



## Review

## Exploring the potential reuse of phosphogypsum: A waste or a resource?



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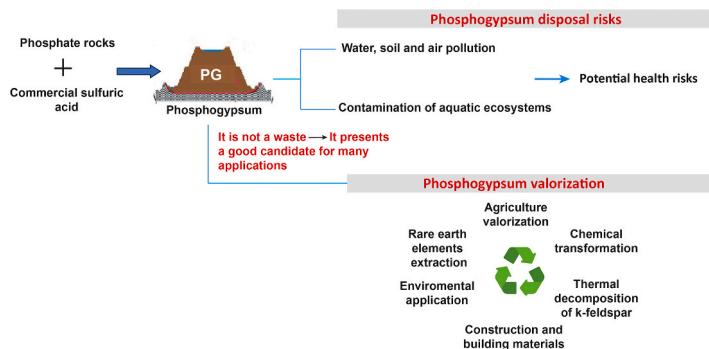
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## HIGHLIGHTS

- A gradual increase in PG production is anticipated in near future.
- Retention mechanisms of trace elements are crucial for their extraction and behavior.
- PG disposal may present a risk of contamination of surrounding environment.
- PG matrix can be used in several applications to reduce its disposal.
- Policies and environmental laws are limiting PG reuse.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Phosphogypsum (PG), the main industrial by-product of phosphate fertilizer industry, primarily consists of calcium sulfate dihydrate. However, it contains various impurities with variable quantities depending on the origin of the phosphate rock. These impurities can restrict the reuse of phosphogypsum as a secondary primary resource. Consequently, large quantities of produced PG are stored in surface stockpiles that occupy extensive land areas and may pose a significant risk of ecological contamination to the surroundings. Researchers have shown growing interest in addressing the worldwide accumulation of this waste material. To gain a comprehensive understanding of the environmental impact of phosphogypsum, it is crucial to explore its properties (e.g., chemistry, mineralogy, radioactivity), and how it interacts with the surrounding environment, enabling well-informed decisions regarding its management and its valorization. In this review, we will i) explore the chemical, radiological and mineralogical characteristics of PG; ii) discuss the environmental concerns related to land discharge and sea disposal; and iii) examine the latest advancements in various valorization techniques developed including agriculture, REE extraction, environmental application, chemical and thermal transformation, and also construction sector. Outlining their limitations and challenges restrict in the global variability of phosphogypsum (PG), technical and economic limitations, and the potential for secondary pollution in select valorization approaches. This requires a thorough assessment and comparison with conventional disposal alternatives.

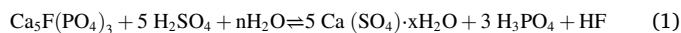
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## 1. Introduction

Industrialization has a major positive impact on the global economy, but it also generates large amounts of waste that can be harmful to the environment. Dealing with this waste is a challenge that humanity must face (Goodship, 2009). One of the critical industries for society is the food industry. The production of fertilizers is essential to maintain agricultural productivity and food production: fertilizers replace the nutrients that crops uptake from the soil. Without the addition of fertilizers, crop yields would decrease drastically.

The extracted phosphate rock (PR) is then converted into phosphoric acid, with 85 % of the PR usually being converted using either a wet or thermal process (Zan et al., 2006). The thermal process to produce phosphoric acid is commonly used in the manufacture of high-grade chemicals, which require a much higher purity. The wet process is an energy-saving process compared to the thermal process, which makes it by far the most common process. It is estimated that 71 % of all produced PR is converted into phosphoric acid by a wet process. This process is accompanied by the generation of PG through reaction (1) (Tayibi et al., 2009):



To procure one tonne of phosphoric acid, approximately 4–5 tons of PG by-product is generated. The phosphoric acid is then further processed to manufacture fertilizer, which accounts up to 95 % of total phosphate rock production (Cánovas et al., 2018a).

The chemical composition and mineralogical properties of PG are affected by the type of phosphate rock, the process used to produce phosphoric acid, the efficiency of the industrial process, the storage plan, and the chemical quality of the applied chemical reagents (Carbonell-Barrachina et al., 2002). The composition and source of the phosphate ore has a major impact on the characteristics of the produced PG. Depending on the type of phosphate rock (magmatic or sedimentary), the impurities present in the PG will differ (Guerrero-Márquez et al., 2017; Santos et al., 2006). Additionally, the process conditions of producing phosphoric acid influence the crystal morphology of the PG, the shape and size distribution, and the distribution of chemical species between the phosphoric acid and the PG (Bolívar et al., 2005). Indeed, the wet process results in the selective separation and concentration of naturally occurring radium, uranium, and thorium. Approximately 80 % of 226-Ra is concentrated in the PG, while approximately 86 % of U and

70 % of Th end up in the phosphoric acid (Sahu et al., 2014; Tayibi et al., 2009).

The management of contaminated PG is a global ecological issue; a substantial mass accumulates in many locations around the world primarily as a result of historical or ongoing phosphoric acid manufacturing processes, such as Florida (>30 million tons per year (Burnett et al., 1996)), Spain (around 2.5 Mt/year (Cádenas et al., 2011)), Tunisia (around 10 Mt/year (Garbaya et al., 2021)), Brazil (5.4 Mt/year (Mazzilli et al., 2000)), Morocco (15 Mt/year (Harrou et al., 2020)), Ukraine (10 Mt/year (Dvorkin et al., 2018)), China (70 Mt/year (Liu et al., 2020)), Jordan (around 3 Mt/year (Al-Hwaiiti et al., 2019)), Turkey (3 Mt/year (KAVAKLI et al., 2016)), Syria (0.35 Mt/year (Al-Masri et al., 2004)), Croatia (8.5 Mt/year (Bituh et al., 2021)), and other parts of the world (Fig. 1). PG production rates will follow fertilizer production rates, recording a sevenfold increase by 2050 compared to 1961 rates and reaching 438 million tons per year. The total stock of PG stored in tailing ponds for the period between 1961 and 2050 will reach almost 11 billion tons by 2050 (Nedelciu et al., 2020). Only a small amount of globally produced PG is valorized (Tayibi et al., 2009).

The management of solid mine waste requires a detailed characterization and a full understanding of the reparation of elements in the origin rock and their distribution in the waste matrix (Elghali et al., 2018). It is now generally acknowledged that the distribution, mobility, availability, and toxicity of chemical elements are determined not only by their concentrations but also by their forms (Parbhakar-Fox and Lottermoser, 2015). Therefore, to predict the chemical availability and to select an efficient strategy for the reuse of a waste product, it is necessary to characterize in detail the reactive minerals present in fresh and weathered material (Jamieson, 2011). Predictive waste quality characterization implies developing an understanding of deposit and waste material geochemistry in relation to both observed and future waste quality at mine sites (Caruso et al., 2008; Maest et al., 2005). Although PG is mainly composed of calcium and sulfur, it contains several impurities such as phosphates, fluorides, sulfates, heavy metals, residual acid, naturally occurring radionuclides, rare earth elements (REEs), and other trace elements (Abril et al., 2009; Rashad, 2017). Acquiring knowledge about the quantities and chemical states of impurities in PG is indispensable for the development of effective techniques that yield a marketable product (e.g., extracting and utilizing REEs) and for establishing subsequent storage and environmental guidelines for stacking. Understanding an element's environmental

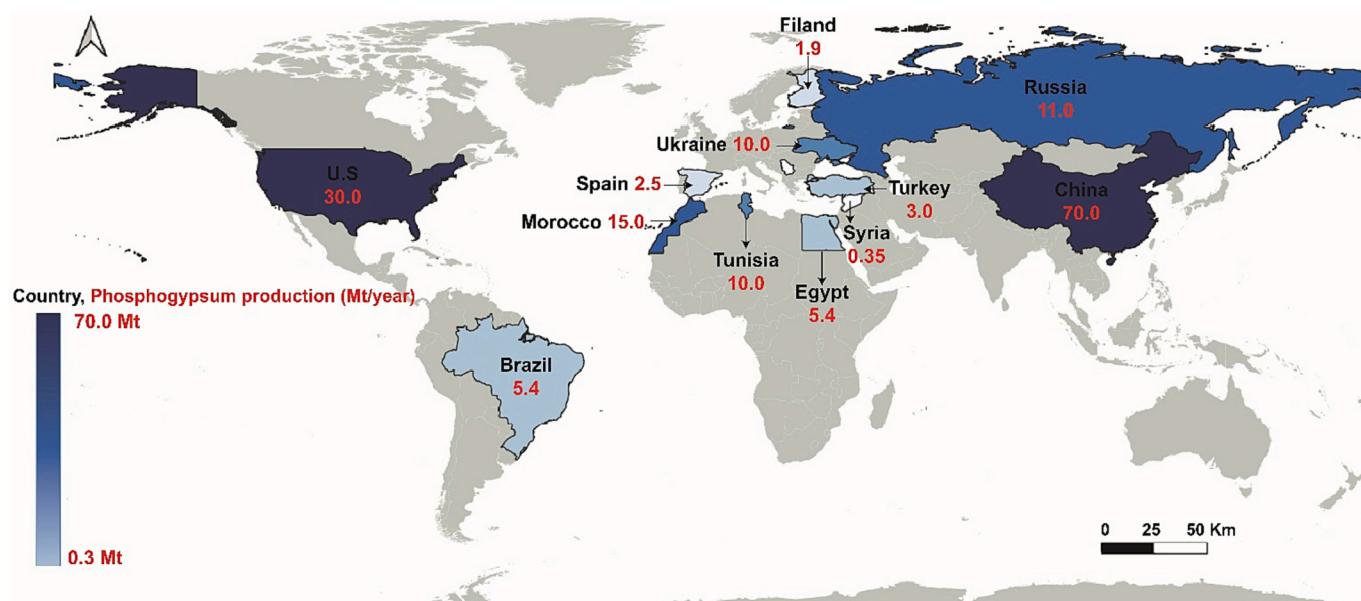
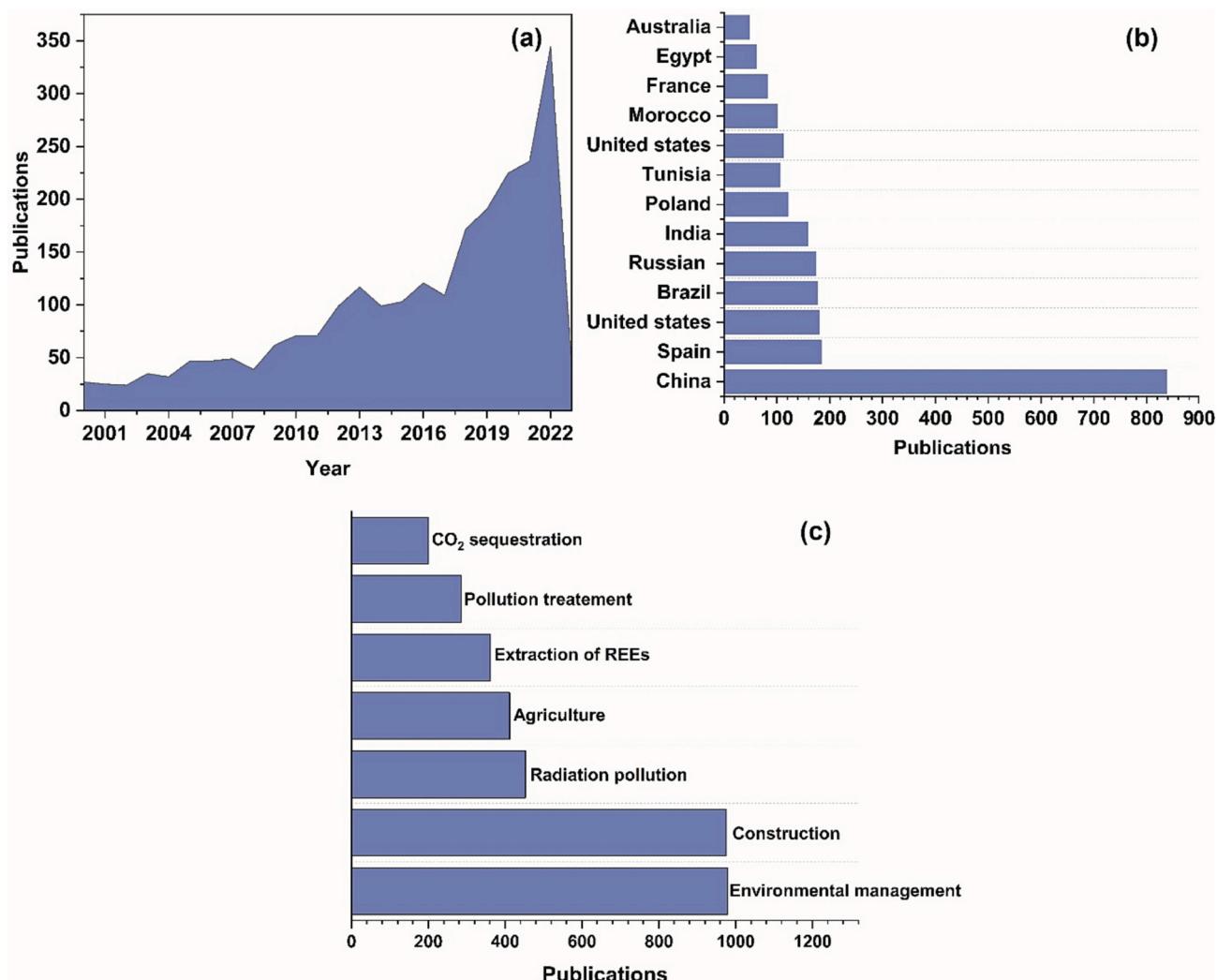


Fig. 1. Repartition map of the annual volume of phosphogypsum generated around the world.



**Fig. 2.** (a) Number of publications dealing with PG in the last 20 years, (b) number of publications per country, (c) main subject of interest for PG research.

chemistry requires precise assessment of its various forms in diverse natural conditions. However, there should be a greater focus on investigating the speciation of trace elements to determine the mechanism by which they are retained within the crystal structure of PG and to identify which forms might pose environmental hazards.

The most common PG management strategies include surface disposal under unsaturated conditions and storage in water bodies under saturated conditions, which may result in serious soil, water, and atmosphere contamination (Tayibi et al., 2009). In specific situations, the necessity for storage arises primarily due to definitional reasons, such as in the United States, where the United States Environmental Protection Agency (USEPA) classifies PG as a valueless waste. Nonetheless, different countries do not share a unified perspective regarding the classification of these wastes. Macías et al. (2017) shed light on this issue, showing the disparity between EU and US regulations on the hazard categorization of these materials. However, in line with modern definitional tendencies, PG should be reassigned as a possible asset. In some countries, PG is disposed of in the ocean, potentially leading to the transfer of toxic elements to sediments and aquatic life, with the risk of local sterilization of the benthic fauna (Gaudry et al., 2007). Progressive changes in environmental regulation, most notably within the European Union in the 1990s and more recently under the International Maritime Organization's London Convention (Cárdenas et al., 2011), have largely eliminated PG discharge to water bodies, causing significantly more PG to be stored on land. Several studies and advancements were carried out

on both valorization and management methods for PG waste. The literature is full of processes and patents describing various methods and technologies capable of producing several by-products from PG. Over the years, research has been conducted to utilize PG as a building material component (Luz et al., 2009; Singh and Garg, 2005), a synthetic gypsum for construction (Lin et al., 2018), and as a raw material in coating mortars (Singh, 2002), and different cementitious systems (Ballim and Graham, 2004). PG can be used in agriculture as a fertilizer or to decrease the pH and electrical conductivity of a saline soil (Kumar et al., 2020; Wu et al., 2022). Thermal or wet decomposition of PG can yield commercial products such as sulfuric acid and alkali sulfates (Zheng et al., 2011). Some calcium-rich compounds are well known to be efficient carbon dioxide sinks via carbonation reactions. As an environmentally friendly application, PG is used as a calcium source for CO<sub>2</sub> mineral sequestration within the framework of reducing greenhouse gas emissions (Contreras et al., 2015; Lachehab et al., 2020).

This paper provides a critical review of the existing data regarding the chemical composition (major, minor, trace elements, and radionuclides), mineralogical properties, and management strategies of PG around the world. A thorough analysis of various PG management strategies was subsequently conducted, considering their effects on the surrounding environment and public health. Finally, the study examines the principal methods of PG valorization, providing a comparative analysis of their industrial, economic, and environmental aspects.

