

## Using cemented paste backfill to tackle the phosphogypsum stockpile in China: A down-to-earth technology with new vitalities in pollutant retention and CO<sub>2</sub> abatement

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# Using cemented paste backfill to tackle the phosphogypsum stockpile in China: A down-to-earth technology with new vitalities in pollutant retention and CO<sub>2</sub> abatement

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**Abstract:** Phosphogypsum (PG), a hard-to-dissipate by-product of the phosphorus fertilizer production industry, places strain on the biogeochemical cycles and ecosystem functions of storage sites. This pervasive problem is already widespread worldwide and requires careful stewardship. In this study, we review the presence of potentially toxic elements (PTEs) in PG and describe their associations with soil properties, anthropogenic activities, and surrounding organisms. Then, we review different *ex-/in-situ* solutions for promoting the sustainable management of PG, with an emphasis on *in-situ* cemented paste backfill, which offers a cost-effective and highly scalable opportunity to advance the value-added recovery of PG. However, concerns related to the PTEs' retention capacity and long-term effectiveness limit the implementation of this strategy. Furthermore, given that the large-scale demand for ordinary Portland cement from this conventional option has resulted in significant CO<sub>2</sub> emissions, the technology has recently undergone additional scrutiny to meet the climate mitigation ambition of the Paris Agreement and China's Carbon Neutrality Economy. Therefore, we discuss the ways by which we can integrate innovative strategies, including supplementary cementitious materials, alternative binder solutions, CO<sub>2</sub> mineralization, CO<sub>2</sub> curing, and optimization of the supply chain for the profitability and sustainability of PG remediation. However, to maximize the co-benefits in environmental, social, and economic, future research must bridge the gap between the feasibility of expanding these advanced pathways and the multidisciplinary needs.

**Keywords:** cemented paste backfill; phosphogypsum; carbon dioxide mitigation; potentially toxic elements; solidification and stabilization

## 1. Introduction

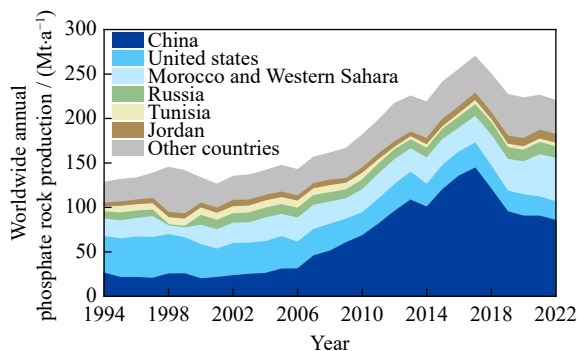
Since the wide-scale application of phosphorus fertilizer for modern agriculture began in the last century, phosphate ores have been excavated for fertilizer production [1–2]. The annual excavation of phosphate rock approximately doubled from 128 to 250 Mt/a in a 25-year range (1994 to 2020, Fig. 1 [3–6]). When raw phosphate ores (fluorapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F)) decompose with concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) at a temperature of approximately 80°C, phosphoric acid and phosphogypsum (PG) are produced [7]. Based on the current roadmap for phosphorus fertilizer production, around 1.5–2.0 t of PG would be generated for each ton of phosphate rock being processed [8]. This means that the annual generation of PG could reach over 300 or even 400 Mt. Considering the increasing global population and growing demand for fertilizer, the PG stockpile is predicted to follow fertilizer production rates in the coming decades [9–12]. In addition, because sulfuric acid is the primary agent used in the wet process of fertilizer production, the resulting PG contains free acidic sub-

stances, such as H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, and HF, thus creating a strong and corrosive solid waste with a pH range of 2–5.

PG disposal currently uses four typical methods: ocean dumping, storage in the mine where the phosphate rock originated, and wet or dry storage in tailings storage facilities (ponds or dams), with the latter two being the most commonly used (Fig. 1). China, United States, and Morocco have the highest number of PG stacks, even though storage sites can also be found in many other countries around the world [5]. Notably, China is not only the world's largest consumer of phosphate fertilizer but also the largest producer of PG by-products (Fig. 2) [4,13]. According to estimates, over 70 Mt of PG is produced in China annually (Fig. 2(a)), but only 30 Mt have been recycled as soil amendment [14–15], cement retarder [16], construction material [17–19], backfill aggregates [20–21], and others (e.g., raw materials for rare earth elements (REE) recovery and CO<sub>2</sub> mineralization) [22–23] (Fig. 2(b)). However, at least in China, a significant gap in terms of reaching the zero-emission goal must be addressed regardless of advancements made in optimizing sustainable PG management [24]. In particular, many past works have

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**Fig. 1.** Worldwide excavation of phosphate ores from 1994 to 2022. Cumulative phosphate ores are obtained from the United States Geological Survey (USGS) database [3–6].

reported that the efficiency of PG recycling is adversely affected by the impurities fraction [2,25]. For instance, when reusing PG as a backfill material, studies reported a decline in workability and mechanical performance with the increase in PG content, which can be attributed to the presence of fluorides and phosphate compounds in the material [5,26]. Meanwhile, investigations on the agricultural use of PG to improve soil structure and crop yield have yielded mixed results concerning the safety of PG application (the leachability of potentially toxic elements (PTEs)) to soils, thus limiting the field applications of this strategy [12,27].

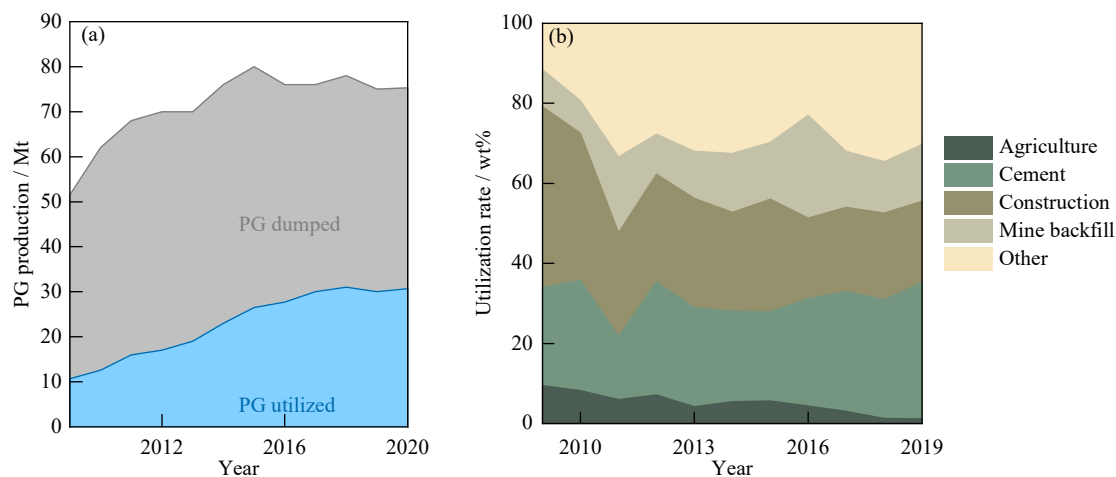
Thus, in recent years, such a hard-to-abate solid waste emission and the inadequacy of planned mitigation approaches have been greeted with growing public consternation, causing a serious disposal issue and disproportionate management expenses [4,6,9,28]. Moreover, recent studies have suggested that the growing need for more PG storage may lead to soil degradation that extends beyond the local land surface and eco-societies—eventually affecting marine and freshwater systems, as well as people and ecosystems far away from the storage locations [1,24,29–30]. For instance, due to the rainwater interaction with exposed PG deposits, fluorine from fluoride minerals (e.g., fluorapatite, fluorite ( $\text{CaF}_2$ ), and malladrite ( $\text{Na}_2\text{SiF}_6$ )) in PG can be channeled back into the soil and aquifer sediments [30]. Although a low

fluoride concentration can help prevent dental caries, a high fluoride intake ( $>1.5$  mg/L) is known to cause dental fluorosis and crippling skeletal fluorosis [31]. Such fluorine redistribution in PG stockpile sites leads to fluoride accumulation in freshwater and drinking water resources. In turn, this can cause excessive retention of fluorides in the body, which has been proven to be a global health concern, potentially affecting 180 million people worldwide [28]. Water eutrophication due to the enrichment of phosphorus is another problematic marker that has placed PG storage under harsh scrutiny [12,21,32]. Studies have proven that the highly soluble phosphate fraction in PG may be directly released into aquatic bodies, causing eutrophication and killing aquatic life [33–34]. Therefore, based on the abovementioned information, the scientific management of PG is required to mitigate the associated environmental risks in the face of increasing global production.

