the concentration of the selected element present in the starting reactant and in the obtained product. And m_i and m_f are the reaction mass (calculate from the reaction of conversion and carbonation with a stoichiometric molar ratio Phosphogypsum/NaOH=2) of each product: PG (1 g), NaOH (0.47 g) Portlandite (0.49 g), Thenardite (0.94 g) and Calcite (0.50 g)

^cError average calculated using the formula: Error (\pm) = [Error (PG) + Error (Portlandite) + Error (Calcite)]/3

Table 8 Average concentrations of trace elements during the preparation of $\text{Ca}(\text{OH})_2$, Na_2SO_4 and CaCO_3 from PG and Soda, data from previous work

Elements	PG	NaOH	$\text{Ca}(\text{OH})_2$		Na_2SO_4		CaCO_3	
	$C^{(a)}$	C	C	$F^{(b)}$	C	F	C	F
<i>Trace elements (mg Kg⁻¹)</i>								
Sr (± 32) ^(c)	435.0	<0.1	611.0	68.2	115.0	24.8	476.0	96.5
Y (± 10)	79.0	<0.1	152.0	93.7	<0.1	<0.1	130.0	87.8
Cd (± 0.1)	0.7	<0.1	1.7	118.0	<0.1	<0.1	1.7	99.9
V (± 0.3)	4.5	<0.1	7.0	75.6	<0.1	<0.1	6.0	88.2
Cr (± 0.7)	10.8	2.2	25.3	104.2	5.0	39.9	19.1	77.6
Ag (± 0.04)	0.7	0.2	1.4	90.7	0.2	18.3	1.3	92.5
Se (± 0.36)	3.8	<0.1	7.1	91.4	0.8	18.8	6.7	97.8
Zn (± 1.56)	7.6	1.0	11.6	69.4	3.2	36.4	13.0	115.3
As (± 0.2)	1.9	0.3	3.2	76.2	0.6	27.6	2.9	94.8
La (± 11.8)	35.5	<0.1	87.7	120.2	0.2	0.5	100.0	117.3
Pb (± 0.53)	4.1	<0.5	9.7	115.0	<0.5	<0.1	10.2	108.7
Cu (± 1.7)	8.9	1.3	11.7	63.1	2.8	29.2	11.1	97.2

^{a,b,c}are mentioned in Table 7

Table 9 Application domains of the products formed from PG

Formed product	Application domains	References
Na_2SO_4	Detergent, paper industry, glass manufacturing, and textile industry	[124, 125]
K_2SO_4	Agriculture	[123]
$(\text{NH}_4)_2\text{SO}_4$	Fertilizer industry	[126]
$\text{Ca}(\text{OH})_2$	Mineral carbonation, formation of calcium oxide CaO nanoparticles and Remineralization of the brine water	[122, 133–135]
CaCO_3	Paint, plastic, paper, cement, food, textiles, rubbers, Adhesives, cosmetic industry, extraction of iron and pharmaceutical engineering	[136–140]
CaF_2	Manufacture of gamma, dental care, treatment of optical Fiber and Fluor industry	[124, 141, 142]

companies extract, treat, charge and commercialize phosphate and its derivatives, in particular phosphoric acid and fertilizers. However, this sector is mainly associated with a large quantity of PG (around 300 MT per year). Generally, the formed PG is commonly stockpiled in open areas or disseminated into aquatic mediums.

Generally, PG use and valorization in different domain of applications, offers some social/ ecological benefits such as:

- Employment opportunity: PG processing creates employment opportunities for people in the surrounding areas (Direct and indirect jobs);
- Intergenerational social equity;
- Avoided land use: The recycling of PG is expected to reduce approximately 12,000 m² of land used for stockpiling of PG, according to [145].