**Table 1**

Concentrations (% weight) of major elements and impurities in phosphogypsum (PG) samples from Morocco and other regions (n.d: not detected, n.m: not measured).

Sedimentary							Igneous
PG Morocco <sup>a</sup>	PG Spain <sup>b</sup>	PG Tunisia <sup>c</sup>	PG Jordan <sup>d</sup>	PG Egypt <sup>e</sup>	PG Florida <sup>f</sup>	PG China <sup>g</sup>	PG Brazil <sup>h</sup>
CaO	32.2–35	37–38.14	32.8–37.2	31.8–35.5	28.3–38.4	n.m	26–37
SO <sub>3</sub>	29.05–44.3	48.1–51.5	37.5–44	39.8–51.2	40.4–53.2	n.m	30–51
Na <sub>2</sub> O	0.18–0.26	0.13–0.86	0.05	0.33–0.42	0.29–0.43	0.04	n.m
P <sub>2</sub> O <sub>5</sub>	0.59–1.09	0.32–0.69	1.11–1.69	1.8–4.7	1.98–2.05	1.21	n.d
Fe <sub>2</sub> O <sub>3</sub>	n.m	0.21–0.34	0.03–0.13	0.15–0.22	n.m	0.06	0.08–3.31
Al <sub>2</sub> O <sub>3</sub>	0.15–0.49	0.18–0.19	0.06–0.11	0.26–0.49	0.17–0.23	0.12	0.08–2.65
MgO	n.m	n.m	0.01–0.07	0.09	n.m	0.12	n.m
K <sub>2</sub> O	n.m	0.03–0.17	0.03–0.06	0.02–0.05	n.m	<0.06	n.m
TiO <sub>2</sub>	n.m	n.m	n.m	n.m	n.m	0.06	n.m
SiO <sub>2</sub>	1.37–1.76	n.m	1.37–1.03	9.18–11.8	5.53–8.29	3.67	0.05–0.26
F	0.67–1.01	n.m	0.55–1.66	0.3–0.79	0.26	n.m	0.05–0.25

<sup>a</sup> Akfas et al. (2023), Abouloifa et al. (2023), Ennaciri et al. (2020a, 2020b), Nasrella et al. (2022), Sebbahi et al. (1997).<sup>b</sup> Guerrero et al. (2021, 2019), Pérez-López et al. (2015), Rentería-Villalobos et al. (2010), Torres-Sánchez et al. (2020).<sup>c</sup> Ayadi et al. (2016), El Zrelli et al. (2018).<sup>d</sup> Al-Hwaiti et al. (2010), Malkawi et al. (2022).<sup>e</sup> El Afifi et al. (2009), Kandil et al. (2016).<sup>f</sup> Rutherford et al. (1995).<sup>g</sup> Chuan et al. (2018), Wei et al. (2020).<sup>h</sup> Da Conceicao and Bonotto (2006).

## 2. Methodology

Recently, the topic of PG has gained increasing scientific attention, with >2880 research articles published between 2000 and 2023 (Fig. 2b). China, with >800 publications, leads the publication around PG (Fig. 2c). To cover this topic, we conducted an exhaustive exploration of literature related to PG. The research focusing on different aspects such as characterization, environmental impact, and valorization from the perspective of the mining circular economy. We conducted an extensive literature search by utilizing two reputable indexed databases, Web of Science and SCOPUS, renowned for their collection of high-quality, peer-reviewed publications. We reviewed a substantial number of articles across various areas related to phosphogypsum, encompassing its properties, environmental evaluations, as well as various articles discussing different approaches for its utilization.

Furthermore, our research extended to include a wide-ranging investigation of international government agencies (e.g., IFA, USEPA, and US-EPA), international organizations (e.g., International Atomic Energy Agency, International Commission on Radiological Protection, International), patent office records, and associations connected to the phosphate industry (e.g., Florida Industrial and Phosphate Research Institute).

## 3. Mineralogical and geochemical characterization of elements in PG

### 3.1. Mineralogical composition of PG

The major mineral phase in PG is gypsum, referred to as calcium sulfate, which is found in three mineral phases distinguished by the degree of hydration: dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ), and anhydrite ( $\text{CaSO}_4$ ) (Freyer and Voigt, 2003; Walawalkar et al., 2016). Quartz is commonly detected in PG and can account for approximately 5 % of the mineralogical composition, depending on the origin of the phosphate (Rutherford et al., 1994). The sensitivity of mineralogical analysis techniques is critical for the identification of trace and nanominerals in PG. The presence of fluorite was revealed by Akfas et al. (2023) and Cánovas et al. (2019) through a detailed examination by scanning electron microscope (SEM) and electron probe micro-analyzer (EPMA). El Zrelli et al. (2018) used SEM and energy dispersive X-ray spectroscopy (EDS) to detect the presence of fluorapatite traces, resulting from the unreacted phosphate during the

acidic leaching. Other mineral phases have been detected in PG, including sphalerite-Cd and minerals of Al and Fe (El Zrelli et al., 2019; Rutherford et al., 1994). Lütke et al. (2020) used a multi-analytical combination of several techniques (X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), EDS, high-resolution transmission electron microscopy (HR-TEM), scanning transmission electron microscopy (STEM), selected area electron diffraction (SEAD), and micro-beam diffraction (MBD)) to deeply characterize PG mineralogy; this approach revealed the presence of many nanominerals that have a size range of approximately 1–100 nm. The results of this study showed the presence of brushite ( $\text{CaPO}_3(\text{OH}) \cdot 2\text{H}_2\text{O}$ ), ankerite ( $\text{Ca}(\text{Fe}, \text{Mg})(\text{CO}_3)_2$ ), calcite ( $\text{CaCO}_3$ ), and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ). The mineral composition of PG may exhibit variations based on factors such as the type of phosphate rock, the contaminants introduced during the manufacturing process, and the age of the stockpile (Lottermoser, 2010; Macias et al., 2017). The investigation of PG samples from an abandoned fertilizer industry allows for the identification of new phases such as hematite ( $\text{Fe}_2\text{O}_3$ ), wusite ( $\text{FeO}$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), zircon ( $\text{ZrSiO}_4$ ), anatase ( $\text{TiO}_2$ ), malladrite ( $\text{Na}_2\text{SiF}_6$ ), chromite ( $\text{FeCr}_2\text{O}_4$ ), and others (Lieberman et al., 2020; Lütke et al., 2020; Sánchez-Peña et al., 2018).

### 3.2. Major elemental composition of PG

Several studies have been conducted to precisely determine the chemical composition of PG. According to Rutherford et al. (1994), the major elemental composition of PG varies depending on the type of wet phosphoric acid process used; on the other hand, the minor element composition may vary greatly following the source of the phosphate rock. Calcium and sulfur dominate the composition of PG, accounting for >90 % of the material (Rentería-Villalobos et al., 2010). Phosphate ore is subject to wide compositional variation and many substitutions in the crystal structure, which may transfer into the PG during the leaching process. The phases of the major elements in gypsum involve various processes, such as the precipitation of these elements in a relatively pure mineral phase, co-precipitation, the formation of solid solutions, and adsorption onto the surface of organic or inorganic compounds (Bisone et al., 2017). Table 1 shows the chemical composition of Moroccan PG compared to those reported from other regions. Moroccan PG consists mainly of Ca and S, with lower levels of impurities (Si, Al, Na, Fe, Mg, Sr, K, and F) (Abouloifa et al., 2023). The chemical composition of PG produced from different sedimentary sources is generally similar. The chemical composition of Brazilian PG, provided by Da Conceicao and

**Table 2**

Concentration (ppm) of trace elements in phosphogypsum (PG) samples from different regions. (n.d: not detected, n.m: not measured).

	Sedimentary						Igneous
	PG Morocco <sup>a</sup>	PG Spain <sup>b</sup>	PG Tunisia <sup>c</sup>	PG Jordan <sup>d</sup>	PG Egypt <sup>e</sup>	PG Florida <sup>f</sup>	PG Idaho <sup>g</sup>
As	<1–1.94	n.m	1–24	4–15	n.m	1.7	<1–2
V	1.89–9	0.72–4.75	3–6.26	n.m	n.m	10–40	n.d
Cr	5.85–11	1.52–20	6.12–13	7–15	n.m	n.m	<10–70
Cu	1.56–5.9	2.2–21	9.60–70	3–4.23	n.m	3.3	10–42
Zn	3–10.12	1.55–8	93–137	16.1–29	n.m	11.1	18
Ga	<1.45	1–3.3	n.m	n.m	n.m	0.5	n.m
Rb	0.36	0.1–2	n.m	n.m	n.m	3	<10–20
Sr	530–630	65–709	1118–1465	1112	n.m	837	610–670
Cd	1.7–3.5	0.13–6	17.7–24.7	0.94–5.05	n.m	<0.2	9–28
Ba	25–63.3	10.8–98	10–30	112–250	n.m	30	20–140
Sc	0.44–9.91	0.61–4.7	n.m	1–2	n.m	<0.05	n.m
Y	127–200	144–190	44.48–94.4	n.m	21.6	49	100–120
La	60.7–87.7	66–86	35–46.3	30–65.7	11.7	34.8	n.m
Ce	39–53	30	49–74.4	13–26.6	234.1	53.6	n.m
Pr	n.m	1–10.3	0.8–1.68	n.m	27.1	4	100
Eu	2.48–3.39	2.3	n.m	n.m	7.91	1.59	n.m
Gd	12.1–12.9	12	n.m	n.m	n.m	7.4	n.m
Pb	0.82–1.93	3.2–6.2	0.90–8.60	1.58–5.58	n.m	n.m	3–7
Th	3.04–5.54	0.22–4	0.74–0.95	0.60–5	n.m	0.7	<1
U	7.28–27.5	1.5–8.3	1.6–4.02	1–16	n.m	2.6	6–13

<sup>a</sup> Agayr et al. (2022), Akfas et al. (2023), Bouargane et al. (2023), Ennaciri et al. (2020a, 2020b).<sup>b</sup> Rentería-Villalobos et al. (2010), Torres-Sánchez et al. (2020).<sup>c</sup> El Zrelli et al. (2018), Hammas-Nasri et al. (2019), Zmemla et al. (2016).<sup>d</sup> Al-Hwaiti et al. (2010), Zielinski et al. (2011).<sup>e</sup> Gasser et al. (2022).<sup>f</sup> Rutherford et al. (1995).<sup>g</sup> Luther et al. (1993).<sup>h</sup> Da Conceicao and Bonotto (2006), Saueia et al. (2013a, 2013b).

Bonotto (2006), showed a very different composition in the concentration of elements. This is most likely due to the different origins between Moroccan (sedimentary) and Brazilian (igneous) PGs. In Brazilian PG, the authors reported lower concentrations of Fe, Ti and P and much higher contents of impurities such as Mg and Si (Da Conceicao and Bonotto, 2006).

The primary composition of PG can be divided into two categories: soluble impurities, which also include “syn-crystallized” impurities, and insoluble impurities.

The salts or  $a^2$ cids not removed during washing of the PG in the filtration step represent soluble impurities, including soluble  $P_2O_5$  in the form of  $H_3PO_4$  or  $H_2PO_4^-$  ions, which can combine with calcium to form monocalcium phosphate  $Ca(H_2PO_4)_2 \cdot 2H_2O$ . According to Silva et al. (2005), these impurities can be incorporated into the gypsum structure, thus forming ardealite ( $Ca(SO_4)_{1-x}(HPO_4)_x \cdot 2H_2O$ , where  $x = 0.5$ ). Fluoride can also be in the soluble form, incorporated into the PG as  $SiF_6^{2-}$  and  $F^-$  ions, which can combine with alkaline elements to form malladrite ( $Na_2SiF_6$ ) or, more rarely, ( $NaF$ ,  $KF$ ,  $MgSiF_6 \cdot 6H_2O$ ), or with ammonium ions ( $NH_4F$ ,  $(NH_4)_2SiF_6$ ). Lehr et al. (1966) have shown that fluorides precipitate as complex crystalline salts, the most common is fluorosilicate ( $H_2SiF_6$ ) in solution and calcium fluoride. The soluble form of these compounds could result in the release of acidity in PG.

Another form of soluble impurities is syn-crystallized impurities: the most common is  $SO_4^{2-}$  ions, which can be easily substituted in the crystal lattice of gypsum by certain phosphate ions, in particular  $HPO_4^{2-}$  and/or  $FPO_4^{2-}$ , because they have the same size, molar mass, and charge ( $AlF_6^{2-}$  ions can also take the place of  $SO_4^{2-}$  ions during the phosphoric acid manufacturing process) (Martynowicz et al., 1996).

Insoluble impurities account for a significant proportion of the impurities in PG. The following impurities are very poorly soluble minerals that remain unchanged during the process of sulfuric acid attack: unreacted apatite, fluorite ( $CaF_2$ ), silica, organic carbon, radioelements, and metals (Fe, Se, Mg) in forms difficult to identify (complex phosphates or sulfates). According to Lehr et al. (1966), ferrous ions could precipitate as  $Fe(H_2PO_4)_2 \cdot 2H_2O$ , and ferric ions as  $Fe_3(H_3O)$

$H_8(PO_4)_6 \cdot 6H_2O$  or  $(Fe, Al)_3(K, NH_4)H_8(PO_4)_6 \cdot 6H_2O$ . The selenium contained in PG could possibly be present in the form of  $CaSeO_4 \cdot 2H_2O$  (Krüger and Abriel, 1991). The presence of silicon is related to quartz, or silicates, or in some cases to feldspars in the presence of Al and Na or K found in PG (Rutherford et al., 1994). Many reactions can take place during the acidic attack result in the formation of insoluble complex of  $P_2O_5$ : like brushite ( $CaHPO_4 \cdot 2H_2O$ ), monetite ( $CaHPO_4$ ), and tricalcium phosphate ( $Ca_3(PO_4)_2$ ). Also, the presence of fluorine could result in the formation of insoluble compounds: the fluorine initially present in most phosphate rocks in amounts ranging from 2 to 4 wt% is released during acidulation, initially as hydrogen fluoride, but in the presence of other elements it can co-crystallize to form  $CaF_2$ ,  $MgF_2$ ,  $K_2SiF_6$ , complex compounds of the chukhrovite type ( $Ca_4SO_4SiF_6AlF_6OH \cdot 12H_2O$ ), or cryolite ( $Na_3AlF_6$ ).  $CaF_2$  and fluorapatite ( $Ca_5(PO_4)_3F$ ) may be the solids controlling the solubility of fluorine in PG. For high concentrations of dissolved aluminum, fluorine precipitates as cryolite ( $(Na, K)_3AlF_6$ ) or chukhrovite ( $Ca_4(SO_4)_2(AlF_6)_2(SiF_6) \cdot 12H_2O$ ) (Mathew et al., 1981). The presence of magnesium alters the fluorine precipitation mechanism, resulting in the appearance of the phase  $MgSiF_6 \cdot 6H_2O$ . This group of fluorosilicates crystallizes in an acicular form, limiting calcium sulfate through vacuum filter. When F, Mg, Na, and Al are present, ralstonite ( $Na_xMg_xAl_{2-x}(F, OH)_6 \cdot H_2O$ , with x ranging from 0.2 to 1.0 and a molar ratio F/OH ranging from 3 to 1) is frequently formed.