We critically elucidate the currently applicable pathways of PG management in this review with a particular emphasis on PG-based cemented paste backfill. This conventional *in-situ* immobilization technique has earned recognition as one of the most effective applications, demonstrating significant full-scale potential and technical benefits. We begin by exporting the status of PG storage in the context of its main physical properties, chemical compositions, mineralogical components, and PTEs bioaccessibility. Next, we discuss the forefront *in/ex-situ* PG remediation pathways, including REE recovery, construction materials, agriculture uses, and the utilization of PG in cemented paste backfill. Finally, we illustrate the potential carbon footprint for the current *in-situ* remediation strategy, investigating what can be implemented and promoted to achieve decarbonization and profitable directions in the future.

## 2. Physicochemical properties of PG and the occurrence of fluorides and phosphates

Here, we analyze aspects relating to the physicochemical properties of PG with different phosphate ores sources and



**Fig. 2.** (a) Annual production and amount of utilized PG in China from 2010 to 2020 [4]. (b) Primary approaches applied in PG recycling and their utilization rates in China from 2009 to 2019, including reuse in agriculture, cement retarder, construction materials, backfill aggregates, and others [13].

different fertilizer production processes, including particle size distribution, permeability, moisture content, chemical compositions, and mineralogical constitutions. Further, we summarized the occurrence of fluorides and phosphates, which are the primary PTEs within PG. These basic investigations and characterizations of PG provide theoretical support and a fundamental basis for its subsequent resource utilization research.

## 2.1. Physical properties of PG

According to the classification standard of the United States Department of Agriculture (USDA), PG can be considered finely granulated powder, silt, or silty-sand material, with its particle size distribution mainly within the range of 10–900  $\mu\text{m}$  [9]. Fig. 3 illustrates differences in maximum PG particle size across storage sites, ranging from 500 to 900  $\mu\text{m}$ , wherein the majority (50%–75%) of particles from all sources are smaller than 75  $\mu\text{m}$ .

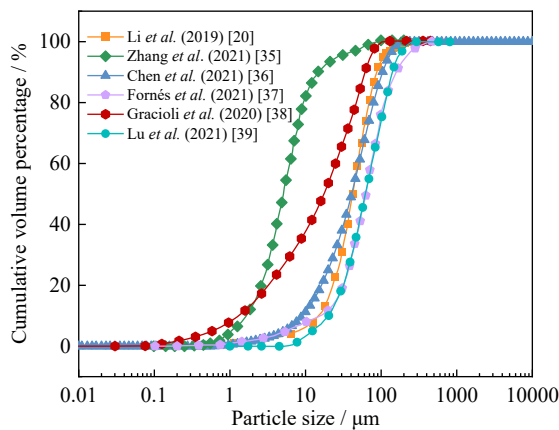


Fig. 3. Typical percentage curves of cumulative PG volume [20,35–39].

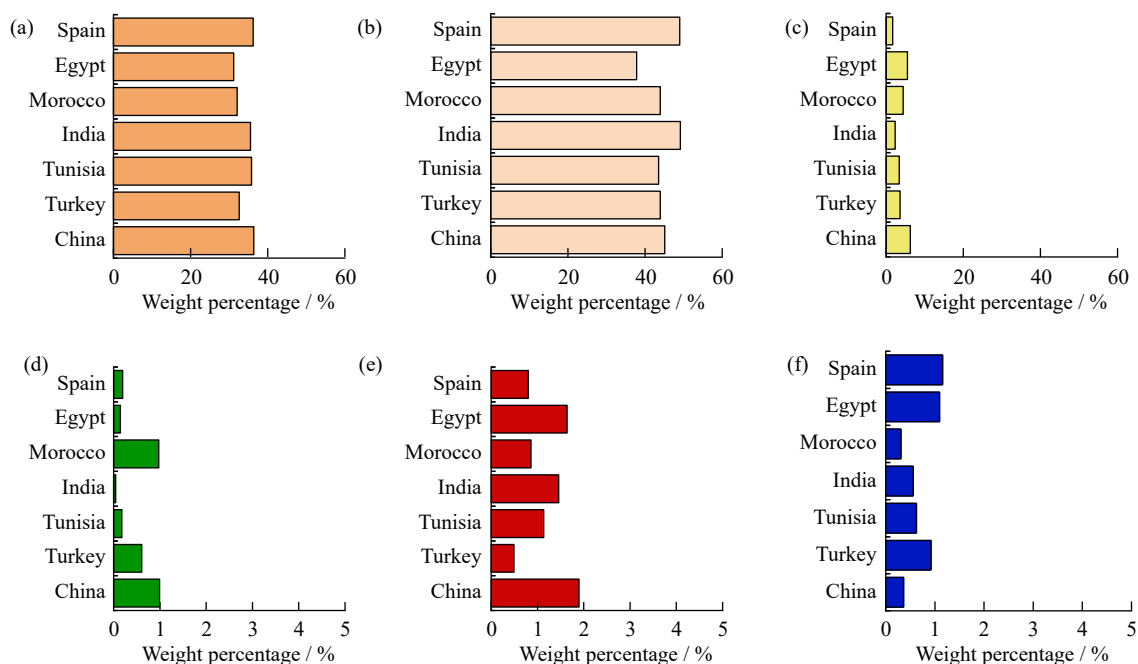
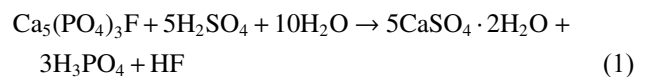


Fig. 4. Chemical compositions of PG from China [19,21,35,47–56], Turkey [57–61], Tunisia [8,46,62–64], India [65–67], Morocco [68–72], Egypt [73–74], and Spain [74–81]: mean weight percentage of (a) CaO, (b) SO<sub>3</sub>, (c) SiO<sub>2</sub>, (d) Al<sub>2</sub>O<sub>3</sub>, (e) P<sub>2</sub>O<sub>5</sub>, and (f) F.

The moisture content of PG ranges from 8wt% to 30wt% and is influenced by the duration of draining after stacking and local weather conditions [9,26,40]. In addition, studies indicate that PG's permeability is influenced by particle size distribution, plasticity, sedimentary layer depth, and weathering process during stacking. Therefore, the permeability coefficient of PG shows great fluctuation, covering nearly three orders of magnitude (approximately from  $2.7 \times 10^{-7}$  to  $2.9 \times 10^{-4}$  cm/s) but remains categorized as low permeability tailings [25,41–42].

## 2.2. Source and fate of fluorides and phosphates: From phosphorite ores to PG

PG properties are dependent upon several factors, including the nature of the phosphate ore used, the type of wet process employed, the disposal method, the plant operation efficiency, and the location of the stack area [43–44]. Typically, during phosphate fertilizer production using a wet process, H<sub>2</sub>SO<sub>4</sub> is the primary agent used for acidulation [26], of which the acidified phosphorite ores (mainly fluorapatite, (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F)) convert to gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), hydrofluoric acid (HF), and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) (Eq. (1)) [45]. Then, the phosphoric acid is filtered and reserved for fertilizer production, with the residues (mostly PG) remaining. However, residual acids tend to remain in PG due to the limitations of the industrial separation procedures, resulting in a strongly acidic pH value (<3) [26] that may gradually increase to a neutral pH value (approximately 6) during the weathering process [46].



The chemical compositions of PGs produced in different countries from 45 cases are tabulated in Fig. 4 [8,19,



21,35,46–81]. Although minor variations can be observed, PG mainly consists of calcium (Fig. 4(a)) and sulfate (Fig. 4(b)), verifying the presence of calcium sulfate species (gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), bassanite ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ), anhydrite ( $\text{CaSO}_4$ )), and sulfuric acid [30]. The detected silicates (Fig. 4(c)) and aluminates (Fig. 4(d)) are assigned to quartz ( $\text{SiO}_2$ ) and aluminum phyllosilicates, which are the typical gangue minerals found in phosphorite ores [82]. Common PG also presents trace amounts of  $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{K}_2\text{O}$ , especially in those exhibited gangue minerals in different types of phosphate ores used [26]. The fraction of phosphates and fluorides, primary PTEs, range from 0.49wt% to 1.90wt% (Fig. 4(e)) and from 0.31wt% to 1.16wt% (Fig. 4(f)), respectively.