In terms of road construction and according to the study investigated by Bentaleb et al., it appears that using PG as a supplement to clay can be beneficial to both environment and economic benefits [146]. In comparison with the alternative used Tounfa (Pit-run) as road construction material, the use of PG in this domain has a Net Present Value (NPV) positive in less period (i.e. NPV: a value of all future cash flows over the entire life of an investment discounted to the present) and a smaller Payback Period (i.e. PP: is utilized to demonstrate the period required by a business/process to regain its investment). In fact, Morocco is planning investments of around 2.8 billion euro for the construction of new rural roads up to 2035. So, Morocco's road industry may represent a potential window for PG utilization and recycling. In the some context and based on a recent economic case study, the PG can be utilized as embankment aggregates in a radius of 29 km keeping a lower cost compared to conventional materials [147]. As concluded by the authors, this manner of doing will lead to various advantages such as air emission reduction, and finite natural resources conservation and protection. Recently, Biyoune et al. analyzed the cost benefit of the salinity reduction of the rejected brine water using PG. Based on the output-materials-global-cost estimation, the gain ratio (output cost/ input cost) was calculated as 1.66 [122]. In the same context, the gain ratio of the PG conversion process (into Na₂SO₄ and (NH₄)₂SO₄) was calculated as 3.43 when using NaOH, whereas this value decreased to 2.02 due to the price of NH₄OH [125]. Carbon dioxide sequestration is also an additional potential economic benefit, as 1 ton of PG can sequester 0.26 tons of CO₂ by reacting it with Ca(OH)₂ obtained from the PG conversion process using NaOH. Exporting the product of CO₂ mineralization reaction, CaCO₃, which is in high demand for, several industries such as construction and paper production, could generate further revenue [148]. Preliminary studies of the techno-economic feasibility of the extraction of rare earth elements (REEs) from PG were evaluated by several researchers. In general, the extraction of REEs

from PG residue could become economically feasible provided that suitable extraction processes are available. Based on the high price of some REEs (Sc, Sm, La and Y) and on the growing demand of these elements, PG by-product can represent an interesting secondary source of REEs.

Life cycle assessment (LCA) is a multi-step system for asserting the lifetime environmental impact of a by-product [146]. The LCA process is normally iterative as the quality and completeness of information and its plausibility is constantly being tested. In all cases, using LCA is a useful approach for comparing PG waste valorization and management methods within the context of Circular Economy (CE). A description of LCA assessment methods that are used in the PG valorization and management field is summarized in Table 10 and explained in detail below.

To the best of our knowledge, few studies dealing with environmental impact and potential applications of PG waste, by applying the LCA methods, have been published [100]. For example, in a recent study the comparison of alternative management methods for PG using comparative LCA calculation was evaluated [149]. The authors used the data base Ecoinvent 2.0 with the assessment method Ecoindicator 99 to compute the ecological footprint of four alternative PG waste management methods: (1) the use of PG in brick production, (2) as soil amendment, (3) in road construction and (4) its disposal in a stack. According to this study, the top ranked method is the use of PG waste as a soil amendment, with second the use of PG as a subbase in road works and third the use of PG in brick production. Disposal of PG waste in stacks, which is the most common management method was ranked as the least preferred one [149]. Using the same LCA approach, up to 30% energy demand reduction and 57% CO₂ release reduction was achieved with a ternary system binder based on gypsum-cement-pozzolan (GCP) binder if PG was used with practically identical performance of mortar material [150]. This method was done by using the LCA program SimaPro 8 software, and by following the ILCD handbook guidelines and International Organization for Standardization standards (ISO 14044). According to these authors, natural gypsum (NG) can be preserved by its replacement with PG. To produce 1t of NG binder about 1.2 t of NG must be excavated, transferred, and treated. Therefore, if the production site is located near to the PG stockpiles, the delivery distance is much shorter and the storage of PG in stocks is avoided. For environmental safety, such a management and valorization approach seem logical and must be supported. Comparing two alternative solutions: (1) landfilling of this waste in large stockpiles, and (2) implementation of REEs recovery technology, Kulczyk et al. evaluate the management of industrial PG waste in the Wizow plant (in Poland) by taking into account both economic and environmental aspects [151]. According to these authors, the recovery of REEs from PG waste

Table 10 LCA approaches for different phosphogypsum's valorization and management methods