### 3.3. Trace elemental composition of PG

In addition to major elemental composition, PG contains various types of trace elements. Incorporated into the PG with different chemical forms, trace elements can be uniformly distributed throughout the lattice structure of PG or can be contained in separate distinct mineral phases. The biggest challenge is not only to determine the trace element concentrations but also the form of the trace elements in the waste, and therefore the availability to the surrounding environment. There is a need to fully understand the chemistry of trace constituents within this industrial by-product to implement the best waste management

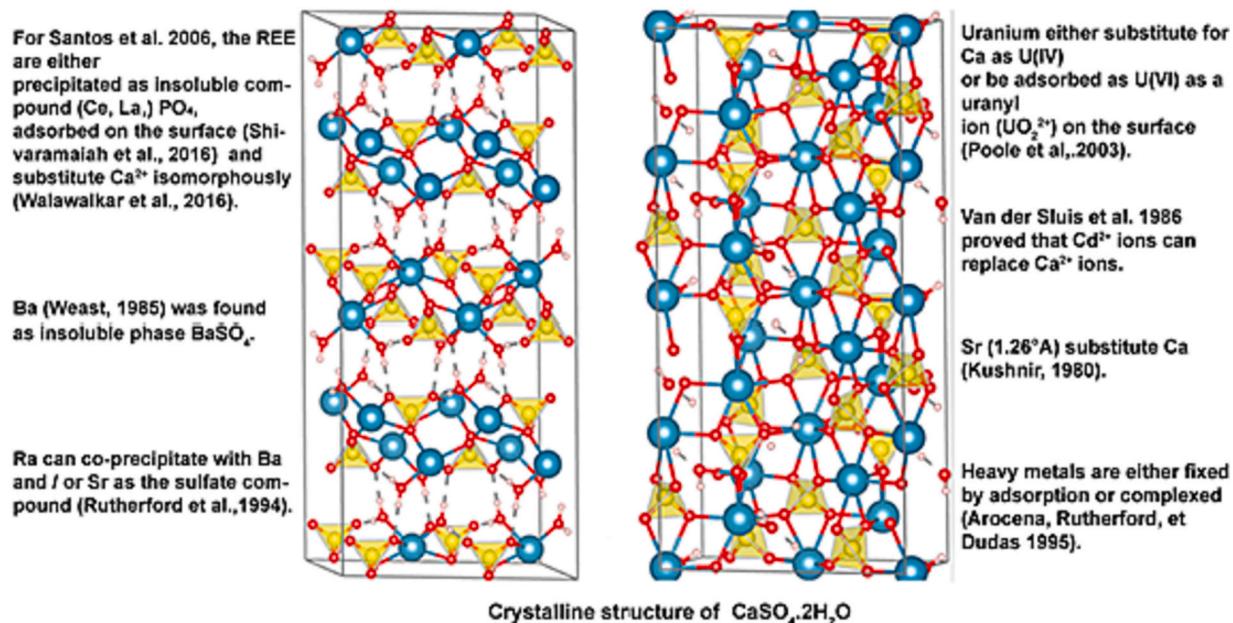


Fig. 3. The main forms of the presence of trace elements in phosphogypsum (PG).

strategies and to identify alternative uses.

Table 2 presents the mean contents of heavy metals and REEs from different origins. A comparison of the trace element composition of PG shows a slight difference between PG from sedimentary origins (Agayr et al., 2022; Bouargane et al., 2023) and a large difference, especially for the Brazilian PG, for those with an igneous origin. Concentrations of La, Ce and Pr in the Brazilian PG were much higher than the PG from Florida.

As shown in Table 2, PG contains a wide range of heavy metals (Carter Jr and Scheiner, 1992; Hamdona et al., 1993), such as lead (Garrido et al., 2005), cadmium (Van Der Sluis et al., 1986), zinc, and copper (Al-Masri et al., 2004), and many trace elements. It also contains varying concentrations of REEs incorporated into the crystal lattice. Metal ions are retained or adsorbed by PG via sorption mechanisms (Liu et al., 2022). Nevertheless, our understanding of the molecular-level chemical and physical processes involved in the retention of metal ions in PG remains incomplete. There is limited knowledge regarding the characteristics, forms, positions, and energy demands associated with metal retention within PG.

To understand and interpret the presence of trace elements in PG, it is necessary to go back and delve into the original structure. Phosphate ores exhibit a wide variation in chemical composition. Apatite is the dominant phosphate mineral in the majority of phosphate deposits. Apatite's physical, chemical, and crystal properties vary greatly (McClellan and van Kauwenbergh, 1991). Some of the elements enriched in phosphorites are known or theorized to substitute for  $\text{Ca}$  in apatite based on crystallographic spacings. Cadmium, Uranium, Strontium, Lead, and Zinc are among these elements (McClellan, 1980). Electrical neutrality is maintained by substituting  $\text{Na}^+$  for  $\text{Ca}^{2+}$  and  $\text{SiO}_4^{4-}$  for  $\text{PO}_4^{3-}$ . In the crystal structure, small amounts of  $\text{CO}_3^{2-}$ ,  $\text{VO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$ , and  $\text{SO}_4^{2-}$  may substitute for  $\text{PO}_4^{3-}$  (Khan et al., 2012). Through the wet process, the impurities naturally present in the PR are partitioned between phosphoric acid and PG according to their solubility and chemical affinity (Rutherford et al., 1994); between 2% and 12% of each trace element in the PR is transferred to the PG, with the exception of Sr (66%), Ce (56%), Y (41%), and Pb (27%) (Pérez-López et al., 2010). The chemical form of trace elements in PG is influenced by the reaction conditions in the acidic medium, and they become uniformly distributed through various retention mechanisms.

The most abundant trace elements in phosphate rock are Sr, Cr, V,

Zn, Ni, and Ba. Some elements, such as Ba, Cd, Cu, Pb, Se, Sr, and Th, are found to be enriched in PG. This enrichment could be attributed to an additional input related to the sulfuric acid used in the phosphoric acid production process (Santos et al., 2002). Furthermore, researchers indicated an uneven distribution of trace elements in PG. According to Arocena et al. (1995) and Rutherford et al. (1994), impurities in PG are more concentrated in small and/or very large particles more than medium-sized gypsum particles. Concerning Cd presence, Van Der Sluis et al. (1986) and Witkamp and van Rosmalen (1991) indicated that  $\text{Cd}^{2+}$  ions can substitute  $\text{Ca}^{2+}$  ions since they have the same charge and ionic radius (0.95 and  $0.99 \text{\AA}$ , respectively). When the concentration of  $\text{H}_2\text{SO}_4$  increases, the incorporation of  $\text{Cd}^{2+}$  increases, but decreases with the presence of halogens. Rutherford et al. (1996) conducted a study on the presence and distribution of Sr and Ba in PG. The results indicate that these elements behave differently: Sr may be capable of substituting into the calcium sulfate dihydrate crystal lattice due to the similarity in ionic radius ( $R = 1.26 \text{\AA}$ ); on the other hand, Ba forms an insoluble sulfate phase ( $\text{BaSO}_4$ ) that is precipitated in the crystal lattice of the PG.

Phosphate rocks contain large amounts of REEs, which can be transferred to the PG during the phosphoric acid production process. Igneous phosphate rocks contain more REEs than sedimentary phosphate rocks (1–2 wt%) (Binnemanns et al., 2015). After the acidulation process, 60 to 80% of REEs (especially the light ones: La to Sm) initially present in the phosphate rock are found in the PG (Habashi, 1985). Because of their importance in many industries, in particular for the transition to green energy, the distribution and textural properties of REEs in PG have gained a huge interest. However, REE geochemistry in PG is still not well defined. There is no experimental evidence of the mechanisms responsible for the incorporation of REEs in PG. However, some hypotheses assume that REEs may be i) structurally incorporated into the gypsum by substituting  $\text{Ca}^{2+}$ ; ii) adsorbed on the gypsum surface; or iii) precipitated as secondary phases (either amorphous or crystalline), which occur adsorbed on the gypsum surface (Fig. 3). Cánovas et al. (2018a, 2018b) suggested that REEs are essentially incorporated in a residual phase that corresponds to a small fraction of the phosphate rock, such as monazite ( $(\text{Ce}, \text{La}, \text{Nd}, \text{Th})\text{PO}_4$ ) or insoluble compounds like sulfates, other phosphates, and silicates distributed homogeneously in different particle size fractions. In addition, sedimentary phosphate rock is mostly composed of fluorapatite, which contains significant concentrations of REEs, Y, and Sc; the most likely source of

**Table 3**

Radionuclide activity concentrations (Bq/kg) in phosphogypsum (PG) of different origins (n.m: not measured).

	PG Morocco <sup>a</sup>	PG Spain <sup>b</sup>	PG Brazil <sup>c</sup>	PG Tunisia <sup>d</sup>	PG Jordan <sup>e</sup>	PG Egypt <sup>f</sup>	PG Florida <sup>g</sup>
(U-238)	174–196	100–160	35–47	30.7–65.9	19–38.7	283–543	132
(Th-232)	3.7–13	n.m	148–190	12.4–19.7	27.2–28.8	28.1–79	312
(Ra-226)	573–845	785–1024	280–467	188–350	475–601	351–596	907
(Pb-210)	n.m	588–827	241–367	163–212.7	425–574	n.m	860

<sup>a</sup> Azouazi et al. (2001), Belahbib et al. (2021), Qamouche et al. (2020).<sup>b</sup> Abril et al. (2009), Bolívar et al. (1996), Dueñas et al. (2010), Gázquez et al. (2014).<sup>c</sup> Canut et al. (2008), Fávaro (2005).<sup>d</sup> Tayibi et al. (2011), Mahjoubi et al. (2000), Reguigui et al. (2005).<sup>e</sup> Abusini et al. (2008), Zielinski et al. (2011).<sup>f</sup> El-Bahi et al. (2017) Mourad et al. (2009).<sup>g</sup> Hull and Burnett (1996).

these elements must be unreacted phosphate found in PG. Another possibility is that secondary minerals form during the acid attack on the phosphate rock. Köhler et al. (2005) proposed that, while REEs are readily released during apatite dissolution in the wet chemical process, they may also be easily precipitated as secondary phosphate phases during the reaction. Fluoride, for example, has previously been reported to be an effective REE scavenger (Borges et al., 2016; Lokshin et al., 2002). This mineral has been detected in solid PG, forming minerals in small grains attached to the surface of the gypsum (Cánovas et al., 2018a, 2018b). As a result, it is hypothesized that phosphate minerals may act as sources of REEs and Y in PG, whereas fluoride minerals may act as a host phase, limiting their mobility. Similarly, Davranche et al. (2015), Marsac et al. (2011), and Wood (1990) consider that trivalent REEs and Y are commonly strongly complexed by hard ligands such as fluoride, sulfate, phosphate, carbonate, organic acids, and hydroxide. Gypsum, the main phase in the PG matrix, could be considered as a mineral phase that could host REEs. Indeed, Akfas et al. (2023) proved, using elemental deportment and microanalysis (EPMA, Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS)), that gypsum can act as the main REE vector, while the mobility of REEs is controlled by fluorite phase. On the other hand, Shivaramaiah et al. (2016) proposed that, due to the rapid PG precipitation in the industrial process, REEs could be present in the form of surface-adsorbed metastable phases in the calcium sulfate crystals. According to Toledo et al. (2004), who studied the incorporation of Ce in PG, Ce is present in the carbonatite form and has an oxidation state of +4. During the chemical attack to produce phosphoric acid, Ce is probably reduced to a more soluble oxidation state (+3) and is more easily leached. Ce<sup>3+</sup> in the presence of Na forms a solid solution during crystallization (Na Ce (SO<sub>4</sub>)<sup>2-</sup> · H<sub>2</sub>O + CePO<sub>4</sub> · 0.5H<sub>2</sub>O). This stabilizes the hemihydrate sulfate structure and slows down the recrystallization of dihydrate sulfate during the hemidihydrate process (Rutherford et al., 1994). The findings of all investigations revealed that REEs are not all present in the same proportions in PG. Monitoring of REEs with different techniques revealed the presence of at least two types of bonds between REEs and PG: a strong binding (for REEs remaining in the final residue) and a weak binding (for REEs migrating with the gypsum).

### 3.4. Radionuclide composition of PG

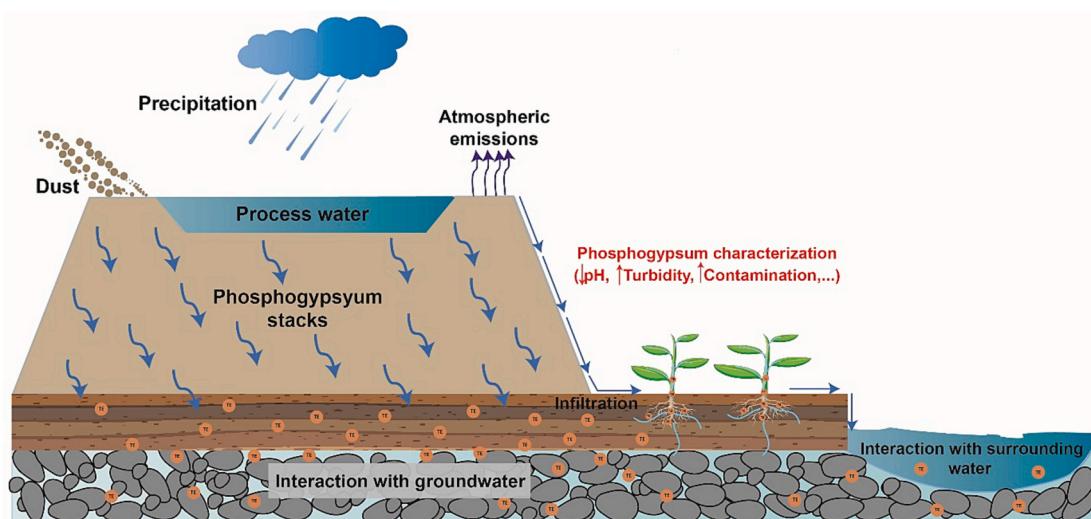
In term of PG radioactivity, sedimentary phosphate ores are naturally enriched in radioactive elements. The radioactivity varies by phosphate rock type and is primarily caused by the U-238 and Th-232 decay series. Because U-235 is not as common in nature as U-238, radiation from this series of decays is not considered a threat. Sedimentary phosphates have high U and Ra concentrations but a low Th concentration, whereas igneous phosphates have a low U concentration but a significant amount of Th (Habashi, 1985). Radionuclide concentrations in enriched ore are typically 100 to 300 % higher than in untreated rock (Santos et al., 2006). In PG, the radioactive elements are essentially

present in the fine particles (<20 µm) (Rutherford et al., 1996; Szajerski, 2020). Table 3 shows the radioactivity of PG produced in different countries.

In the structure of apatite, uranium is commonly found in the U(IV) and U(VI) oxidation state (Górecka and Górecki, 1984). Most researchers agree that U(IV) replaces Ca in the structure of apatite due to the similarity in ionic size between U<sup>4+</sup> and Ca<sup>2+</sup> (0.97 and 0.99 Å, respectively) (Qamouche et al., 2020). U(VI) can be adsorbed on the crystal surfaces of the apatite as the uranyl ion (UO<sub>2</sub><sup>2+</sup>) (Hull and Burnett, 1996), complexed with clay minerals (Rutherford et al., 1995), or fixed in the exterior part of the structure by various adsorption process. Uranium is very soluble as U(VI) (uranyl ion, UO<sub>2</sub><sup>2+</sup>) in the acidic conditions, explaining why >80 % of the U originally contained in the raw material remains in the phosphoric acid (Bolívar et al., 2009; Mazzilli et al., 2000). Lin et al. (2018) used X-ray absorption spectroscopy (EXAFS) to study U speciation in PG under different pH levels. EXAFS fitting results suggested that uranyl PG occurs most likely as carbonate complexes, with uranyl (UO<sub>2</sub><sup>2+</sup>) the dominant species at the Ca site. Additionally, U may be present as UO<sub>2</sub>HPO<sub>4</sub> adsorbed on the surface of gypsum (Al-Bassam, 2007), as uranyl fluorides for pH 4–7.5, or as sulfates or phosphates for pH < 5.

Generally, levels of Th-232 radionuclides in sedimentary phosphates are much lower than in igneous phosphates. Thorium appears in its +IV oxidation state and is able to co-precipitate with minerals such as iron and manganese oxides (Roselli et al., 2009). Thorium forms poorly soluble complexes with fluorides, hydroxides (formation of Th(OH)<sub>4</sub> for pH > 5), and phosphates, or relatively soluble complexes with chlorides, nitrates, and sulfates (Periéz et al., 1996). Furthermore, it was also suggested that Th(IV) could probably substitute for Ca in the structure of apatite due to the similarity in ionic radius (R = 1.12 vs R = 0.99 Å) (Saueia and Mazzilli, 2006). During the chemical attack of phosphate rocks, the Th equilibrium is disrupted; it migrates according to its chemical properties and/or its solubility, and thorium is fractionated between the phosphoric acid and PG.