Other studies have indicated that the fluoride content is related to the nature of phosphate rock, while the variation of phosphates depends on the specific type of wet process [37]. For instance, a high percentage of phosphates may get lost in the coarse fraction and remain in PG residues when the crushing and screening settings in the beneficiation facilities are inappropriate for recovering the phosphate product in the fine fraction due to the differential friability of the excavated phosphate ores [83–84]. Regarding the fluoride content difference, many studies have reported that hydroxy (hydroxyapatite  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) and chlorine (chlorapatite  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ ) can take the place of fluorides because of the ability of anions to substitute for fluoride ions in fluorapatite [85–86]. However, the exact extent to which substitution may take place is controlled by many factors, such as prevailing conditions during apatite formation and the subsequent weathering process [83,87].

Despite the fact that chemical analysis provides gross information on the bulk PG samples, detailed characterizations are still required to advance our understanding of fluorides and phosphate changes from phosphate ores to PG residues, which are important preconditions for the subsequent remediation. Many advanced techniques have been used to bridge this knowledge gap, including X-ray diffraction for examining the mineralogical evidence [43,88], scanning electron microscope with energy dispersive X-ray spectroscopy (SEM–EDS) [20,47,62] and electron probe micro-analyze with wavelength dispersive spectrometry (EPMA–WDS) [21] for identifying PG morphology and elemental distribution, solid-state nuclear magnetic resonance for determining possible F and P speciations [48–89], Fourier-transform infrared spectroscopy (FTIR) for revealing the functional groups' vibrations [21,49], and X-ray photoelectron spectroscopy for determining the potential binding mechanisms of F and P in PG [90–91].

The concentration of PTEs is not the only factor to consider when assessing PG toxicity. In fact, the speciation of PTEs also plays a role in determining their potential hazard. As shown in Fig. 5, PG samples have a well-defined crystalline structure, with the typical morphology of rhombic and orthorhombic-shaped crystals and with small solid particles that are adsorbed on the surface [8,21,92]. Furthermore, the

elemental mapping characterization illustrates that P is mainly scattered on the surface of gypsum crystals (Fig. 5(b), (e), and (h)) [8,21,92], possibly assigned to water-soluble and/or insoluble compounds precipitation ( $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  and  $\text{Ca}_3(\text{PO}_4)_2$ ) and  $\text{SO}_4^{2-}/\text{HPO}_4^{2-}$  substitution in the gypsum crystal lattice [21,29]. In addition, the presence of phosphate could also be attributed to the surface complexation of  $\text{HPO}_4^{2-}$  on silicates (e.g., feldspars and muscovite) at acidic conditions, as the formation of Al–Si–F–P–O complex (Fig. 5(d) and (e)) verifies the co-existence of phosphate and aluminosilicates due to the weathering process [21]. The detected fluorides may be classified as acids (i.e., hydrofluoric acid (HF) and forms of hexafluorosilicic acid ( $\text{H}_2\text{SiF}_6$ )), sodium fluoride (NaF), calcium fluoride ( $\text{CaF}_2$ ), and fluorosilicate complexes (e.g.,  $\text{Na}_2\text{SiF}_6$  and  $\text{CaSiF}_6$ ) [26,93–94]. Fig. 5(c) and (f) reveal that similar to P speciation, F is evenly distributed on the surface of gypsum particles, with a clear interface observed. Moreover, the elements of Si and F (Fig. 5(c)) also demonstrate a coexisting preference [92]. This is because the silica reacts with the generated HF and forms  $\text{H}_2\text{SiF}_6$  during the wet process, during which the acid may convert to a variety of mineralogical speciations.

### 2.3. Spatial distributions of fluorides and phosphates: Geogenic and anthropogenic factors

Aside from the sources of PTEs (variable concentrations of fluorides and phosphates in PG from different regions), geogenic and anthropogenic activities can accelerate the accumulation and transportation of fluorides and phosphates from PG to stockpile sites, resulting in contaminants spread over large spatial regions [24,95]. Therefore, especially considering the vast amounts of PG that have been produced and dumped, there is a need to build and fortify long-term isolation (e.g., geopolymers and clay barriers) in the stockpile sites, which is an important preparatory to prevent the formation of new acidic and polluted leachates before the *in/ex-situ* remediation. A case study of the PG stockpile site in Spain [30] suggests that geogenic weathering is the dominant factor affecting trace pollutants' spatial distribution. The long-term dynamic wet–dry cycles driven by evaporation, rainfall, and recharge induced a high concentration of PTEs in the PG-brine deposits system, with the sampled brines and residues reflecting seasonal changes in the local weather conditions (Fig. 6). Therefore, appropriate actions to abate these compounds should be implemented in the current roadmap of PG storage, especially given the substantially high concentrations of pollutants present in mobile forms [30]. Similarly, a field investigation in Hongfeng Reservoir, one of the largest artificial water bodies along the Yangtze River (China), indicates that the P concentration increase is partially caused by a PG storage pond located only 800 m from the Yangchang River [96]. The profile distribution of P fractions suggests that, due to the absence of an efficient wastewater treatment facility and reliable leachate barrier, high P concentration PG leachates are discharged directly into the Yangchang River through surface runoff and eventually make their way into

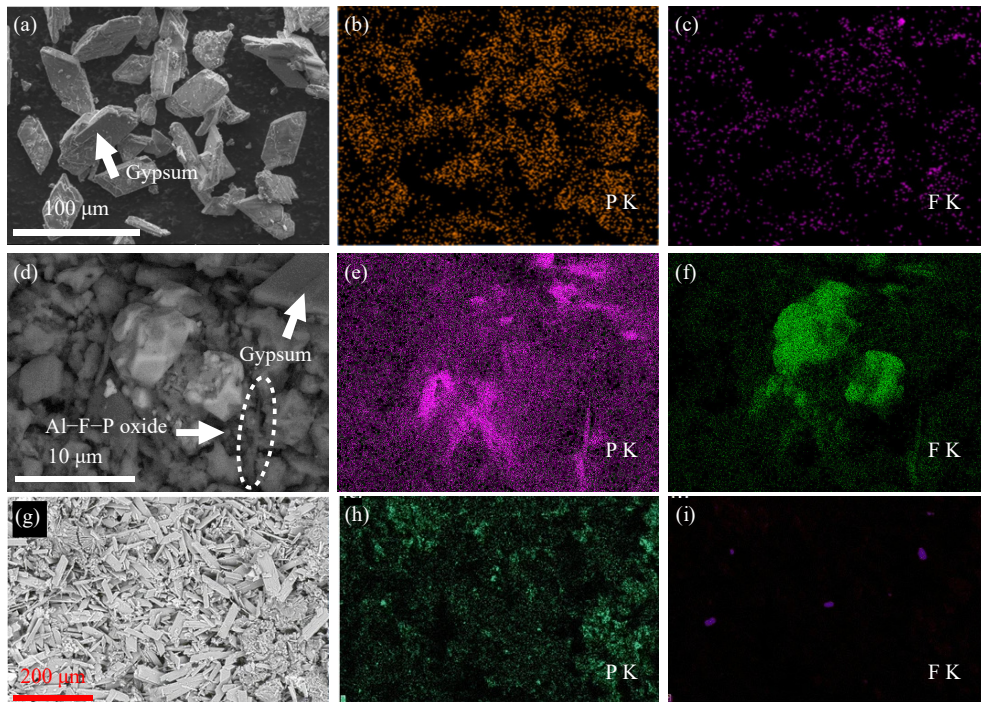


Fig. 5. SEM images of different PG samples: (a) morphology of PG samples from literature [92] and distributions of (b) P and (c) F correlated to image (a); (d) morphologies of PG samples from literature [21] and distributions of (e) P and (f) F correlated to image (d); (g) morphologies of PG samples from literature [8] and distributions of (h) P and (i) F correlated to image (g). (a–c) Reprinted from *Constr. Build. Mater.*, 311, X.B. Li and Q. Zhang, Dehydration behaviour and impurity change of phosphogypsum during calcination, art. No. 125328, Copyright 2021, with permission from Elsevier. (d–f) Reprinted from *Environ. Res.*, 214, Y.K. Liu, Q.S. Chen, M.C. Dalconi, *et al.*, Retention of phosphorus and fluorine in phosphogypsum for cemented paste backfill: Experimental and numerical simulation studies, art. No. 113775, Copyright 2022, with permission from Elsevier. (g–i) Reprinted by permission from Springer Nature: *Environ. Sci. Pollut. Res.*, Characterization of phosphate rock and phosphogypsum from Gabes phosphate fertilizer factories (SE Tunisia): High mining potential and implications for environmental protection, R. El Zrelli, L. Rabaoui, N. Daghbouj, *et al.*, Copyright 2018.