PG's type of valorization	LCA method or software	Database	Results	References
Chemical conversion into paper	LCI/ Simapro	Ecoinvent 3 emission	The findings from LCA indicate that the PG based paper are not environmentally friendly in some aspects and also not economically profitable compared with conventional products;	[145]
Construction Industry	SimaPro	Ecoinvent	With the alternative PG-binder up to 30% of energy can be saved and 57 wt.% of CO ₂ emissions can be reduced;	[150]
	SimaPro 7.3.3	CEN TC350 standards	It found that transport had a marked effect on the categories of eutrophication and noncarcinogenic effects. The greatest impact was found when gypsum was transported to a recycling plant at a distance of 50 km	[152]
REEs recovery	Eco-indicator 99	–	The REEs extraction from PG is cost-effective but requires significant financial investment, and it is characterized by a relatively high degree of risk;	[151]
Soil amendment	Eco-indicator 99	Ecoinvent 2.0	Use of PG waste as soil amendment to correct calcium levels in agricultural land has a lower environmental footprint than using NG;	[149]

is considered as a cost-effective and economical process. But it is characterized by a relatively high degree of risk. This is due to the volatility of prices of REEs, as well as a novel, not previously tested technology. [145] proposed a new LCA calculation methodology for PG transformation into useful products. They apply process engineering principles for developing symbiotic pathways on the chemical transformation of PG and to assess the sustainability of these pathways from social, environmental and economic objectives. There are several indicators that affect the PG chemical transformation, including in first degree; Global warming potential (GWP), Eutrophication potential (EP) and Solid Waste Impact (SWI). The effect of other indicators such as human toxicity, land use, water body and ecosystem toxicity, is negligible [145]. In this study, two life cycle inventories for the PG conversion into CaCO₃ and Na₂SO₄ (using NaOH and Na₂CO₃ mediums) were investigated. The process that utilizes NaOH has the highest energy demand compared to that utilizes Na₂CO₃. The formed Na₂SO₄ could be used in a neighboring industry for paper fabrication, while the formed CaCO₃ is largely used in Cementous materials production. Suarez et al. were used life cycle assessment (LCA) methodology to evaluate the environmental impact of primary and secondary gypsum (i.e., PG, NG (natural gypsum), RG (red mud) and construction and demolition waste (CDG)) production and its application in the production of Portland cement. This study demonstrates that the process of burning natural gas in a furnace to dry gypsum has the greatest environmental impact on all environmental categories, except for respiratory inorganics and land occupation, in the production of NG [152].

Conclusions and recommendations

The untreated PG generated by several phosphoric acid production units, not only poses an environmental threat because of the impurities it contains, but also constitutes an economic loss. Thus, it is necessary to find an alternative recovery way. PG contains mainly calcium sulfate, which can be easily recovered and therefore, has an interesting economic value to exploit. Research might be pursued to find the best ways of recovering this waste. The treatment of PG could be very advantageous technology because it allows us to eliminate the maximum impurities present in this waste, especially the soluble impurities such as P₂O₅ and fluoride. For that, we have shed some light on various ways to purify the PG. The alkaline medium is generally considered to be the best solution to dissolve PG waste, it is therefore recommended to study the conversion of this waste in a novel alkaline solution or in special mixture of alkaline solutions. Based on this literature review, we recommend that the appropriate selection of solubility enhancement techniques should be deemed to be key to revolutionizing the industrial valorization of PG waste. Also, extracting REEs from this waste (considered as a secondary source of REEs) by hydrometallurgical procedures appears to be a sustainable approach with cost-effective and environmentally benefits. Finally, this review can be used as a guide and work of reference to compare, study and applying different processes to valorize the high amounts of PG produced annually.

As described above, the valorization of PG has attracted the interest of much scientist and engineers in recent decades, giving rise to several technologies to valorize this

waste. For this purpose, the authors support and recommend pilot-studies of PG application as a soil fertilizer and as additive in the building materials production (cement, bricks...). Many applications of PG valorize only a few quantities of this material. The use of PG in road construction is also of most interest. It represents the most promising method of valorization and management of PG, where large amounts of PG are used. Chemical transformations of PG seem to be preliminary studies, and may suffer from technical and economic constraints (energy and reagents consumption, complex development, secondary pollution ...). Therefore, more clarifications are needed to determine the most environmentally friendly transformation.

Declarations

Conflict of interest The authors declare that they have no competing interests.

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