Radium, one of the decay products of U-238, constitutes the major source of radioactivity in PG. Radium belongs to the alkaline earth elements and is therefore divalent and has similar properties to Ca, Sr, and Ba (Qamouche et al., 2020). Due to the chemical and crystallographic properties of Ra-226, it probably does not occupy a position in the crystal lattice of gypsum (Froelich et al., 1988). Radium has an ionic radius of approximately 1.52 Å (Ames and Rai, 1978; Vdovenko and Dubasov, 1975), which is too large for isomorphic replacement of Ca. Radium can co-precipitate with Ba and/or Sr as a sulfate compound (RaSO<sub>4</sub>), which is less soluble than gypsum (Azouazi et al., 2001). It was reported that radium sulfate (along with barium sulfate) could form crystals in the rhombohedral system, while CaSO<sub>4</sub> · 2H<sub>2</sub>O crystallizes in the monoclinic system (Rutherford et al., 1994), indicating that Ra-226 is more likely to be associated with the finer hemihydrate particles than the larger dihydrate particles. Even though Ra is considered to be relatively immobile, it was suggested that not all Ra-226 in PG originates



**Fig. 4.** Environmental impact of stocking phosphogypsum (PG) on the surface (TE = trace elements).

from precipitation of sulfate compounds during the acidic attack: some radium could have survived the sulfuric acid attack and transferred directly from the phosphate rock (Guimond and Hardin, 1989). Rn-222 is one of the Rn gas isotopes produced in significant amounts by PG from sedimentary origins (Dueñas et al., 2007; El-Didamony et al., 2013). Rn-222 is produced by the alpha decay of Ra-226. The radioactive gas has a relatively short half-life of 3.82 days and produces Po-218 through alpha decay (Gijbels et al., 2018). Rn-222 is an inert noble gas that is harmful to the environment because it is highly mobile and eventually decays to form two radioactive daughters with relatively long half-lives: Pb-210 and Po-210 (Pensko et al., 1980). The Ra-226 content and distribution, the emanation coefficient, the atmospheric pressure, and the radon diffusion coefficient influence the exhalation rate of Rn-222 from a source such as PG. Exhalation rates are greatly influenced by cracks and crusts on the surface of the PG (Ackers et al., 1985).

The presence of Po-210 and Pb-210 are detected in higher concentrations in sedimentary phosphate rock, particularly in the small particles of PG. Polonium, found inside the gypsum network, was detected in the form of insoluble quadrivalent polonium sulfate (80 %) and simple polonium sulfate (20 %) (Al-Masri and Al-Bich, 2002; Rutherford et al., 1996). Lead precipitated with sulfates or carbonates to form insoluble compounds that control lead solubility in the environment (Al Attar et al., 2011). Lead could also precipitate as PbS under reduced conditions or adsorb onto clays and organic materials (Rutherford et al., 1995).

#### 4. The impact of PG management strategies on the environment

PG waste has been an environmental challenge in several countries for many years, especially with the increase in the volume produced due to the huge global demand for fertilizer. The management of this “waste” presents a serious problem because of the incorporation of many impurities that could present a harmful threat to the surrounding environment. Currently, there are two main management strategies used for PG: surface disposal or discharge to the sea. Both are subject to numerous questions and limitations regarding their effectiveness in ensuring sustainable management and their impact on the environment. According to Bilal et al. (2023), >86 % of PG is stored on land or discharged in the sea or in waterways, while only 14 % is recycled. In this situation, site-by-site studies and assessment of management strategies using appropriate tools are required to ensure the success and efficiency of each strategy and to make short-, medium-, and long-term planning decisions, considering the growing awareness of the environmental problem and legal framework evolution.

##### 4.1. Disposal on the surface

Surface storage of PG in waste dumps is a common waste management strategy adopted by many phosphate producing countries around the world. The storage of PG on the surface without any previous treatment can cause serious environmental contamination of soil, water, and atmosphere (Fig. 4). To construct dumps, large areas must be allocated. These areas frequently exceed the size of industrial production sites. When large areas are set aside for PG storage, the natural landscape is altered, soil functioning is disrupted, and the appearance of the surrounding landscape is distorted (Chernysh et al., 2021). In the same context, PG disposal presents a financial burden related to transportation and remediation of the storage facilities. The transportation of PG to dumps results in high costs that could reach about 18 % of the cost of construction of the phosphoric acid production itself. Operating costs are approximately 12 % of the cost of raw material processing. Hilton (2010) estimated an approximate handling and storage cost of \$1.50 per ton of PG produced, giving a lifetime storage cost of around \$25 per ton.

###### 4.1.1. Risks of water and soil contamination

PG wastes are frequently disposed of in large stockpiles near phosphoric acid plants and are exposed to weathering processes that can result in serious environmental damage (Tayibi et al., 2009). This is due to the enrichment of the interstitial space of PG with highly harmful residual acids (i.e., phosphoric–sulfuric–hydrofluoric acids rich in metal (loid)s) (Lottermoser, 2010), and the presence of variable hazardous components. Hazardous spills and leakages are often responsible for polluting groundwater and reaching aquifers. The leaching behavior of major contaminant elements is largely dictated by their pH, solubility, and sorption properties. These factors are affected by various chemical and geochemical processes such as solid–solution partitioning, complexation, sorption, redox reactions, and solubility (Groenenberg et al., 2012; Li et al., 2007). Some studies have highlighted the effect of the presence of bacteria on the decrease in the mobility of metals (Heijmans and van Gemerden, 2000; Sarmiento et al., 2009). A variety of measuring techniques can be used to assess leaching, such as static batch leaching tests (a mixture of solid waste and water that is agitated and filtered) (Townsend et al., 2003), kinetic leaching tests (which simulate field conditions) (Elghali et al., 2023), and pH-static leaching tests (which evaluate solubility/sorption/precipitation under different pH conditions) (Luo et al., 2019). Moreover, the presence of heavy metals and their accessibility can be assessed by examining both their total concentrations and speciation using sequential extraction methods (Tessier et al., 1979). In recent decades, geochemical modeling has been

applied to predict the behavior of contaminants present in PG (Rabi and Mohamad, 2006). This method is used in many areas to examine and formulate the mass transfer in groundwater, known as reactive transport modeling, which analyzes the solutes carried by water flow through the soil. It involves combining transport modeling with reaction modeling through molecular diffusion and hydrodynamic dispersion (Bethke, 2022; Grace et al., 2016). Several studies have been conducted on PG stockpiles to assess their potential environmental impact.

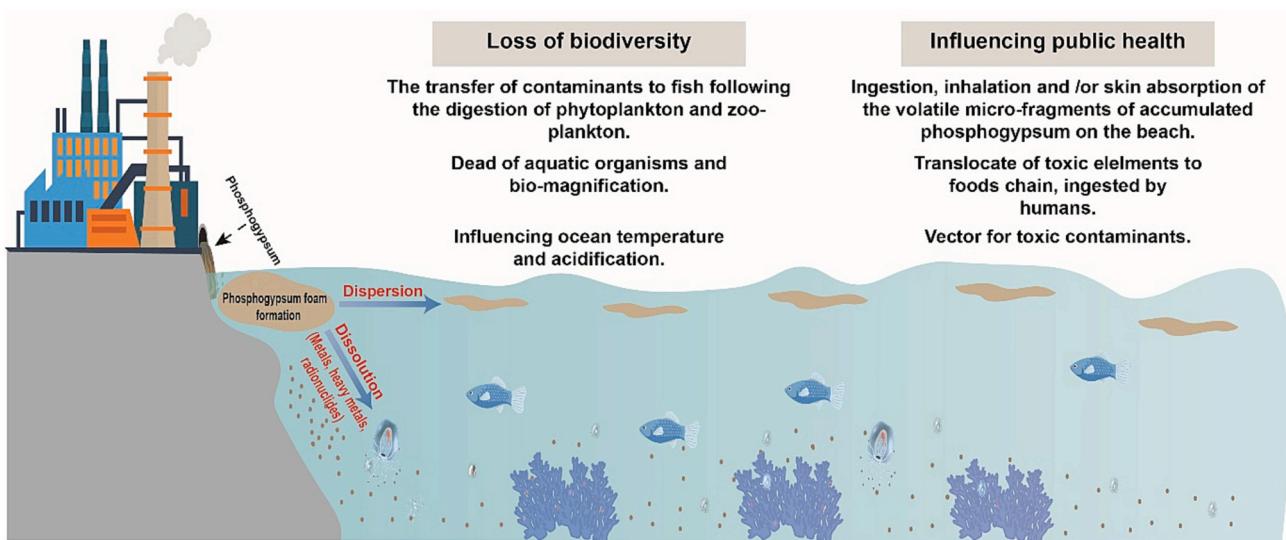
The management of PG is complicated by the presence of high concentrations of fluoride, which can leak and pollute groundwater. Studies conducted by Gago et al. (2012), Melki and Gueddari (2018) and Wang et al. (2019) have demonstrated that fluorine compounds released by PG can reach the soil through dry deposition, rainfall, or the decay of fluorine-contaminated plant matter. The physicochemical parameters, rain intensity, and soil type affect how fluoride is spread in the environment (Liteplo et al., 2002). Fluoride tends to accumulate in the topsoil layer due to the presence of iron, aluminum hydroxide, oxide, and silicate compounds (Luther et al., 1996). The spatial and vertical distribution of F reveals that the concentration of total and water-soluble fluoride (TF and WSF) decreased with distance from the industrial region, up to 2500 m. It was also noted that the 0–40 cm vertical soil profiles had more TF and WSF than the deepest 40–100 cm layers. Regarding associated health risks, the main exposure pathways of fluoride for children and adults were determined to be oral ingestion and dust inhalation.

In southwestern Spain, a large industrial complex for the production of phosphoric acid and fertilizer was located at the city of Huelva, where sedimentary phosphate rock was processed from 1965 to 2010, generating an average of about 2.5 million tons of PG annually. The majority of the PG was stored in big stacks located 1 km away from Huelva, covering 1000 ha (Grande et al., 2000). The spatial variability and the long-term evolution of the concentration of impurities in PG dumps have been investigated to contribute to the knowledge of the geochemical characteristics and leaching behavior of pollutants. Bisone et al. (2017) studied the behavior of elements presents in PG stacks in Spain over a 20-year period. It was observed that, despite the size of the stacks, they were relatively homogenous with little variation in depth. pH was determined to be the main factor influencing the leachability of  $F^-$ ,  $PO_4^{3-}$ , and Cd, with these elements being more extractable following leaching tests. This ultimately makes them a serious threat to both freshwater and marine environments. Pérez-López et al. (2010) evaluated the potential of PG stacks as a source of mobile toxic impurities through total digestion and sequential extraction. The results demonstrated that the leaching of mobile pollutants from the surface stack may lead to negative impacts. For each ton of PG, they estimated the mass of mobile pollutants released to be approximately 700 g Sr, 110 g Fe, 55 g Y, 30 g Ce, 12 g Cr, 11 g Ti, 5 g Zn, 4 g each of Cu and Pb, 3 g each of V and Cd, 2 g each of As and Ni, and 1 g U. Multiplied by 100 million tons and 20–25 tons per hectare, this enabled them to calculate the risk of PG in estuarine areas. In a subsequent study, Pérez-López et al. (2011a) investigated how pollutants interact with ecosystems over time. They collected pore-water samples at different depths of a PG stack in Spain and assessed the capacity of the salt marshes of the Tinto River to mitigate contamination from the landfill. The geochemical characterization indicated oxygen depletion in the deepest zones, which decreased the dissolution of contaminants in pore-water solution, even though it was found that the concentration of most pollutants increased with depth. Vásconez-Maza et al. (2019) examined the spatial distribution of heavy metals in the same spatial area by combining geochemistry, electrical resistivity tomography, and statistical methods. The large volume of PG generated during the production process, as well as the multiple physical and chemical characteristics observed, make it difficult to fully control this waste. The results showed the pond was highly acidic and saline, and the metals (Cd, As, Cu, and Zn) exceeded legal limits, with Cr rising to five times the This study concluded that these heavy metals in the pond have the potential to reach agricultural

soils, posing a risk to human health. In a recent study, conducted by Millán-Becerro et al. (2023) the focus shifted to understanding how weathering factors influenced the hydraulic response of a PG stack. Additionally, they delved into the hydrochemical characteristics of strongly acidic and polluted effluents resulting from leaching during various hydrological conditions, emphasizing the behavior of pollutants during both dry and rainy periods. Their observations revealed a slight increase in pollutant release from PG stacks during rainy periods, with estimated contaminant discharges into the estuary, such as  $PO_4$ , As, and U, totaling approximately 5000, 6.9, and 3.0 t/yr, respectively. The transfer of heavy metals to human-consumed products poses a serious ecological and human-health risk. El Zrelli et al. (2015) and Al-Masri et al. (2004) conducted separate studies that identified heavy metal contamination and ecological risks in the coastal regions surrounding the industrial facilities in Gabes City, Tunisia, and Syria, respectively. They assessed the leachability of Cd, Cu, U, and Zn through both continuous and batch leaching experiments. The results demonstrated that PG served as the principal source of most pollutants, particularly Cd, Zn, and Cr, which could readily leach into water and, subsequently, the surrounding environment. This implies the necessity for immediate intervention to prevent PG from being stored on the surface in contact with either water or acids.

PG has been classified internationally as a TENORM (Technologically Enhanced Naturally Occurring Radioactive Material). This classification is given to naturally occurring radioactive material that has had its radioactivity concentration or potential human exposure heightened above natural levels due to certain human activities (Beddow et al., 2006; Değirmenci, 2008; Luca et al., 2009; Máduar et al., 2011; Moreira et al., 2018). In response to the concern over high radionuclide concentrations in PG, the USEPA has set rules governing radioactive emissions from PG sources (U.S. EPA, 2010). The exposure of PG piles to weathering conditions may cause the dissolution/leaching of radioactive elements from the PG, potentially resulting in higher radioactivity levels in nearby soils or the transfer of these elements to water and living beings (Reijnders, 2007). The potential radioactive environmental risks of disposed PG have been measured in several studies. Azouazi et al. (2001) conducted a radiological study of Moroccan PG using gamma spectrometry, specifically examining the potential leaching of Ra-226, a uranium decay product, in aqueous solutions. The experiment consisted of mixing 20 g of PG with 50 mL of distilled water for 20 h at various pH levels (2.10–8.84), revealing an average Ra-226 leaching rate of 26.4 %. Although a nearby phosphate mine yielded water with 0.2 Bq/L of Ra-226, below the 1 Bq/L safety limit, concerns persisted regarding PG's potential for radioactivity dispersion in the environment. In a related study in India, Haridasan et al. (2002) reported the mobility of Ra from PG disposal using water and rainwater to mimic natural conditions. Based on the laboratory results, the maximum Ra-226 activity in the leachate was 0.53 Bq/L when PG was exposed to natural weather conditions (rain), while the minimum was 0.07 Bq/L. Leaching results proved that PG may enhance Ra-226 levels in the disposal environment. Although the leaching of radium may be slow under field conditions, given the quantity disposed and that most of Ra-226 in phosphate rock is entrained in PG, emphasis is required to assess the radioactive impact of PG. Olszewski et al. (2016) observed similar findings near Poland's Martwa Wisła river, where they investigated a PG stack's surroundings. Following the stockpile's closure and recultivation, concentrations of radioisotopes like Po-210, Pb-210, U-234, U-235, and U-238 decreased compared to previous levels. However, concerns persist about the possibility of incomplete stockpile security, potentially resulting in higher levels of more soluble uranium radioisotopes in the Martwa Wisła river water.

To simulate the influence of solution composition on the leaching of radionuclides, El Afifi et al. (2018) investigated Ra-226 leachability from PG waste in Egypt using a wide range of solution including synthetic, natural, saline, and solutions with anions or cations. Ra-226 activity concentration in PG was  $461 \pm 12$  Bq/kg, exceeding USEPA limits.



**Fig. 5.** The main environmental impacts of disposing phosphogypsum (PG) in sea water.

When exposed to different mixtures, approximately 4.5 % to 11 % of Ra-226 was released. Exposure to irrigation water extracted 80 % of Ra-226, posing environmental risks if consumed by humans or animals and contaminating surface and groundwater. Similarly, [Lysandrou and Pashalidis \(2008\)](#) conducted a study to examine how solution composition, including acidity and salinity, affected U leaching from PG stacks in Cyprus using both deionized water and seawater. They sampled three areas with varying characteristics, including A1 and A2 representing aged and fresh PG, and A3 with high salinity due to seawater exposure. The study found that increasing salinity significantly enhanced PG solubility, particularly for calcium and uranium leaching. This resulted in higher uranium content (75 Bq/kg) in A1 compared to 40 Bq/kg in A3, where seawater leached uranium, leading to its migration to the adjacent sea. Geochemical modeling indicated that uranium likely eluted from PG in the form of fluor complexes, confirming that the nearby sea becomes the destination for released uranium from Cyprus PG due to effective elution by saline water and the formation of stable uranium (VI) carbonate complexes.