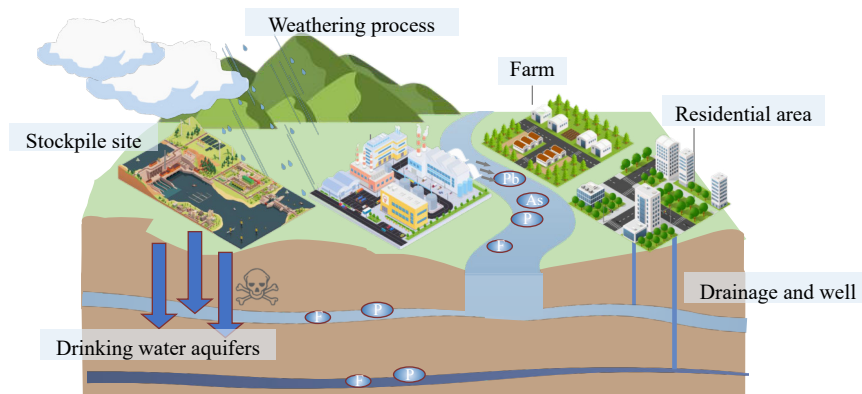


Fig. 6. Redistribution of PTEs in dumped PG is due to the dynamic interactions of groundwater and the weathering process.

the reservoir [96].

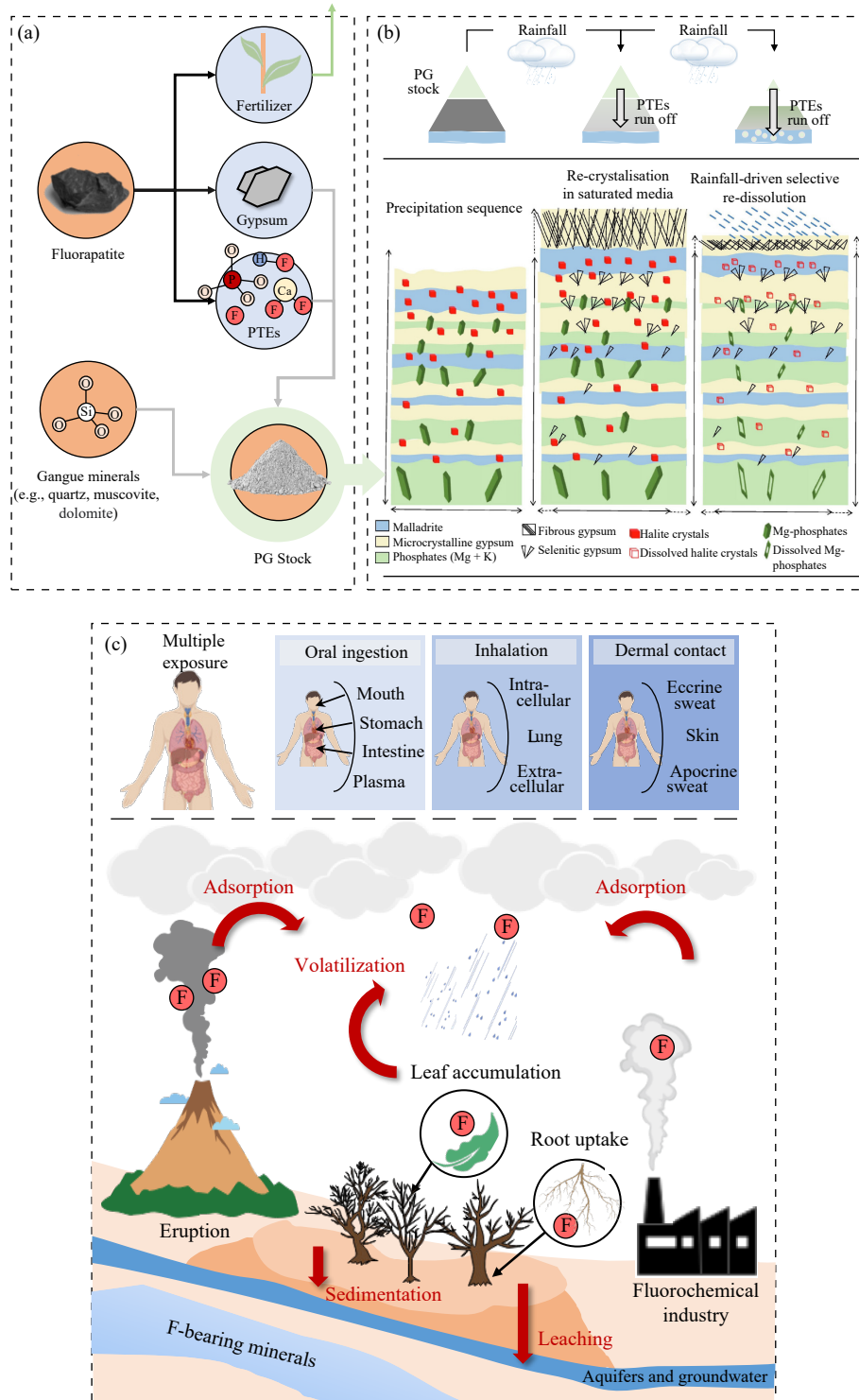
Apart from geogenic factors, anthropogenic activities are also the main drivers of PTEs emissions. For instance, during the phosphorus fertilizer manufacturing process, the material can release a large amount of gaseous and particulate PTEs in surrounding areas apart from the massive generation of PG solid waste [29,97]. Furthermore, the surface soil in a phosphate chemical factory has a high F content, whereas it is much lower in deep soil, suggesting that F in the atmospheric deposition is probably a vital contributor to the industrial area [29]. In addition, occasional accidents in chemical plants can

lead to increased PTEs concentration in the soil, with a previous report demonstrating that the accidental spillage of hydrofluoric acid might pollute the surrounding area within a 1000 m radius of the spillage site [98]. Notably, improper engineering procedures and practices can cause potential secondary pollution even though the remediation application is expected to advance the sustainable management of PG. Usually, a stabilized PG stack is at a relatively steady state and may not cause any dust problems; however, dust pollution is typically observed during the excavation and shipping procedures as well as during the maintenance of access roads [65].

**2.4. Bioavailability of fluorides and phosphates: Toxicity to flora and fauna**

Increased PTEs concentration in the ground body of stockpile sites partly due to the weathering process has been widely reported [27,91,99]. Although the mineralogical spe-

ciation and spatial distribution investigations of fluorides and phosphates provide a basis for the interactions of the PTEs and stockpile sites, their toxicity is contingent on bioavailability because these toxic impurities are bio-accumulative in both the environment and the food chain (Fig. 7(a) and (b))



**Fig. 7.** Spatial distributions of PTEs in PG due to the weathering process and anthropogenic activities and the potential exposure risks: (a) fluoride and phosphate transformation from phosphate ores to PG stock; (b) mechanisms controlling the evolution of the brine-evaporation deposits system [30]; (c) major natural and anthropogenic fluxes in the biogeochemical cycle of fluorides and *in-vitro* bioaccessibility of fluorides posed by multiple exposure routes. (b) Reprinted from *Sci. Total Environ.*, 700, R.N. Lieberman, M. Izquierdo, P. Córdoba, et al., The geochemical evolution of brines from phosphogypsum deposits in Huelva (SW Spain) and its environmental implications, art. No. 134444, Copyright 2020, with permission from Elsevier.