Using geochemical modeling, [Burnett and Elzerman \(2001\)](#) assessed the potential for radionuclide release from PG stacks in Florida, where about 40 million tons are stockpiled each year in the central and northern parts of the state. Sampling was conducted from monitoring wells around and within the Piney Point stack, employing two analysis methods: examining stack fluids, groundwaters, and soils linked to the gypsum stacks and geochemical modeling. The stack fluids exhibited notably high uranium and Pb-210 concentrations, with moderate levels of Ra-226. When acidic stack solutions encountered buffered conditions, they led to elevated levels of uranium and Pb-210, suggesting potential precipitation. Geochemical modeling demonstrated that the sulfate and phosphate complexes of the radionuclides were significantly increased, leading to a negatively charged solution with species that were highly mobile within the stacks. The low pH indicated limited solid precipitation in freshwater, yet high dissolved chemical species and specific ion concentrations caused oversaturation. The findings of this study indicate that, while PG stacks do contain significant amounts of dissolved radionuclides, removal mechanisms appear to prevent large-scale radionuclide migration to the underlying aquifer.

#### 4.1.2. Atmospheric contamination

Storing PG in open piles may lead to the emission of radioactive materials and can be a health risk to those who work on the site or live nearby. The worldwide mean of Ra-226 in PG is 1000 Bq/kg ([USEPA, 2002; IAEA, 2013a, 2013b](#)). This causes a problem due to the emanation

of Rn-222 from the alpha-decay of Ra-226, a radionuclide classified by the USEPA as a group A human carcinogen. As a result, the disposal of this material is regulated under the National Emission Standards for Hazardous Air Pollutants (NESHAP) and the National Emission Standards for Radon Emission from PG Stacks ([US-EPA, 1986](#)). Rn-222 is a gaseous element that can be released into the air; Rn-222 can also be resuspended into the air by wind and vehicular traffic. This may result in potential radiological risks due to external exposure of workers in the PG storage area ([UNSCEAR, 1982; Bigu et al., 2000; Papastefanou, 2001](#)). Another matter of concern is the release of nanoparticles produced during the production of PG that have the potential to reach neurons, which could lead to the development of neurological diseases such as Alzheimer's and Parkinson's ([Bernhoff, 2012; Calderón-Garcidueñas et al., 2020; Caricchio et al., 2019](#)). Moreover, those who reside near mines have a higher rate of psychological disorders such as depression and anxiety ([Joaquin et al., 2018](#)).

According to [Mas et al. \(2006\)](#), accumulated PG located in salt marshes in Huelva (Spain) raise local gamma radiation levels to 5–38 times the normal rate (0.74 Bq/m<sup>2</sup>/s). Radon equivalent radiation for one square meter of soil measured 2–7 times the normal rate, which means that 9 min of exposure per day equals an annual dose of >10 mSv/year. This value is significantly higher than the recommended worldwide exposure limit of 2.4 mSv/year ([UNSCEAR, 2002](#)), and may pose a health risk to site workers or residents ([US-EPA, 1986](#)). [Dueñas et al. \(2007\)](#) explored the same region to measure Rn-222 exhalation from active, restored, and unrestored inactive PG stacks over 24 h. The Rn-222 exhalation of active PG stacks (0.523 Bq/m<sup>2</sup>/s) was two times higher than that of unrestored inactive stacks, while the Rn-222 exhalation of restored PG stacks was eight times lower than that of active stacks. It should be noted that all the recorded values were lower than the aforementioned EPA limit value ([EPA, 1998](#)).

In contrast, [Gezer et al. \(2012\)](#) assessed the radiological characteristics of disposed PG in Turkey. They examined the annual effective doses received by members of the public and workers by using generic exposure scenarios. Samples were collected from various layers of PG stacks and measured with a gamma-ray spectrometer. Their study revealed that both the general public and workers received annual effective doses below the 1 mSv/year limit. Meanwhile, [Al Attar et al. \(2011\)](#) investigated the radiological impact of Syrian PG piles on the environment. The study found a mean Ra-226 activity of 318 Bq/kg and evaluated gamma radiation from the PG stacks. The annual effective dose was merely 0.082 mSv/year, suggesting that the presence of PG piles had no significant impact on Rn-222 concentration or gamma

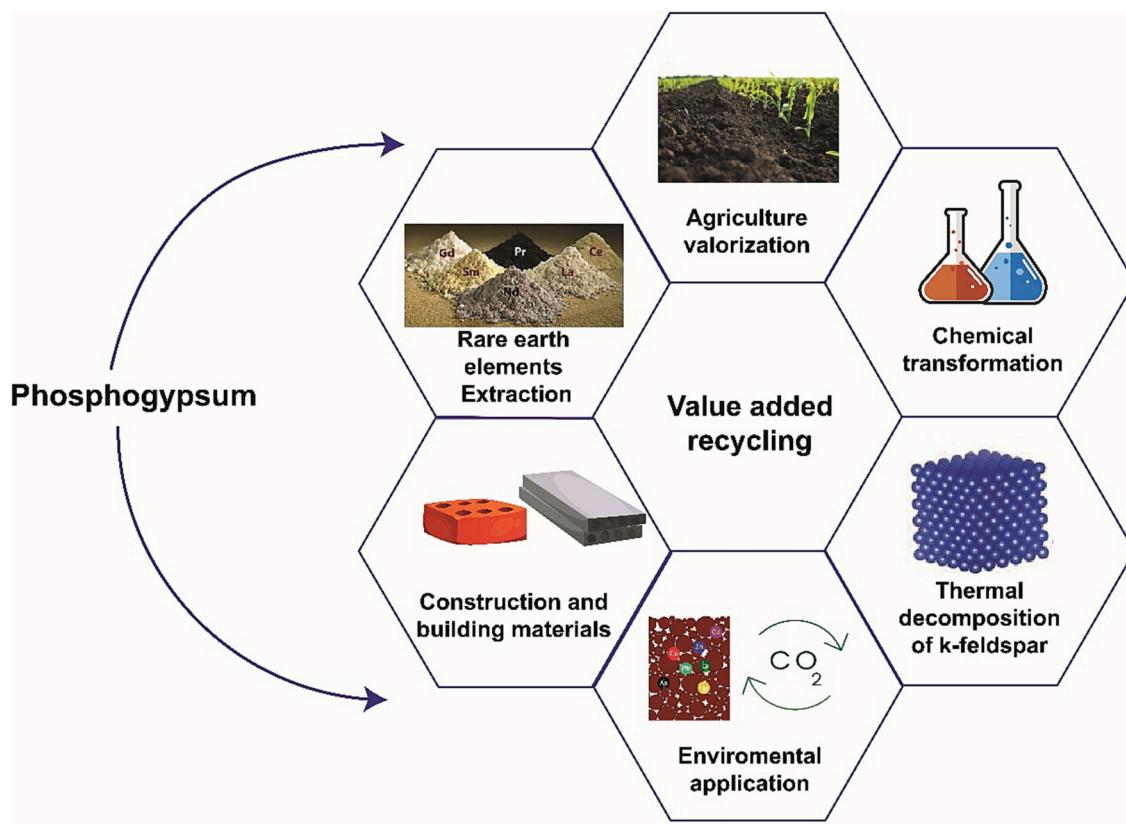


Fig. 6. Potential valorization pathways of phosphogypsum (PG).

radiation levels in the area.

#### 4.2. Dumping PG in the sea

Metallic pollution is regarded as one of the most serious and potentially dangerous threats to natural marine systems and human health (Bastami et al., 2015; Gao and Chen, 2012). Metal pollution in the aquatic environment and its effects on natural ecosystems have received increased attention in recent decades (Ayadi et al., 2015; Aziz et al., 2023; Förstner and Prosi, 1979; He et al., 2005; Islam et al., 2015). The dumping of PG waste in the marine environment is seen as a major cause of contamination in the ocean. When this waste is dumped in coastal areas, it can lead to a local change in the pH of the seawater, which in turn can affect the behavior of trace elements and determine the proportion that is dissolved. The presence of calcium sulfate and other salts in the waste can cause the concentrations of heavy metals to increase near the release point (Contreras et al., 2015; El Samad et al., 2014; Pérez et al., 2016). This has raised awareness about the potential risks of marine life contamination by PG pollution (Fig. 5).

The Tunisian Chemical Group has been releasing hundreds of tons of PG into the sea each day, posing a threat to the marine ecosystem in the region (Ayadi et al., 2015; Darmoul, 1988; Darmoul et al., 1980; Rabaoui et al., 2015, 2014). In the absence of official data, it is estimated that between 1000 and 13,000 tons are being discharged daily without any form of treatment. According to a Facility for Euro-Mediterranean Investment and Partnership (FEMIP) and World Bank study, the Gabes region is now one of the most polluted areas in the Mediterranean Sea (Benoit and Comeau, 2012). Studies have been conducted to assess the potentially harmful effects of the impurities released by PG into seawater. Within this context, El Zrelli et al. (2019) conducted a study to evaluate the sediment quality and environmental/ecological dangers in the central Gulf of Gabes, which has been heavily impacted by industrial activities. Their analysis revealed the presence of fluoride, trace

elements (Sr, Cd, Cu, Zn, Cr, and V), and radionuclides from the U-238 decay series (Ra-226, Th-232, Pb-210, U-234, and Po-210). The average concentrations of the analyzed metals were found in this order: Zn > Cd > Cr > Pb > Cu > Hg. It was revealed that the metallic pollution status of the surface layer of Gulf of Gabes is obvious, very worrying, and requires rapid intervention. The coastal area surrounding the Gabes City chemical complex has experienced negative impacts on biodiversity, such as the local reduction and disappearance of *Posidonia oceanica* meadows, since the establishment of the phosphate fertilizer industry in Gabes City (Darmoul, 1988). Despite the seriousness of the ecological situation of the Gulf of Gabes, dumping PG into the marine environment still occurs.

The Estuary of Huelva in Southwestern Spain is a crucial marsh ecosystem facing severe pollution challenges due to historical mining activities in the Iberian Pyrite Belt and ongoing industrial operations in the Huelva Industrial Estate (Borrego et al., 2013). The pollution in the estuary is attributed to various contaminants, including sulfates, metals, and metalloids, transported by the Tinto and Odiel Rivers. Furthermore, the disposal of PG waste from 1965 to 2010 has further contributed to the pollution of the estuary (Nieto et al., 2013; Torre et al., 2019; Pérez-López et al., 2011a, 2011b). In the same region, Papaslioti et al. (2018) investigated the environmental impact of PG leachates on estuaries, focusing on pH's influence on water chemistry, mineralogy, and precipitated materials. The results showed that the levels of Al, Fe, Cr, Pb, and U decreased significantly with an increase in pH due to sorption and/or precipitation processes. Nonetheless, this research sheds light on the PG stack's significant contribution to the release of toxic elements (Co, Ni, Cu, Zn, As, Cd, and Sb) to coastal areas, as up to 80–100 % of their initial concentrations behaved conservatively in the mixing solutions. It is also important to note that these wastewaters are highly acidic and, combined with their high concentration of trace elements, represent a significant contribution to the pollution of the Huelva Estuary and, consequently, the Atlantic Ocean. Pérez-López et al. (2011b) quantified pollutant inputs into the Huelva Estuary from PG disposal,

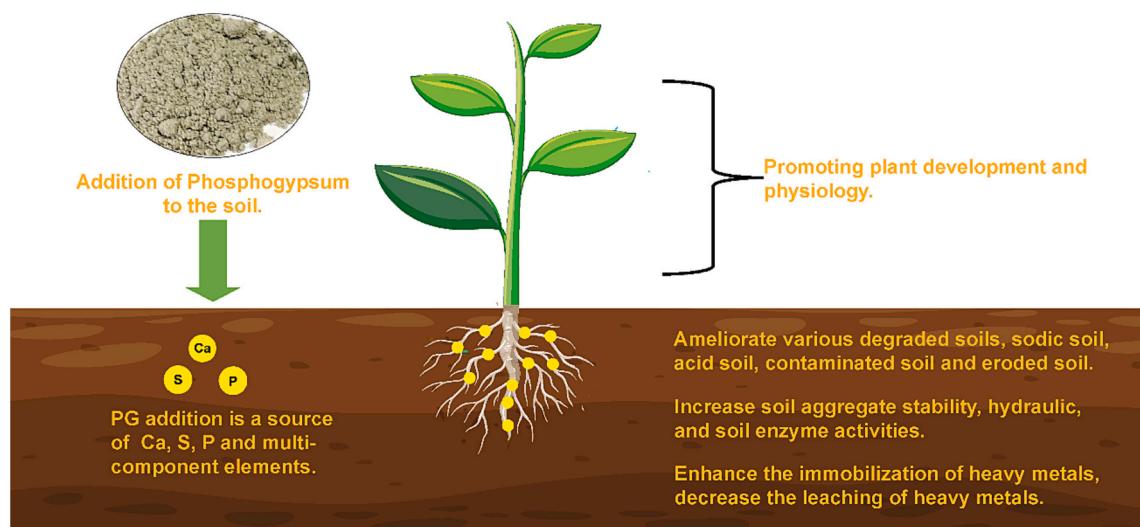


Fig. 7. The main advantages of using phosphogypsum (PG) in agriculture.

with Fe, Zn, As, and Cd being the most prominent, entering the estuary at rates of 42 tons, 12 tons, 6.9 tons, and 1.6 tons annually, respectively. The geochemical signatures of tracers elements such as REE and Cl/Br ratio was assessed by Pérez et al. (2016) to evaluate long-term impacts on coastal environments. Samples collected from various areas revealed potential contamination even in ostensibly restored regions. These solutions exhibit a low pH of 1.9 and contain concentrations of 6100 mg/L for phosphorus (P), 1970 mg/L for sulfur (S), 600 mg/L for fluorine (F), 200 mg/L for ammonium ( $\text{NH}_4^+$ ), 100 mg/L for iron (Fe), 10–30 mg/L for zinc (Zn), arsenic (As), and uranium (U), as well as 1–10 mg/L for chromium (Cr), copper (Cu), and cadmium (Cd). These results emphasize the need to develop effective restoration strategies to manage and mitigate the pollution of the Huelva Estuary from PG.

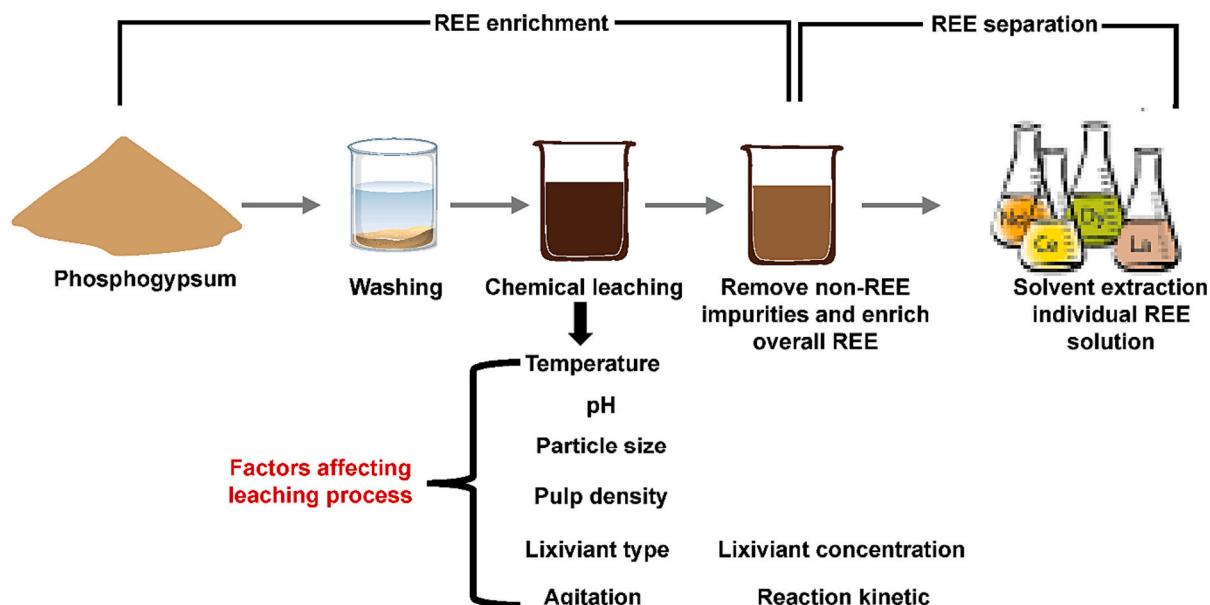
In Morocco, considerable volumes of PG are dumped into the Atlantic Ocean in proximity to Safi and Jorf Lasfar: two major chemical industry locations. Kaimoussi et al. (2002) presented a diagnosis concerning the state of the coast of the city of El Jadida, in which the authors revealed the existence of a variety of concentrations of certain heavy metals (Cd, Cu, Zn, Fe, and Mn) detected in four species of algae. The presence of these metals is due to the rejection of PG waste without any preliminary treatment. Gaudry et al. (2007) examined the impact of PG discharge on the Atlantic Marine Environment using two analytical techniques capable of detecting multiple elements. The authors used inductively coupled plasma mass spectrometry (ICP-MS) and instrumental neutron activation analysis (INAA) to measure the concentrations of 47 elements in various PG samples involved in the study. Algae were used as a bio-accumulator of heavy metals in the Jorf Lasfar region to identify the signal of heavy metal pollution. *Ulva lactuca* Linnaeus was chosen to detect heavy metal pollution (Cu, Ni, As, Cd, Pb, Cr, Ag, Mn, Th, U) close to the location of the waste rejection. It was found that the algae collected near the phosphate industry's sewage system had higher levels of heavy metals than background algae, indicating pollution even 6 km away from the site. The elevated concentrations of toxic or radio-toxic elements observed in the marine environment can be hazardous to marine flora, fauna, and human life since it is at the top level of the food chain. This study emphasizes the importance of industrially reusing PG, especially as the rising production volume could potentially lead to higher concentrations of pollutants at the sediment interface and in long-lived plants (Ennaciri and Bettach, 2018; Wędrychowicz et al., 2019).

## 5. The potential strategy for PG recycling: reuse of PG as a secondary raw material

To address environmental and economic issues associated with the storage and disposal of PG, numerous valorization routes have been explored in recent years, such as in agriculture, REE extraction, the energy sector, chemical transformation, environmental applications, and construction applications (Fig. 6). However, in order to utilize PG as a raw material rather than a waste, a substantial shift in perspective, regulatory framework, and the environmental laws in the PG-producing countries is imperative (International Fertilizer Industry Association, 2016). Additionally, technical, and economic limitations make it difficult to employ strategies that would consume large amounts of PG and achieve the goal of mass consumption. It is also important to consider the potential for secondary pollution that could result from the various valorization routes and compare it to the pollution caused by traditional disposal. Despite these obstacles, numerous studies have highlighted the many opportunities to use PG in a variety of applications (Ajam et al., 2009; Bouchhima et al., 2013; Huang and Lin, 2010; Meskini et al., 2021; Rashad, 2017; Shen et al., 2007; Zhao et al., 2015a, 2015b). Therefore, the recycling of PG could be an eco-friendly, safe, and cost-effective solution. Recycling PG offers an eco-friendly, cost-effective solution, aligned with policies advocated by organizations like the International Fertilizer Association (IFA) (Hilton et al., 2020), the Environmental Protection Law of the People's Republic of China, and the United States Environmental Protection Agency, promoting PG reuse in sectors such as construction and agriculture.

### 5.1. Agriculture

PG can be used as an amendment to decrease the salinity of soils, and also as a low-grade fertilizer supplying calcium and sulfur together with traces of  $\text{P}_2\text{O}_5$  remaining in the PG matrix (Plyatsuk et al., 2019; Belyuchenko et al., 2010). The absence of the requirement to purified PG from  $\text{P}_2\text{O}_5$  is beneficial for agricultural use, as  $\text{P}_2\text{O}_5$  is an essential element for soil (Sheudghen and Bondareva, 2015). In the agricultural sector, PG is used mainly for i) treating acidic or metal-rich soils (Rodríguez-Jordá et al., 2010; Takahashi et al., 2006), ii) improving crop yield and soil structure (Tang et al., 2006), iii) reducing soil erosion (Zhang et al., 1998), and iv) increasing the availability of Ca, P, and S (Fig. 7). These nutrients are traditionally considered amendments that improve the physio-chemical properties of soils (Delgado et al., 2002) by providing calcium in the soil depth and reducing the aluminum saturation, which contributes to the deepening of the plant root system and



**Fig. 8.** Hydrometallurgical route for rare earth element (REE) extraction from phosphogypsum (PG) schemes developed at the lab scale.

favors the absorption of water and nutrients (Alcordo and Rechcigl, 1993).

Due to its residual acidity and the presence of hazardous elements such as heavy metals and radioactivity, the use of PG as a soil amendment is limited. In 1992, the USEPA forbade its use due to its radioactive properties, with the exception of PG with an average radium concentration of <370 Bq/kg. To guarantee the long-term safety of using PG in soil, research has been conducted to investigate the mobility and bioavailability of contaminants that may be present (Enamorado et al., 2009; Hurtado et al., 2011; Quintero et al., 2014; Smaoui-Jardak et al., 2017; Wang, 2020). Papastefanou et al. (2006) studied the Ra-226 content of PG and found that it ranged from 261 to 688 Bq/kg. In soil amended with PG, the radionuclide was between 50 and 479 Bq/kg (average 205 Bq/kg), while in regular cultivated fields it was between 37 and 54 Bq/kg (average 48 Bq/kg). To assess the migration of Ra-226, an examination was conducted on rice samples originated from cultivated fields amended with PG. The outcome revealed an elevated concentration of Ra-226 in samples collected from these fields compared to others. In the same context, Nisti et al. (2015) carried out a column leaching experiment using a mixture of typical Brazilian sandy clay soils and PG. They reported a low release of metals and radionuclides (i.e., As, Cd, Ni, Cr, 226-R, 210-Pb, and Th-232) from Brazilian PG-amended soils at doses 10 times higher than those required to achieve 50 % soil base saturation (around 15 g PG/kg soil). Saueia et al. (2013a, 2013b) evaluated the availability of metals (As, Cd, Cr, Co, Cu, Hg, Ni, Pb, Se, Zn) and radionuclides (Ra-226, Ra-228, and Pb-210) using leaching with ethylenediaminetetraacetic acid (EDTA). The results were compared with those obtained from the most common phosphate fertilizers. The obtained results demonstrated that the metals and radionuclides were not available to the environment, indicating that the use of PG in agriculture is safe in terms of contamination by such elements. The presence of fluoride (F) in soil has become an increasing concern because of its toxicity to microorganisms, plants, animals, and humans (Allibone et al., 2012; Mazzilli et al., 2012; Garg and Malik, 2004). Cui et al. (2021) conducted a study to understand the leaching characteristics of F in soil. Several sources were investigated, including fertilizers, pesticides, PG, and atmospheric deposition. Despite having a substantial F concentration, PG-covered soil had the lowest proportion of F released (0.18%). Compared to PG, phosphate fertilizer-treated soil leached 5.47 kg F ha<sup>-1</sup> per year, posing the greatest environmental risk to deeper soil and groundwater. Therefore, PG had little effect on F leaching in soil.

Fluoride-containing agricultural materials may leach more F from surface soils than industrial sources. On the other hand, Abril et al. (2008) and Enamorado et al. (2014) have directed attention to the cumulative effect of PG amendments on cultivated soils and plants. The authors concluded that Cd levels in tomato shoots and fruits were lower than, but close to, food safety limits. Indeed, the authors stated that accumulated PG amendments >16 g PG/kg soil would be sufficient to exceed such a limit. Al-Hwaiiti and Al-Khashman (2015) found similar results, noting that PG amendments had caused contamination in soils and vegetables (tomatoes and green peppers) grown in soils amended with Jordanian PG. According to Mazzilli et al. (2012), soils amended with PG were heavily polluted with Cd, moderately polluted with Cr and Ni, and slightly polluted with Pb, Cu, Zn, and V. It was also noted that adults and children who consumed vegetables grown in PG-amended soils were ingesting significant amounts of the studied metals, but the daily intake of metals (DIM) and health risk index (HRI) values both indicated no health risk. The use of PG as a fertilizer has been examined by researchers to limit ammonia volatilization. Lim et al. (2017) and Prochnow et al. (1995) examined the effect of using PG on the loss of N. The results indicated that N retention was increased due to the formation of ammonium salts ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), which avoid nutrient imbalance by reduction of the N/P ratio. The authors revealed an increase in the reduction of ammonia with an increasing rate of PG addition during composting. Outbakat et al. (2022) investigated the effects of PG amendments on salinity and sodicity stress and concluded that it can be used to reclaim saline and saline-sodic soils with no adverse impacts on the environment. Leaching tests were conducted to check the leachability of impurities from PG, and the results showed that it can be used as an amendment without any negative environmental impacts.

In summary, utilizing PG in agriculture holds potential benefits due to its widespread availability and absence of technological barriers. However, concerns arise from impurities within PG that may be absorbed by plants, posing risks to air and water quality. Therefore, environmental and public health impacts must be considered, especially when employing large PG doses (Silva et al., 2022). Notably, repeated applications of high PG doses (12–24 t/ha) can substantially raise soil's total and water-soluble fluorine content (Trigub, 2009). Field studies are essential to determine appropriate dosages and prevent the spread of hazardous elements. Overall, further research is necessary to assess the risks associated with PG use, prioritizing public health and environmental protection.

## 5.2. Extraction of REEs

Rare earth elements are often referred to as industrial vitamins due to their wide range of uses in energy production, high-tech manufacturing (e.g., smartphones and lamps), and for their special properties like catalytic activity, strong oxidation resistance, and chemical corrosion resistance (Bagguley, 1978; Bandara et al., 2014; Grandell et al., 2016; Innocenzi et al., 2014; Tunsu et al., 2015). With the growing demand for REEs, more attention is being paid to their extraction from solid waste such as PG. The extraction of REEs from PG could be a promising route in its valorization, especially given the complexity of its management in relation to the massive quantity produced to meet the world's increasing demand for fertilizer. Due to the low concentration of REEs in PG and their occurrence as complex mineral phases, REE extraction from PG could be extremely difficult, both technologically and economically (Mukaba et al., 2021). Despite this fact, the large volume of PG, currently estimated to be 200–300 million tons per year, makes it a potential source of REEs (Brückner et al., 2020); it can be considered as a high-tonnage/low-grade source of REEs. Therefore, several studies have been carried out to investigate the feasibility of extracting REEs from PG by developing different physicochemical and hydrometallurgical processes (Fig. 8). In the developed process, the first step aims to extract the valuable elements from REE-bearing materials, performed frequently using aqueous extractants. Following dissolution, additional steps are required to concentrate and separate elements of interest. The ultimate goal is to achieve the highest purity by refining and purifying the element to create a marketable product.

To increase the concentration of REEs in PG, various physical and chemical methods have been explored. Yang et al. (2019) investigated physical techniques like hydrodynamic separation, flotation, grinding, and high gradient magnetic separation (HGMS). Yang (2017) conducted tests combining these methods, leading to an increase in REE content in PG from 0.13 to 7.3 wt%. Milling PG was also considered to enhance REE leaching efficiency, with centrifugal ball milling showing improved extraction with longer times. Rychkov et al. (2018) and Lütke et al. (2023) reported an improvement of REE leaching from PG by investigating the effects of mechanical treatments (grinding and ultrasonic impact) and chemical activation (sorption onto an ion exchange resin). In the experiment, a small fraction of REEs was leached from PG with  $H_2SO_4$ . Instead, the simultaneous application of grinding and ultrasonic treatment to reduce the particle size increased the recovery of REEs by a factor of four. The low recovery was explained by the strong chemical bonds between the REEs and the gypsum crystals. Lambert et al. (2018) proposed microwave irradiation to enhance REE leaching from PG, achieving optimal results at specific power and duration settings (at either low power (600 W) and short duration (5 min) or high power (1200 W) and long duration (10 min)). Microwave heating created pores in the gypsum matrix, facilitating lixiviant infiltration and converting gypsum into more soluble crystals. The conventional method for extracting REEs from PG involves direct leaching with strong inorganic acids like  $HNO_3$ , HCl, and  $H_2SO_4$ . Various studies have employed this approach (Gasser et al., 2022; Grabas et al., 2019; Ismail et al., 2015; Laurino et al., 2019; Reid et al., 2017; Salo et al., 2020). Controlling reaction parameters, including contact time, solid-to-liquid ratio, temperature, chemical agent concentration, particle size, and agitation speed, is required for direct PG leaching. Different acids have been tested for PG leaching. For instance, Walawalkar et al. (2016) developed an  $HNO_3$ -based technique to extract REEs, achieving an 85 % recovery rate with increased acid concentration. Hammas-Nasri et al. (2016) conducted another experiment using a two-step process of  $H_2SO_4$  leaching. Under normal conditions, PG has a low solubility due to the common ion effect, but the low cost of  $H_2SO_4$  makes it a good candidate. HCl-based leaching of REEs from PG yielded moderately low results, attributed to calcium sulfate's poor solubility in HCl due to the salting-out effect. Ismail et al. (2015), improved REE leaching efficiency from PG with a two-step HCl (1.5 M) extraction, raising average extraction

levels from 51 % to 81 %. Moreover, due to the limited solubility of PG, its complete dissolution to recover only REEs is economically unfeasible because the concentration of REEs to be extracted is low. Hammas-Nasri et al. (2019) enhanced REE enrichment in PG by treating it with a 25 g/L salt solution followed by a 60 g/L  $Na_2CO_3$  solution. Using the salt solution alone enriched REEs by 81 %, while adding  $Na_2CO_3$  raised this value to 84 %.

Exploring carbonation and recrystallization methods for PG can facilitate indirect REE leaching and material development while enabling REE extraction by manipulating PG's microstructure. Carbonation, a well-documented process, can convert PG into calcium carbonate ( $CaCO_3$ ) or ammonium sulfate (AS) fertilizer, with  $CaCO_3$  being enriched in REEs (De Beer et al., 2014; Kolokolnikov and Kovalev, 2009; Mattila and Zevenhoven, 2015; Mulopo and Iku-Omoregbe, 2012). Pure  $CaCO_3$  has many different commercial and industrial uses, such as the production of concrete (Portland cement) or lime (stabilizing soil and neutralizing acid), water treatment, and flue gas desulfurization (Kandil et al., 2017). This technique shows promise in increasing REE concentration before extraction by dissolving  $CaCO_3$  with inorganic acids. (Masmoudi-Soussi et al., 2019). According to the literature, REEs do not crystallize within the lattice structure but rather exist in separate phases, which presents a great opportunity for REE extraction and recrystallization of technically pure PG (Genkin et al., 2017). The dissolution and recrystallization of PG with a focus on REE recovery is a new area of research that has been reported (Koopman and Witkamp, 2000). Several trials, both at the laboratory and larger scale, have been conducted in this perspective. For instance, Genkin et al. (2017) described a method that removed over 98 % of REEs by recrystallizing PG-dehydrate in an acidic medium with calcium nitrate. Although solvent extraction was proposed for REE recovery, this process faced cost and waste management challenges. An increase in  $Ca^{2+}$  ions was beneficial for REE recovery but caused a decrease in the quality of the targeted PG. Koopman and Witkamp (2000) suggested using ion-exchange resin to recover leached REEs during the recrystallization of PG-hemihydrate to PG-dehydrate, resulting in up to a 53 % decrease in REEs in the final residue. However, this method also extracted calcium ions, generating significant calcium sulfate waste. Another research area involves synthesizing calcium sulfate whiskers (CSWs) from high  $CaSO_4$  content in PG (Sheng et al., 2018; Sun et al., 2016a, 2016b). CSWs have been widely used in a variety of applications, including reinforcing materials in plastics, paper mills, rubbers, bone and tissue regeneration grafting materials, filters, paints, and other products (Miao et al., 2015; Qi et al., 2017). To date, little effort has been made to develop a combined process that could achieve both CSW synthesis and REE extraction sequentially (Zhou et al., 2021).