[24,30]. Fluoride is not considered essential for plants; in fact, it has a negative impact on vegetation, either limiting its growth or prohibiting the action of anti-oxidative enzyme systems [100–101]. Typically, root fluoride accumulation in areas receiving fluoride contaminations is the primary factor for the excessive intakes of fluoride in plants [100]. Consequently, the fluoride taken up by the root might be readily transported and retained in the leaves through the xylem as  $F^-$ ,  $F-Al$  complexes, or less prevalent  $F-Ca$  complexes (Fig. 7(c)) [102]. However, small amounts of fluoride can directly enter leaves (cuticle or stomata) by adsorbing atmospherically emitted fluoride, which is the form of gaseous HF or silicon tetrafluoride ( $SiF_4$ ) [102]. As a result, plants with excessive fluoride uptake may transfer to the higher trophic levels of the food chain, leading to severe risks to mammals. Apart from ingesting contaminated crops, the inhalation of fluoride-bearing dust and fluoride-polluted groundwater may also put vulnerable people at great risk. Field studies have reported that the amounts of atmospheric fluoride concentration in PG storage sites are typically double the permissible airborne threshold due to the prevailing winds in these regions [103]. Geological hazards (e.g., volcanic eruptions) can also contribute to soil fluoride contamination and enhance the fluoride exposure risks of creatures through the uptake of fluoride-containing volcanic ash deposits [104]. Regarding the phosphates cycle, several reports indicate that the dumping of PG adversely affects the authigenic phosphorus content in stockpile sites [9,105]. Notably, although phosphate can reach the soil body easily, its availability is low due to its fixation with iron, aluminum, and calcium, which may precipitate as insoluble forms [1]. In other words, phosphate cannot be taken up by plants but may be exported from the soil to water bodies through a variety of pathways even though the total phosphate content of the soil may be close to the saturation of its storage capacity due to this anthropogenic phosphate input; this is one of the primary causes of eutrophication [106].

### 3. Value-added use of PG dumps

Concurrently, the sustainable management and comprehensive utilization of PG is becoming a critical problem due to stricter legislative requirements, which should be inclined toward the direction of large dosage, high added value, and industrial exploitation prospects [107–108]. The growing issue of soil pollution caused by PG deposits also represents one of the biggest challenges for reaching the “zero-emission” goal [32,109]. Considerable research has been conducted on reusing PG materials (*ex-situ* and *in-situ*), such as raw materials for REE recovery, soil amendments, retarders in cement manufacturing, and solidification/stabilization purposes. However, field and industrial applications have not achieved commercial-level outputs, which are restricted by numerous factors, such as cost, technology barriers, production capacity, and potential secondary pollution [9,25]. Especially given that PG contains a large number of impurities

with complex components, a considerable risk of leaching after generating resource products is presented. We discuss below four different recycling approaches by identifying the associated mechanisms and applicabilities, as well as by clarifying the challenges and outlook of implementing the strategy on a large scale.

#### 3.1. *Ex-situ* pathways: REE recovery, construction materials, and agriculture applications

With the growing interest regarding sustainable resource development and environmental processing of indispensable elements, extracting REE from PG has become a promising strategy to reduce the consumption of natural resources and promote the high value-added valorization of solid waste. Although PG has a relatively low REE content (ranging only from 0.05wt% to 2.00wt% [22,110] or an average of 0.45wt% according to the wet-process procedures and sources of phosphorite ores applied in fertilizer production), it can be considered a valuable anthropogenic source [22,26,111]. The common extraction technology includes three steps: (1) water/solvent-washing pretreatment procedures to collect the solid components; (2) valuable REE dissolution and enrichment by agent digestion; (3) separation and purification of REEs from the collected liquid solutions [110].

Many works have been conducted to optimize and improve the extraction efficiency of valuable metals, such as by controlling reaction temperatures [22], various acid concentrations and types [112], multiple physicochemical pretreatments [113], and ion exchange resin [22]. In this sense, as evidenced by many studies [21,111], the extraction process is technically feasible, implying that both the economy and sustainability of the resource recovery could be competitive (Fig. 8) [114]. However, processing PG for REE extraction has not yet been industrially realized. To date, existing technical methodologies cannot be used for low-cost extraction due to the high cost of field trials and low content of rare metals compared with common ore minerals (e.g., bastnäsite and monazite), which have average contents ranging from 2wt% to 20wt% [22]. As a result, the PG extraction process is highly challenging and can cause industrial application failure. In addition, the tiny and complex occurrence phases co-existing with REE in PG could limit the efficiency of further selective extraction schemes. If the impurities have not been removed, their presence can inhibit the emulsification of extraction systems and decrease product purity [22,112].

Another interesting possibility of PG utilization is recycling PG as a construction material (e.g., retarders for cement manufacture and alternative gypsum sources for building cementitious materials, Fig. 9 [115]). The introduction of PG in the construction materials matrix showed certain advantages, while some properties deteriorated [9,26,116]. Recently, studies have indicated that the incorporation of PG can effectively enhance the mechanical properties of construction materials, including fly ash, ground-granulated blast-furnace slag, geopolymers, or Portland cement-based pastes [26,117]. The results are also encouraging for reducing the specimen's



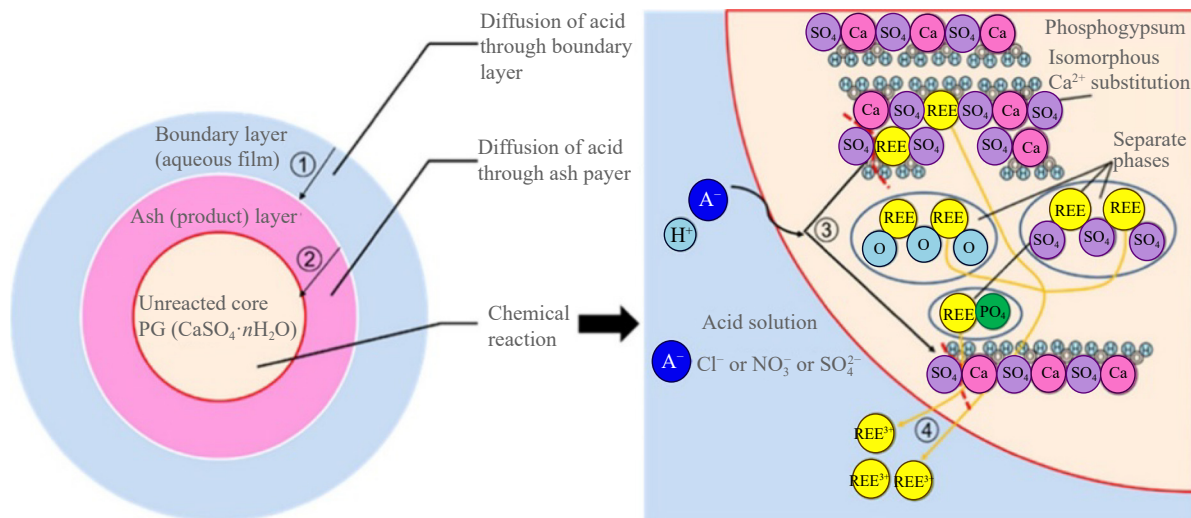


Fig. 8. Schematic diagram of the REE extraction process from recycled PG samples, including Step 1—diffusion of leachate through the aqueous film, Step 2—diffusion of leachate through the product layer, Step 3—PG lattice bonding break, and Step 4—recovering the released REE. Reprinted with permission from S.C. Li, M. Malik, and G. Azimi, *Ind. Eng. Chem. Res.*, vol. 61, 102-114 (2022) [114]. Copyright 2022 American Chemical Society.