A new trend is developing in which organic acids are used instead of mineral acids. Organic acids are more eco-friendly because they are easily degradable. Citric acid ( $C_6H_8O_7$ ), in particular, has shown promising performance for REE leaching from PG. Gasser et al. (2019) studied the leaching of REEs from PG using different concentrations of weak acids, such as boric acid, malic acid, and citric acid, at different retention times. It was found that the leaching efficiency of the total REEs by a citric acid solution is more favorable than that using boric or malic acid solutions. The authors investigated the efficiency of the process under different conditions; it was observed that the maximum leaching efficiency was provided after three leaching cycles. Analysis of different REEs in the final product indicated that a 1.0 mol/L citric acid solution has high leaching selectivity for Er (89.4 %), Ce (88.2 %), and La (81.8 %) and lower leaching selectivity for Pr (71.9 %) and Y (40.7 %). El-Didamony et al. (2012) explored the use of organic solutions of tri-n-butyl phosphate (TBP), tri-n-octylphosphine oxide (TOPO), and a mixture of TBP + TOPO in kerosene to recover REEs from PG. The leaching of PG with 0.5 M TBP for 2 h at 55 °C resulted in a recovery yield between 66 and 73 % for total REEs. Subsequent steps using the organic solutions of TBP and TOPO with molar concentrations between 0.7 and 0.9 increased the efficiency of REE removal. Despite the

**Table 4**

Leaching of rare earth elements (REEs) from phosphogypsum (PG) using different approaches.

Approach	REE content (wt%)	Leaching agent	S/L	Time (h)	Temperature (°C)	Efficiency (%)	Reference
Direct leaching	0.034	90 % H <sub>2</sub> SO <sub>4</sub> + 10 % H <sub>3</sub> PO <sub>4</sub> 3 M HNO <sub>3</sub>	1/6.7	1	72	49	Al-Thyabat and Zhang (2015)
	0.048	2 M HCl 4 M H <sub>2</sub> SO <sub>4</sub>	1/3	3	25	66	Ismail et al. (2015)
	0.022	10 % HNO <sub>3</sub> 1.5 M HCl	1/1.3	1–2	60	50 51	Hammas-Nasri et al. (2016)
	0.02	1.5 M H <sub>2</sub> SO <sub>4</sub> 1.5 M HNO <sub>3</sub>	1/8	0.33	80	23 57	Walawalkar et al. (2016)
	0.032	1.5 M HCl	1:15	1	85	Nd: 80 Dy: 99 Y: 99	Lambert et al. (2018)
	0.44	10–30 % H <sub>2</sub> SO <sub>4</sub>	1/7.5	2	50	72	Rychkov et al. (2018)
	0.035	3 M HNO <sub>3</sub>	1/30	8	25	85	Cánovas et al. (2019)
	0.17*	2.5 % HNO <sub>3</sub>	1/7.5	0.25	25	59	Laurino et al. (2019)
	0.44	10–15 % H <sub>2</sub> SO <sub>4</sub>	1/3	4	20	50	Grabas et al. (2019)
	1.7	1 g/L H <sub>2</sub> SO <sub>4</sub>	1/8	24	–	45–75	Virolainen et al. (2019)
Organic leaching	0.041	15 % H <sub>2</sub> SO <sub>4</sub>	1/3	2	100	60	Masmoudi-Soussi et al. (2020)
	0.048	Na <sub>2</sub> CO <sub>3</sub>	1/3	3	25	Ce: 76.9 Er: 75 Pr: 65.3	Gasser et al. (2022)
	2.6	H <sub>2</sub> SO <sub>4</sub> 2.9 M H <sub>2</sub> SO <sub>4</sub>	1/6	4.3	275	95	Brückner et al. (2020)
		2.5 M HCl	1/20	0.33	55	90	Salo et al. (2020)
		2.5 M H <sub>2</sub> SO <sub>4</sub>	1/30	0.33	45–85	Nd: 94.6 Dy: 86.1	Li et al. (2022)
		2.5 M HNO <sub>3</sub>					
	0.040	0.7 M TBP - 0.9 M TOPO 0.5 M Na <sub>2</sub> CO <sub>3</sub> + TPB-TOP	1/1	2	55	70	El-Didamony et al. (2012)
		Spent medium. ( <i>Gluconobacter oxydans</i> , 220 mM gluconic acid)				Y: 91.2 Ce: 36.7	
	1.3	<i>Gluconobacter oxydans</i> NRRL, B85	1:50	24	25	Nd: 42.8 Sm: 73.2 Eu: 50 Yb: 83.7	Antonick et al. (2019)
	1	Sulfate-reducing bacteria	–	24	20–22	60	Salo et al. (2020)
	0.6	<i>Acidithiobacillus thiooxidans</i>	–	0.33	30	52.5	Tayar et al. (2022)

promising results, REE leaching using organic acids presents certain drawbacks, such as the loss of organic reagents that enter the gypsum matrix and the high costs associated with the amount of organic solvents consumed. Therefore, further research and development is needed before organic leaching can be implemented at a large scale (Table 4).

Bioleaching is an emerging technology with potential for recovering REEs from PG (Corbett et al., 2017; Hopfe et al., 2018; Zhang et al., 2018). It offers higher metal selectivity at lower concentrations, making it environmentally friendly due to its slow process, low temperature and pressure conditions, and avoidance of aggressive reagents. Heterotrophic microorganisms, known for producing organic acids and metal-binding molecules, are commonly used in REE extraction via bioleaching. Organic acids like citric, oxalic, and malic acids lower the leaching pH, while metal-binding molecules act as chelating agents. (Dev et al., 2020; Fathollahzadeh et al., 2019). Bioleaching of PG for REE recovery is typically accomplished through column or heap leaching processes using either anaerobic or aerobic microorganism species such as *Gluconobacter*, *Acidithiobacillus*, *Acetobacter*, or *Desulfivibrio* (Brandl et al., 2016). Phosphate-solubilizing microorganisms (PSM) have also been identified and used to solubilize REEs from various minerals such as PG (Corbett et al., 2017). According to Brandl et al. (2016), a mixed culture of sulfur-oxidizing bacteria was able to extract 55–70 % of REEs from PG after 30 days of incubation at a pH of 1.5–1.8. The authors attributed the leaching of REEs to sulfuric acid produced by the sulfur-oxidizing bacteria. Antonick et al. (2019) reported the use of gluconic acid-dominated biolixiviant for REE extraction, although it performed less efficiently than conventional H<sub>2</sub>SO<sub>4</sub> acid leaching. More trials on industrial PG were suggested by the authors. Tayar et al. (2022) explored a two-step bioleaching process using *Acidithiobacillus thiooxidans*, resulting in improved REE extraction (98 % Nd, 60 % Ce, 58 % La, and 62 % Y) compared to one-step bioleaching (28 % Nd, 17 % Ce, 18 % La, and 30 % Y) due to PG's acid consumption. However, further

research into the cost-effectiveness and environmental impacts of bioleaching is needed to determine its viability for large-scale REE recovery from industrial PG (Brandl et al., 2016). While bioleaching has lower yield and rates than chemical leaching, its effectiveness is determined by various factors, such as the ability of the microorganisms to oxidize and leach the REEs, the particle size of the REE-bearing mineral, the pH of the leaching media, and the temperature (Costis et al., 2021; Rasoulnia et al., 2021).

Overall, exploring the possibility of a secondary source of REEs could have a major effect on the economies of countries without primary sources. However, the low REE concentration in PG compared to other metals makes direct leaching costly and ineffective. To enhance the feasibility of REE recovery from PG, a comprehensive understanding of hydrometallurgical processing techniques, identification of REE-bearing phases in PG, and the development of selective leaching methods are crucial.

### 5.3. Environmental application

Research explores the eco-friendly use of PG for reducing air pollution and carbon dioxide (CO<sub>2</sub>) sequestration to mitigate greenhouse gas emissions. PG is currently employed for CO<sub>2</sub> capture through mineral carbonation, known for its high reactivity (95 %) and rapid carbonation rate (Wang et al., 2021; Zhang et al., 2020). This process combines CO<sub>2</sub> with naturally occurring minerals dissolved in a liquid solution to form stable carbonates. PG's advantages include its abundance, low cost due to its waste material status, and the stability of resulting carbonates. Additionally, the resulting carbonates are stable and not easily broken down. Mineral carbonation is usually carried out in a basic medium under atmospheric pressure (Lu et al., 2016; Mattila and Zevenhoven, 2015; Sun et al., 2016a, 2016b). Zhao et al. (2015a, 2015b) developed a one-step process using ammonia and carbonation under pressure,

achieving nearly complete carbonation (97 %) in 5 min, producing reusable calcite and ammonium sulfate. This process, which is similar to the method described by Habashi (1985). The calcite and ammonium sulfate produced in this process can be reused as raw materials. Cárdenas et al. (2011) adopted a different approach by dissolving PG using NaOH to produce  $\text{Na}_2\text{SO}_4$  and portlandite ( $\text{Ca}(\text{OH})_2$ ). They noticed that portlandite was remarkably effective at capturing  $\text{CO}_2$  through carbonation, even in harsh environmental conditions, and converting it into calcite. Nevertheless, they also noted that all metal(loids) present in the PG were transferred to the portlandite and then to the calcite. In addition to producing pure  $\text{Na}_2\text{SO}_4$  that could be used by industries such as detergents and paper, the resulting  $\text{CaCO}_3$  could be used for acid mine drainage remediation due to the low amount of metal(loids) transferred from PG to calcite compared to the amounts present in acid mine drainage. Contreras et al. (2015) found that radionuclides, especially  $^{226}\text{Ra}$ , showed strong chemical affinity with Ca during PG carbonation, leading to hazardous materials regulated by the EU. To address this issue, Ding et al. (2019) explored ammonium acetate in PG carbonation, aiming for high-purity calcite and to concentrate impurity in slag. However, these methods often use pure reagents like ammonia and soda, raising costs and energy consumption. An alternative approach involves using industrial by-products like caustic liquid waste from aluminum anodizing plants, which has been studied for its effectiveness in  $\text{CO}_2$  sequestration. (Romero-Hermida et al., 2017). The effectiveness of using this liquid waste reactive agent has been investigated in several studies through bubbling into aqueous media and weathering (Esquivias et al., 2018). Despite the potential benefits of utilizing PG for  $\text{CO}_2$  sequestration, there are still a few obstacles that must be addressed. The sequestration process is not very efficient, and it is uncertain if it can be scaled to the levels necessary to make a major difference in atmospheric  $\text{CO}_2$  concentrations. Additionally, there are worries that the impurities found in PG, such as heavy metals and radionuclides, could leach into the environment should it be used for  $\text{CO}_2$  sequestration.

Heavy metals pollution of the surrounding water has been a major concern of industrial activity. There are available technologies to successfully decrease metal concentrations in industrial effluents; however, these technologies are usually expensive, especially for developing countries. This encourages research into low-cost technologies based on cheap materials or wastes (Fu and Wang, 2011; Sud et al., 2008). To overcome this problem, PG has been used as a low-cost adsorbent for the removal of heavy metals from industrial wastewaters. This process involves ion exchange, where metal ions in wastewater replace calcium ions on PG's surface. Balkaya and Cesur (2008) conducted an experiment in which they mixed a batch of PG with 0.4 % lime milk to neutralize water-insoluble impurities. They tested the adsorption of Cd on this pre-conditioned PG by adding a dosage of 10 g/L of sorbent. They found that this process had a high Cd removal rate of around 99 %, but it was highly pH dependent. The removal was primarily due to adsorption at pH values around 9, but it could be slightly improved by the precipitation of cadmium hydroxide at pH values above 9. A similar approach was followed by Cesur and Balkaya (2007) to study the adsorption of Zn (II) using pre-conditioned PG. The experiment resulted in a high adsorption capacity controlled by pH conditions. Mousa et al. (2016) used PG as a raw material to prepare hydroxyapatite nanoparticles via thermal activation (600 °C). This mineral has been known for its ability to retain metals and anions in water treatment (Sundaram et al., 2008; Zhu et al., 2008). These latter authors found that lead adsorption by hydroxyapatite nanoparticles was very rapid, and equilibrium was attained within 5 min; this encourages adoption of this material as an economical source of sorbent for lead ions from wastewater. To enhance the retention capacity of PG, many authors tried to prepare mineral assemblages using PG and other materials. Kadirova et al. (2014) and Lopes et al. (2013) tested the joint application of PG, kaolin, and red mud for As adsorption. The authors reported a significant increase in the adsorption of As using PG that could be used as a low-cost inorganic sorbent material. In summary, in the cited studies, the reuse of PG for

adsorption was shown to be particularly effective in removing heavy metals such as lead, zinc, and copper from aqueous solution. Meanwhile, further studies should be performed to enhance the adsorption ability of PG and to overcome its dependence on some physicochemical parameters, such as the pH of the solution.

#### 5.4. Chemical transformation

In recent decades, the chemical transformation of PG has become a promising valorization route to obtain raw materials of economic interest. The Merseburg ammoniacarbonation process has been used to convert PG into ammonium sulfate, an excellent fertilizer, and calcium carbonate, which is a useful product for acidic water neutralization (Cánovas et al., 2018a, 2018b). This process is currently being used commercially in China, India, and Indonesia. Almost all radionuclides in the PG migrate to the calcium carbonate, leaving the ammonium sulfate fertilizer product radioactively lower than most natural materials (IAEA, 2013a, 2013b). Despite this, the process has seen only limited application in practice due to abundant supplies of ammonium sulfate from other industries. Idboufraise et al. (2022) adopted this approach to convert Moroccan PG to  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{CaCO}_3$ . The study aimed to establish a relation between the molar ratio  $\text{OH}^-/\text{Ca}^{2+}$  and its effect on the efficiency of the conversion process. The pure compounds  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{CaCO}_3$  were obtained for a molar ratio  $n(\text{NH}_4\text{OH}/\text{PG}) = 4$  (i.e., 0.6 M of  $\text{NH}_4\text{OH}$ ) under fixed conditions:  $t = 3.5$  h,  $T = 25$  °C,  $S = 500$  rpm, and  $V_{\text{CO}_2} = 20$  mL/min. Using this method, the Moroccan PG studied in this research could be classified as an efficient source of calcium and sulfate. Kolokolnikov and Shatov (2008) conducted a chemical transformation of PG into calcium carbonate and sodium sulfate using washing soda ( $\text{Na}_2\text{CO}_3$ ). They examined the reaction at temperatures ranging from 40 to 90 °C and  $\text{Na}_2\text{CO}_3$  concentrations of 240 to 260 g/L. They found that the transformation rate increased with temperature, and that 80 to 90 °C and 20 to 30 min resulted in a 96 to 98 % conversion. A similar paper by Ennaciri and Bettach (2021) compared the transformation of PG and pure gypsum into valuable products. The authors concluded that the PG conversion showed attractive results regarding the required time for conversion, the lack of costly or specific conditions, and the resulting high purity products ( $\text{CaCO}_3$  and  $\text{Na}_2\text{SO}_4$ ) that could be used in environmental and construction applications. Another option is the conversion of PG to calcium sulfate and potassium sulfate: two products that are of great importance in agricultural and industrial fields. For this purpose, Lachehab et al. (2020) performed the transformation of PG in the presence of KOH and  $\text{CO}_2$ . A simultaneously developed process for the sequestration of  $\text{CO}_2$ , which results in the production of  $\text{CaCO}_3$  and  $\text{K}_2\text{SO}_4$  was studied. The authors mentioned the high efficiency of the approach and suggested that it presents a safe and permanent solution for the storage of PG and carbon dioxide. Based on a phase diagram study, Laaboubi et al. (2022) developed a new crystallization pathway for the conversion of PG to solid  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  by using the quaternary reciprocal system  $\text{Na}^+/\text{K}^+/\text{Cl}^-/\text{SO}_4^{2-}-\text{H}_2\text{O}$ . In this process,  $\text{Na}_2\text{SO}_4$  is first produced from the conversion of PG waste. Then, the recovered  $\text{Na}_2\text{SO}_4$  reacts with potassium chloride (KCl) to produce glaserite ( $\text{NaK}_3(\text{SO}_4)_2$ ). Finally, the intermediate chemical glaserite is dissolved in a KCl solution and transformed into  $\text{K}_2\text{SO}_4$  solid. A benefit of this approach is that the phase diagram provides a guide for optimal conditions of salt crystallizations, and high purity product characterized by minimal transformation of radionuclides originally found in PG.