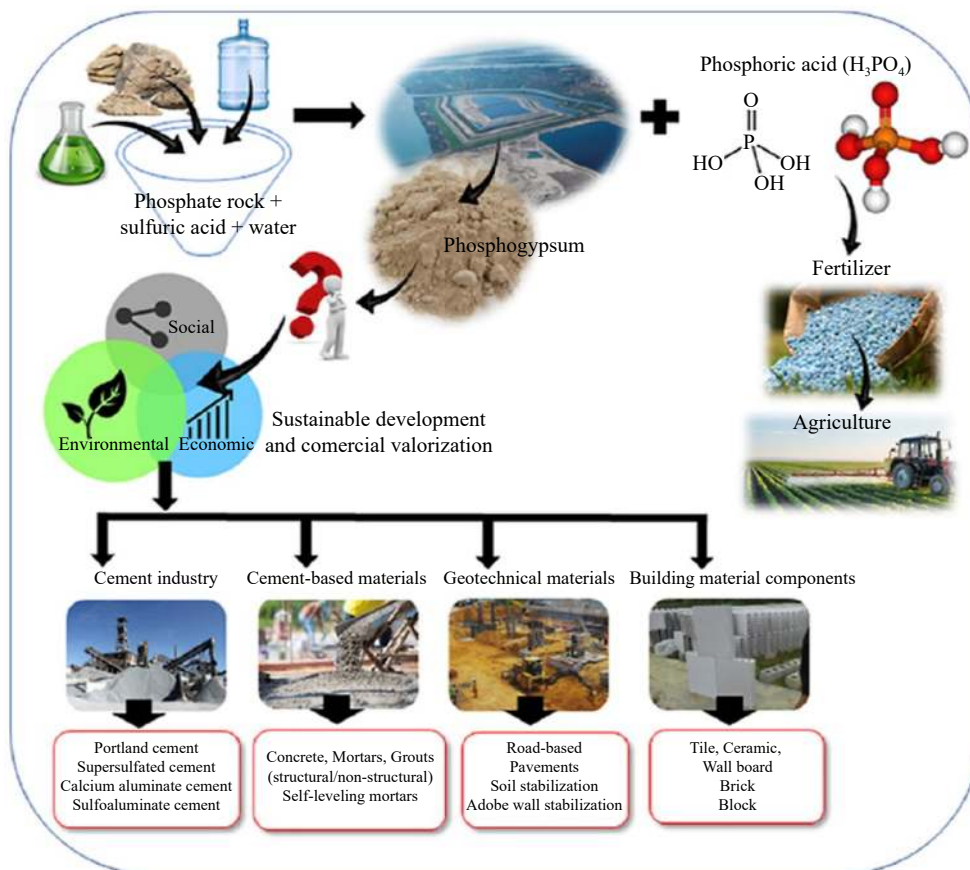


Fig. 9. Potential valorization of PG in eco-efficient construction [115]. Reprinted from *J. Build. Eng.*, 44, B.R.S. Calderón-Morales, A. García-Martínez, P. Pineda, and R. García-Tenório, Valorization of phosphogypsum in cement-based materials: Limits and potential in eco-efficient construction, art. No. 102506, Copyright 2020, with permission from Elsevier.

density [56], increasing fire resistance [26], and optimizing resistance to water erosion [118]. However, these benefits can only be observed at relatively low PG replacement contents (approximately 2.5wt% to 10wt%) [26]. Studies have reported that the fire resistance and compressive strength decreased accordingly with higher amounts of PG fraction

[26,117]. In addition, the shortages of PG incorporation in the construction materials matrix included decreasing workability [119], which can lead to a high possibility of drying shrinkage deformation [59], linear expansion, and mechanical deterioration of the samples at later periods [26], and increased thermal conductivity [120].

Furthermore, safety concerns about the leaching of PTEs impurities from PG-incorporated materials have been cited as the main defects that limit the commercial use of PG [121–122]. Several trials have been conducted to remove or at least reduce the PTEs content from raw PG to guarantee its safe use in the construction field, including NaOH washing [48], calcination [117], and bio-washing [91]. However, the exact influence of pretreatment on the physicochemical properties of the PG-incorporated matrix and information about the costs of using different pretreatment methods still require further investigations to obtain general conclusions. Therefore, reusing PG in construction materials has a potentially positive effect on increasing the consumption of PG and mitigating the soil pollution caused by PG storage. Prior to stepping into field trials, the safety analysis of its long-term impacts on surrounding environments and the profitability of applying pretreatment should be clarified in advance.

As indicated in the previous section, the primary components of PG are calcium, sulfate, potassium, and phosphate, many of which are essential for plant growth and crop nutrition [25]. Therefore, scholars have attempted to use large-tonnage PG to increase crop fertility [9,123–124]. PG has also been used as an amendment to eliminate the salinity of degraded soil (e.g., saline, sodic, acidic, and alkaline soils) (Fig. 10) [27,125–126]. Compared with industrial gypsum-amended soil, PG demonstrates favorable hydraulic conductivity, desalinization efficiency, and phosphate conservation capacity by reducing electrical conductivity and exchangeable sodium percentage of the soil body [125,127]. However, the direct application of PG in agricultural soil faces severe restrictions and problems due to its strong acidity and abund-

ant PTEs contents. Therefore, essential pretreatments and/or additional supplements (e.g., biochar [124], lime [128], and lignin sludge [123]) are required for PG utilization in agriculture to avoid the transfer of these elements to the food chain. In addition, although phosphate is the mandatory nutrient for crop yield, the eutrophication of natural water and soil bodies due to the excess phosphorus loads can stimulate the rapid growth of aquatic organisms and waste resources [110,124]. Therefore, the successful commercialization of recycling PG is far from an apparent breakthrough. For this reason, scientists should focus on the direct use of PG, with particular emphasis on quality assurance, safety, variability in PG composition, soil type, and cultivated crops.

### 3.2. *In-situ* solidification/stabilization pathways: PG-based cemented paste backfill

First developed in the late 1950s for sludge management, cemented paste backfill (CPB) technology is currently considered one of the ideal technologies for the remediation of solid waste due to its convenience and effectiveness [129–130]. This technology can reduce the potential migration of PTEs by changing the physical and chemical properties of the wastes [131–132]. In the context of phosphorite ore mining, the preparation of PG-based CPB mainly relies on the use of PG for the alternative aggregates of CPB, thus resulting in a mixture consisting of binder (usually ordinary Portland cement, OPC), PG, and water [20,43,133]. Subsequently, these homogenized mixtures are transported into mine goaf to mitigate the massive stockpiling of PG and support the underground structures of the phosphorite excavated area [20,134] (Fig. 11). Unlike the PG application in con-

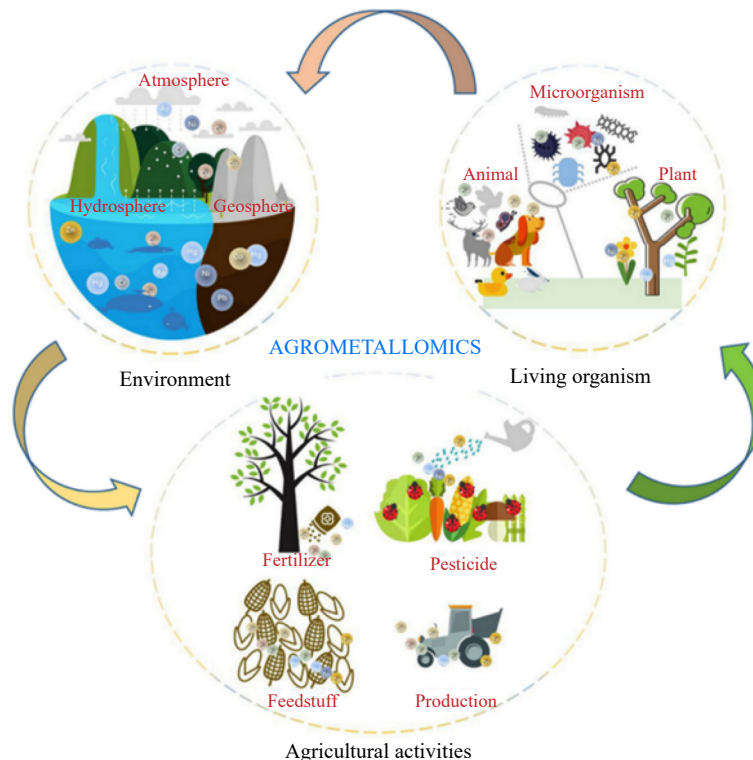


Fig. 10. Application of PG in agricultural remediation [126]. Reprinted by permission from Springer Nature: *Int. J. Environ. Sci. Technol.*, Application of phosphogypsum in soilization: a review, J. Qi, H. Zhu, P. Zhou, et al., Copyright 2023.

struction materials, which requires high-quality mechanical property thresholds to ensure the structural safety of the urban architectures, the acceptable mechanical performance of PG-based CPB mixtures is much lower (approximately only 2 MPa at 28 d) [26,43,47]. Another difficulty of commercial valorization comes from the redistribution of impurities (Fig. 6). In particular, due to the complexity of underground structures (e.g., long-term exposure to percolating water/groundwater and the interference from the processed mining operation), hazardous substances—despite already being immobilized by binders—may leach out and contaminate groundwater systems as well as fauna and flora [88, 135–136]. Therefore, the current projects mainly focus on modifying and purifying PG in advance and identifying PTEs retention mechanisms after solidification/stabilization (Fig. 12), ensuring that this strategy can be used as an ecological restoration pathway [20–21,48,91,137]. Therefore, the effect of PG on the mechanical properties of the CPB matrix, the immobilization mechanisms of PTEs, and the proposed optimization strategies are reviewed and discussed in this section.

### 3.2.1. Influence of PG on the mechanical properties of CPB mixtures

The unconfined compressive strength of CPB mixtures is considered one of the critical parameters that directly affect safety performance. Beyond strength parameters, the setting time and workability of PG-based CPB mixtures, influenced by factors such as particle interactions and mix proportions, are considered integral aspects of practical utility. However, preliminary studies have suggested that the inclusion of PG may impart negative alterations to the hydration processes, thereby influencing compressive strength and other mechanical properties.

To date, OPC remains the most conventional binder used in PG remediation. In the general formulation of PG-based CPB mixtures for optimal performance, minimum proportions (approximately 20wt% of binders) are required to strike a delicate balance between meeting structural safety and sustainability requirements while maximizing the efficient utilization of resources [20,43,138]. Nevertheless, opting for a lower binder content can yield a more permeable mixture,

enhancing workability and potentially increasing profitability. However, there exists a trade-off, as this might compromise the mechanical properties of the hardened mixture and increase the risks of PTEs leaching. Therefore, the selection of the appropriate OPC content within this range should be based on the specific engineering requirements of the project, in which factors such as permeability, compressive strength, and overall sustainability are equally considered.

Moreover, the physicochemical properties of PG, including density, particle size distribution, and impurities, exert varying degrees of influence on the strength of CPB mixtures. Notably, when the particle size distribution of PG adheres to Fuller's ideal curve, the strength development of hardened mixtures surpasses that of batches deviating from this curve [47,139]. Likewise, to optimize the particle size distribution of aggregates, Shi *et al.* [51] incorporated modified quartz sand, an inactive reactant in cementitious systems, in the mixing process of CPB mixture preparation. The results indicate that this approach optimizes the aggregate gradation, thereby promoting hydration reactions and enhancing strength development (approximately 20.5% higher than that of control groups). Furthermore, the inherent impurities of PG can affect the hydration reactions and hardening processes of the CPB mixtures. For instance, strength development was found to be correlated with phosphate types, with adverse effects exhibiting the following hierarchy:  $H_3PO_4 > KH_2PO_4 > Ca_3(PO_4)_2$  and  $K_3PO_4$ , where  $H_3PO_4$  demonstrated the most significant adverse impact on strength [32]. The insights gained from geochemical modeling and experimental characterization suggest that the deterioration is predominantly linked to the phosphate species formation. In particular, the dissolved phosphates precipitate and form calcium-phosphate complexes after initial hydration, thereby coating cement particles in a protective manner [140]. Similar to the influence of phosphate on the development of mechanical properties, fluorides could also act as triggers for degrading pore structure formation and hydration product precipitation. When fluoride contents in PG increase from 0.003wt% to 3.100wt%, the CPB's strength at the curing age of 90 d drops from 2.19 to 1.36 MPa at a rate of >38% [138].

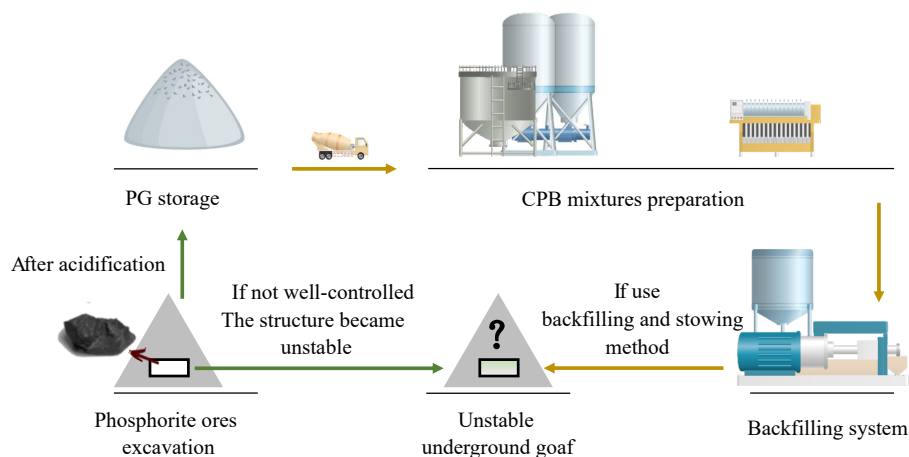
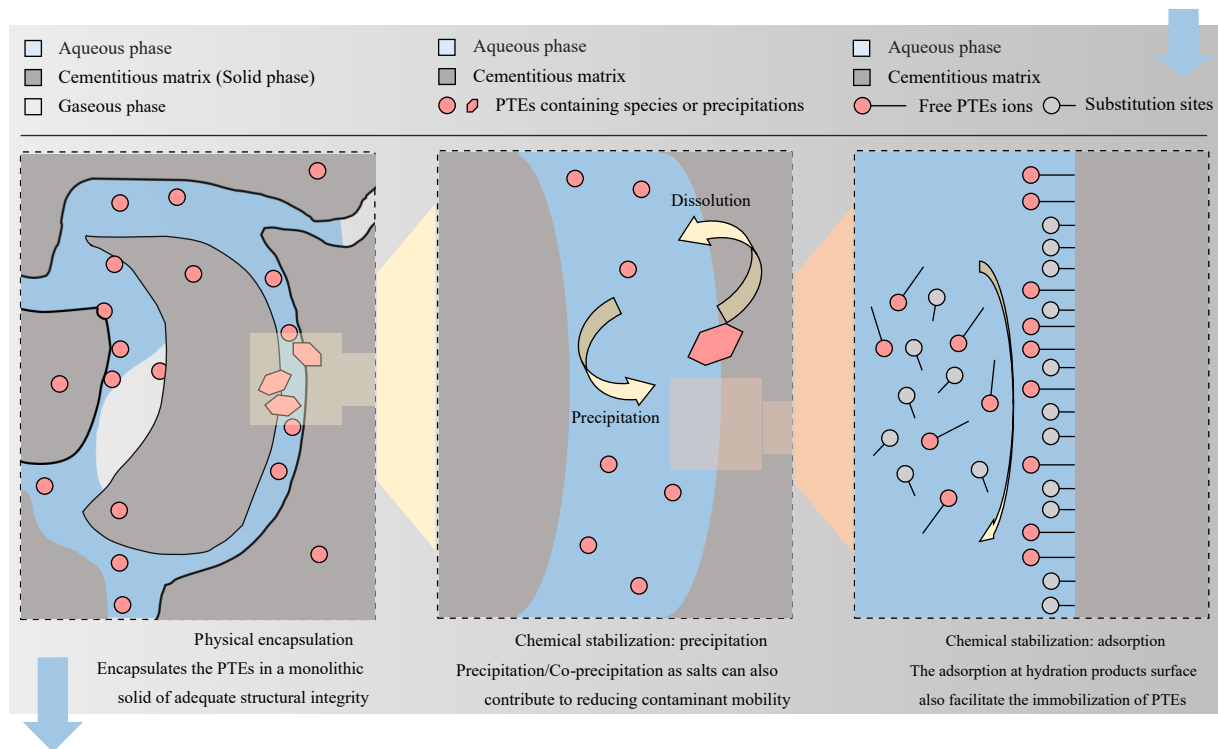


Fig. 11. Flow-process diagram of CPB mixture preparation and backfilling process.