Transforming PG into marketable products is a promising way to recycle this waste. However, there are challenges to address. Secondary raw materials like calcite, ammonium sulfate, or sodium sulfate often compete with cheaper products. To overcome this, extracting economically valuable materials from these by-products is essential. Additionally, the transfer of elements like REEs and pollutants during the transformation of Ca minerals must be studied. Some techniques involve energy and chemicals, potentially limiting their cost-effectiveness in industrial applications.

### 5.5. Thermal transformation

The decomposition of PG into its primary components, CaO and S, is a process that has been explored to both make use of the materials and address environmental issues (Yan et al., 2014; Yang et al., 2013; Zhao et al., 2017). Therefore, PG decomposition has been explored under a variety of experimental settings, including reducing gases (CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>) and reacting with various forms of carbon such as coke, coal, and charcoal (Strydom and Potgieter, 1999; Taher, 2007). However, it appears that our understanding of the reductive decomposition of PG to SO<sub>2</sub> is limited. Most studies have used thermogravimetric analysis, which provided insufficient data to explore the decomposition behavior of PG to SO<sub>2</sub>. As a result, the reaction conditions and reducing agents remained inadequate, leading to challenges in controlling the process effectively (Zheng et al., 2011). Various studies have been conducted to explore the process performance (He et al., 2022; Ma et al., 2010; Yang et al., 2012), but the decomposition of PG is limited by its high temperature, necessitating optimization of the reaction parameters. Among these studies, Yang et al. (2013) examined the use of sulfur as an alternative for coke during PG decomposition. Using thermodynamic simulation and experimental data, the authors found that the final decomposition temperature of PG was 993 K through the first step of the process, which was consistent with the experimental results. However, the actual decomposition temperature was 250 K lower than the thermodynamic simulation of calcium sulfate. This discrepancy was attributed to the impurities in the PG. The enthalpy for the sulfur reduction process was 27.95 % lower than that for the coke reduction process at 1473 K per mole of SO<sub>2</sub>, making the novel approach more attractive for industrial use due to its reduced energy consumption. To further optimize the temperature, Zheng et al. (2018) conducted the decomposition process in the presence of an Fe catalyst. The authors observed a series of competitive gas–solid/solid–solid reactions in the presence of an Fe catalyst during the decomposition process. At temperatures lower than 1000 °C, the main substances present were CaS and CaSO<sub>4</sub> (anhydrite). Intense competition between CaO and CaS occurred between 1050 and 1100 °C. By introducing a series of Fe oxides, the decomposition temperature of PG was significantly lowered to below 700 °C, thereby forming a catalytic reaction system. Recently, Sun et al. (2022) found that Fe-P slag, which is a solid waste mainly composed of iron phosphide (FeP) and di-iron phosphide (Fe<sub>2</sub>P), can dramatically decrease the decomposition temperature of PG to 800 °C, and the CaSO<sub>4</sub> conversion could reach approximately 97 %.

PG decomposition was also applied for extracting potassium from K-feldspar. As soluble potassium resources are limited and there is a widespread lack of potassium in soils worldwide, especially in Africa (Zhong et al., 2017), K-feldspar (KAlSi<sub>3</sub>O<sub>8</sub>) is a much larger and more secure source of potash ore with reserves of >1.0 10<sup>10</sup> t. Thus, the production of potash fertilizer from K-feldspar is critical to reduce the consumption of soluble potassium resources (Huang et al., 2011). In this perspective, Lu et al. (2021) studied the decomposition of K-feldspar in the presence of PG using coke as a reducing agent. HSC Chemistry software was used to determine the equilibrium compositions of the PG–K-feldspar–coke system. The authors obtained a high PG decomposition rate of 99.40 % at 1150 °C for 25 min, when the mass ratio of coke to PG and K-feldspar to PG was 0.07 and 0.43, respectively. A coupling process comprising the activation of K-feldspar with PG at high temperatures was investigated as a method of extracting K<sub>2</sub>SO<sub>4</sub> and mineralizing CO<sub>2</sub> (Gan et al., 2016; Wang et al., 2014). Under specific activating conditions (T = 1200 °C), the K-extraction and CO<sub>2</sub>-mineralization yields exceeded 87 % and 7.7 %, respectively. The potassium extraction process follows an ion exchange interaction of Ca<sup>2+</sup> from CaSO<sub>4</sub> with K<sup>+</sup> from K-feldspar, and CO<sub>2</sub> reacts with CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> (Zhong et al., 2017). K<sup>+</sup> ions react with Ca<sup>2+</sup> ions to generate K<sub>2</sub>SO<sub>4</sub>, and the remaining molecular skeleton forms the electrical neutral phase CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>. Ca<sup>2+</sup> is released after the CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> is dissolved by H<sup>+</sup>, which originates from the ionization of H<sub>2</sub>CO<sub>3</sub>. Finally, the Ca<sup>2+</sup> reacts with the

HCO<sub>3</sub><sup>-</sup> to form CaCO<sub>3</sub>. Despite the improvements in potassium extraction, there are still challenges in terms of reducing energy consumption, decreasing greenhouse gas emissions, and increasing SO<sub>2</sub> concentration levels in the flue gas. Therefore, further research should focus on developing an efficient and cost-effective process to produce potassium fertilizer with a low energy requirement.

### 5.6. Application in construction and building materials

Over the past years, various methods of recycling PG in construction and building materials have been investigated. It has been used as a replacement for natural gypsum in the production of plaster, wallboard, and cement (Layr, 2020). In addition, its importance has been noted due to the gap in natural and flue gas desulfurization (FGD) gypsum supply reported by the EU Renewable Energy Directive (Haneklaus et al., 2022). Various authors have looked into the advantages and limitations of using PG in construction materials (Amrani et al., 2020; Calderón-Morales et al., 2021; Men et al., 2022; Rashad, 2017; Tayibi et al., 2009; Qin et al., 2023). There are several potential benefits for using PG in construction materials. It is often more readily available and less expensive than natural gypsum, and it can help to reduce the environmental impact of the construction industry by reducing the demand for mined gypsum. However, there are also some potential drawbacks to employing PG in construction materials. The presence of soluble phosphorus, fluorine, and organic matter in PG has adverse effects on PG reuse. Therefore, pre-treatment is required before reusing PG. For this reason, many methods to obtain PG that is safe and suited for secondary usage have been studied (i.e., washing, wet sieving, alkaline neutralization, and addition of extractant solutions). Liu et al. (2019) found that washing PG with ionized water is an effective way to eliminate certain water-soluble substances from the surface of the crystals and improve the functional features and mechanical properties of cemented paste backfill (CPB). However, P<sub>2</sub>O<sub>5</sub> and other components can only be eliminated through thermal treatment at 130–150 °C; the process is expensive and may not be practical. Al-Hwaiji (2015) and Valkov et al. (2014) proposed an alternative solution, which consists of treating PG with sulfuric acid and heating at 70–100 °C for 1–2 h at a specific ratio of sulfuric acid to solids. This method produces PG that is free of hazardous impurities and can be used in road construction and the production of cement and various building materials. Recently Calderón-Morales et al. (2021) and Liu et al. (2020) found that fluoride and phosphate could be effectively removed from PG with Ca(OH)<sub>2</sub> treatment. Qin et al. (2023) also proposed the use of Ca(OH)<sub>2</sub> or Al<sub>2</sub>(SO<sub>4</sub>) to neutralize the acidity of PG and effectively immobilize the soluble P<sub>2</sub>O<sub>5</sub> and heavy metals, allowing PG to serve as a substitute for calcium sulfoaluminate (CSA) cement. Another major factor limiting the application of PG in construction materials is the presence of radionuclides. The use of PG-manufactured building materials, which can release radioactivity into the environment, is a concern because people spend a large portion of their day indoors (Kovler, 2009). This type of chronic exposure to low levels of ionizing radiation has the potential to cause health problems that may not appear until 5–30 years after exposure (Sievert and Failla, 1991). The International Atomic Energy Agency (IAEA, 2013a, 2013b) revealed in a study that, in certain cases, the use of PG in house construction for structural panels might expose an occupant to an annual effective dose of >1 mSv. However, for other uses of PG in home construction, such as in cement, bricks, plasterboard, and tiles, the annual effective dose received by the occupant is unlikely to exceed 1 mSv. Therefore, restrictions on such uses are not necessary. Kovler (2009) reported that PG building materials can cause two types of radiation exposure: external and internal. External exposure comes from direct gamma radiation, while internal exposure is largely caused by inhaling radon (222-Rn) and its short-lived decay products (Ju et al., 2012). It is important to monitor radon gas in the environment because radon is an inert gas that can easily move through porous materials such as building materials; this is critical for radiological protection. In general, these

**Table 5**

Potential applications of phosphogypsum (PG) with advantages, limitations, and associated solutions. (REEs = rare earth elements).

PG valorization	Advantages	Limitations	Solutions
Agriculture	Soil structure and crop yield improvement. Reclaim sodic soil by Ca amendment. Reduce Na saturation in soils. Control surface sealing and reduce runoff and soil erosion. Control N losses. Increase soil phosphorus content.	Presence and lixiviation of radionuclides ( $^{238}\text{U}$ , $^{226}\text{Ra}$ , $^{210}\text{Pb}$ , $^{210}\text{Po}$ , $^{232}\text{Th}$ , and $^{228}\text{Ra}$ ) in soils. Contamination of soils by metals (As, Cd, Cr, Ni, Se, Hg, and Pb) present in PG. The migration of pollutants from PG-amended soils to agricultural products to consumers.	Research should be conducted to determine a method for removing radionuclides and heavy metals from PG. Monitoring the effect of long-term use of PG on the consumers.
Extraction of REEs	Promising secondary source of REEs. High leaching rate using strong acids. Possibility of bioleaching.	Low concentration of REEs in PG. Complexity of the determination of the mineral phase locked REE in PG. A second source of environmental pollution through the use of mineral acids.	
Environmental application	Carbonation of $\text{CO}_2$ using PG to produce stable $\text{CaCO}_3$ . Low-cost material to absorb heavy metals from wastewater.	Only low levels of $\text{CO}_2$ do not make major difference in atmospheric $\text{CO}_2$ concentrations. pH dependence of the process of absorption of heavy metals.	
Thermal decomposition	Production of $\text{SO}_3$ largely used in the production of $\text{H}_2\text{SO}_4$ . Decrease the temperature of decomposition of K-feldspar and increase the release of K in solution.	The process requires high temperature. Expensive process	
Industrial sector	Preparation of ammonium sulfate used as fertilizer. Production of calcium carbonate. Production of potassium sulfate.	Require the use of expensive reagents. The process could be cost-effective on an industrial level.	More attention should be paid to the transfer of pollutants from PG to product.
Building and construction	Additive to building materials to produce cementitious materials for construction. Important mechanical properties.	The presence of radioactive elements that could present a threat to the surrounding environment.	Safety analysis. Site-by-site analysis.

findings cannot be extended to each PG deposit since radionuclide content varies widely among sites.

Another issue with recycling PG is that many applications only use small amounts, which is not enough to absorb the large amounts of PG produced by the fertilizer industry. To make PG recycling more viable, we need technologies that are both inexpensive and capable of using large amounts of PG. One potential possibility could be using PG in road construction, which can consume up to 25,000 tons per lane kilometer. Many authors studied the possibility of recycling PG as road base fillers. The use of PG in the transportation sector was primarily concerned with roadbed filler and altering asphalt for road engineering projects. Combining PG and foamed asphalt yielded a product with the same mechanical properties as natural foamed asphalt (Cuadri et al., 2021). To the same end, Zmemla et al. (2022) conducted a study where a mixture of 46.5 % sand, 46.5 % PG, and 7 % cement was prepared and its mechanical strength was discussed. The prepared mixture was subjected to conventional compressive and tensile strength tests, as well as Young's modulus test. The results showed that the early and final compressive strengths of the stabilized material were higher than those of conventional road subgrade materials, reaching 2200 and 3500 kPa at 28 and 360 days, respectively. To overcome pavement diseases, Li et al. (2019) added 10 % gypsum to road base course binder (RBCB). They observed reduced dry shrinkage and an 82 % decrease in reflective cracks in semi-rigid subgrade pavements, extending road service life. The application of PG in highway engineering is still in its early stages, with most research focusing on the impact of PG on road bases or pavement materials. Before applying PG in this field, a safety analysis must be conducted. Despite this, research into the effects of PG on road bases and pavement materials has been the main focus so far. Advantages, limitations, and solutions for each valorization pathway are presented in Table 5.

## 6. Research needs

Further comprehensive research is needed to enhance our understanding of PG and establish a suitable management strategy. A greater focus should be placed on investigating how elements associated with PG are retained and released. Moreover, investigations should be

conducted to determine the availability of heavy metals and their binding minerals to evaluate the environmental impact of PG. It is also crucial to find optimal methods for restoration of PG, reducing its acidity, and minimizing the leaching of toxic pollutants, thereby mitigating its effects on soil, air, and water (Millán-Becerro et al., 2022). Addressing this concern requires further efforts, whether through conventional treatment methods or the development of new disposal approaches. In the short term, there is a projected increase in PG generation due to the growing global fertilizer demand, necessitating the exploration of technical advancements in PG processing. This area of research would encompass novel technologies, such as chemical, thermal, and mechanical methods, for processing PG. Also, achieving universal adoption will demand a fundamental change in mindset and, in certain instances, modifications to regulations that stem from an improved comprehension of the diverse, proven, and safe alternatives at hand. Embracing this shift will manifest in unique ways across different regions.

## 7. Conclusion

The phosphate fertilizer industry is growing to meet global agricultural needs, but it also generates a significant amount of PG. This review paper investigates PG's mineralogical and chemical properties, including trace element content. Research reveals that PG characteristics vary depending on factors such as the type of phosphate rock, production processes, and storage duration. However, the forms of retention and incorporation are still based on hypotheses, necessitating detailed investigations to determine their impact on the environment. PG is either stored on land surfaces or disposed of in the sea. Worldwide studies indicate that large-scale land-based PG storage may pose risks like water contamination, dust emissions, and radioactive pollution. Historically, some PG has been discharged into the ocean, leading to environmental threats to marine ecosystems and coastal water quality. To address these issues, the International Fertilizer Association (IFA) proposes two approaches for 100 % legacy waste elimination from PG: utilization and prevention. Research into PG utilization encounters challenges including social, political, technical, and economic barriers that hinder its adoption. Precise cost comparisons with alternative

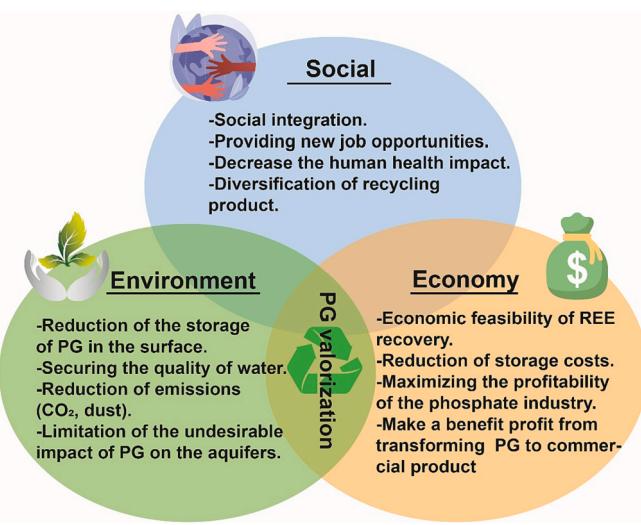


Fig. 9. Integrated sustainable development to recycle phosphogypsum (PG).

solutions are essential to find cost-effective and feasible reuse strategies (Fig. 9). Additionally, it's crucial to assess potential secondary pollution from PG reuse while considering often-overlooked social factors.

#### CRediT authorship contribution statement

**Fatima Akfas:** Conceptualization, Formal analysis, Writing – original draft, Writing – review & editing. **Abdellatif Elghali:** Conceptualization, Writing – review & editing, Supervision. **Abdelmaula Aboulaich:** Conceptualization, Writing – review & editing. **Manuel Munoz:** Conceptualization, Writing – review & editing. **Mostafa Benzaazoua:** Conceptualization, Writing – review & editing. **Jean-Louis Bodinier:** Conceptualization, Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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