**Fig. 12. Immobilization mechanisms of PTEs in stabilized PG, including encapsulation, precipitation, and adsorption.**

### 3.2.2. Immobilization mechanisms of PTEs into CPB mixtures

With the versatile solidification/stabilization (typically using OPC) of PG, past studies suggest that phosphorus is immobilized in CPB mixtures in the forms of calcium-phosphate species (e.g., hydroxyapatite and tricalcium phosphate) [21,32,141] or captured and encapsulated by hydration products (e.g., calcium silicate hydrates (CSH) and ettringite) [51,142]. Furthermore, fluoride tended to precipitate as sparingly soluble fluorite ( $\text{CaF}_2$ ), aluminum fluoride complexes ( $\text{AlF}_3$ ), and fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) [21,88,143–144]. Similar to phosphate retention, the main hydration products (portlandite, CSH, and ettringite) of clinker phases also play a role in fluoride immobilization [21,32,48]. Although the PG-based mixtures prepared by OPC have acceptable PTEs retention under laboratory conditions (e.g., using ultrapure water as the extraction leachate), their ability under harsh conditions is under significant scrutiny, because they are vulnerable to many factors, such as water erosion, permeability, atmospheric carbonization, physical degradation, micro/macro structures, and chemical and mineralogical compositions [20,145].

Apart from the experimental characterization, geochemical modeling is equally important and urgently required as a useful tool to estimate the release of pollutants from the stabilized mixtures [21,146–149]. The results from the simulations suggested that different roles of the captured phosphates and fluorides had varying pH values [1,21,36]. When the pH is below 5,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{CaH}_2\text{PO}_4^-$  are the main solubility-controlling phases, whereas, around the neutral and alkaline pH conditions, sparingly soluble calcium phosphates species (e.g., hydroxyapatite and calcium fluoro-

phosphate) become the main phases. In comparison, the main controls of fluoride at acidic conditions are mainly assigned to Al–F complexes ( $\text{AlF}_3$ ,  $\text{AlF}_2^+$ , and  $\text{AlF}^{2+}$ ) when the pH values increase to neutral and alkaline conditions, after which calcium fluoride, calcium fluorophosphate, and CSH matrix take the roles of fluoride capture [21,88]. Geochemical modeling adequately explains the PTEs retention mechanisms and sheds new insights into the existing experimentally observed capabilities. However, there is still a need to improve the thermodynamic database curation and analytical tools, as well as to extrapolate the obtained results to a larger scale (local and regional) while considering the impacts of soil hydrology [24]

### 3.2.3. Optimization strategies: PG pretreatment

Apart from investigations on clarifying and quantifying the PTEs immobilization roles, finding an eco-friendly pathway to optimize *in-situ* solidification/stabilization has also garnered considerable interest. Different studies have delved into purification pretreatments for PG, such as solution washing pretreatment (e.g., water washings [47,137,150], bio-washing [91], hot aqueous ammonium sulfate solutions [151], and base washings [48,152]). In addition, thermal treatments [44,73] and physical screening [153] were also conducted. These investigations revealed that after purification, PG yielded a similar performance as natural gypsum. Therefore, this purification step has become a pivotal practice in CPB technology, because it ensures that PG is pretreated harmlessly to remove or passivate PTEs and organic substances. In this way, the properties are optimized, and the potential applications of CPB technology in various mining engineering endeavors are broadened.

As a relatively practicable and effective method of impur-



ity removal, solution-based washing finds widespread use in industrial applications. During the water/base-washing procedures of PG pretreatment, most soluble impurities can be removed by water rinsing, filtration leaching, and mechanical dehydration, thus optimizing the hydration kinetics and improving the mechanical properties of CPB mixtures [47–48]. However, previous studies have underscored the constraints of the water-washing method in removing considerable lattice-bounded impurities, particularly co-crystallized  $P_2O_5$  within the gypsum lattice. Moreover, this approach produces substantial volumes of wastewater that require secondary treatment, thus increasing energy consumption. In efforts to refine this procedure, screening was integrated into washing protocols, with scholars using wet sieving (300 mesh sieve) before water-washing and flotation. This preliminary screening effectively separates impurities in PG, particularly phosphorus, chloride, and organic matter, thus providing a favorable foundation for the subsequent purification of PG [153]. In the context of base-washing procedures, the soluble phosphates and fluorides can be transformed into insoluble or partially soluble substances by adding alkaline substances (e.g., CaO,  $NH_3 \cdot H_2O$ , and NaOH) and changing the pH of the PG system [26,48]. This transformative process effectively mitigates the adverse impacts associated with soluble phosphates and fluoride, thus contributing to the overall improvement of the PG-CPB system.

The efficacy of calcination as a pretreatment method has been mainly attributed to eutectic phosphorus mitigation. In particular, calcination demonstrates distinct advantages in the precise and targeted removal of eutectic phosphorus compared with other conventional PG pretreatment methods. In the process of calcination, soluble phosphate was transformed into water-insoluble and harmless pyrophosphate ( $CaP_2O_7$ ), facilitating the simultaneous expulsion of organic matter through evaporation. The efficiency of eutectic phosphorus removal was also intricately related to the calcination temperature, as evidenced by the work of Smadi *et al.* [154], where PG was subjected to varying temperatures (170, 600, 750, 850, and 950°C). Their results suggested a significant increase in the compressive strength of the thermally pretreated PG-CPB mixtures, with the highest strength observed at 850 and 950°C. This optimization is related to the enhanced hydraulic properties of thermally pretreated PG, which activates the activity of cementitious binder [73].

While calcination in PG pretreatment has proven effective in eliminating specific impurities, it is essential to acknowledge that its constraints also limit its overall applicability. For example, the challenges of heightened energy consumption at rising temperatures not only contribute to increased operational costs but also environmental concerns. Elevated greenhouse gas (GHG) emissions, particularly when fossil fuels are used for heating, exacerbate the environmental impact. In addition, economic considerations, such as the costs associated with establishing calcination facilities, can potentially impede its widespread adoption.

#### 3.2.4. Optimization strategies: Binder optimization

In recent years, developing alternative binders and refin-

ing mix proportions have been recognized as two key approaches to optimize the retention capacity of sensitive PTEs and improve the engineering properties of CPB mixtures. The appropriate proportioning of CPB constituents, mainly including OPC, common chemical admixtures, and PG, can also improve the mechanical performance of hardened mixtures, thus enhancing the physical encapsulation of PTEs. It has been shown that the cementitious content can vary by up to 20wt% and still lead to the equivalent strength (approximately 1.5 MPa) of CPB mixtures [42,88,140]. Otherwise, for the same cementitious proportion, there could be up to a 90% difference in CPB compressive strength (from 1.4 to 0.2 MPa at the same OPC content of 10wt%) [32]. These variations indicate that the use of similar CPB mix proportion scenarios could lead to the unnecessary overuse of cement due to inconsistencies in the physicochemical properties of different batches of PG. In fact, just a 0.5wt% reduction in cement consumption can save hundreds of thousands of dollars per year [109]. Therefore, beyond the current research roadmap, advanced designs must be introduced to provide the same functionality at a lower operating cost, thereby addressing the issue of CPB performance of different PG sources.

In addition, previous studies have confirmed the potential of various additives, including modified quartz [51], silica fume [155], fly ash [156], ground-granulated blast-furnace slag [48,155], red mud [156], calcium aluminate cement [157], and  $\gamma-Al_2O_3$  [88]. These additives can improve the immobilization performance of PTEs and the support of underground structures. Specifically, substituting OPC with modified quartz as an alternative binder has been proposed to physically optimize aggregate gradation, thereby fostering hydration reactions and enhancing the mechanical properties of CPB mixtures. Notably, the unconfined compressive strength values of CPB with modified quartz at 60 d (1.82 MPa) exceeded that of the control group (1.51 MPa) by 20.5%. The presence of aluminate-rich materials, such as red mud, fly ash,  $\gamma-Al_2O_3$ , and calcium aluminate cement, played a significant role in forming crystalline hydration products, particularly ettringite. This is because PG is mainly composed of calcium sulfates (gypsum, bassanite, and anhydrite) that can react with the aluminum released from these aluminate-rich materials and then promote the ettringite precipitation. This process can further fill the pores of the CPB microstructure and improve the densification of the mixture matrix [156]. Instead, the inclusion of silica-rich substitutes primarily contributes to the formation of CSH, facilitating strength development at later curing ages (from 7 to 28 d). However, we must also acknowledge that while alternative binders may offer superior engineering performance, challenges related to material availability, binder transportation, costs, and technical limitations of each specific case can render them impractical from the technical and resource perspectives. Unfortunately, many of the proposed methodologies have yet to achieve commercialization in existing enterprises.

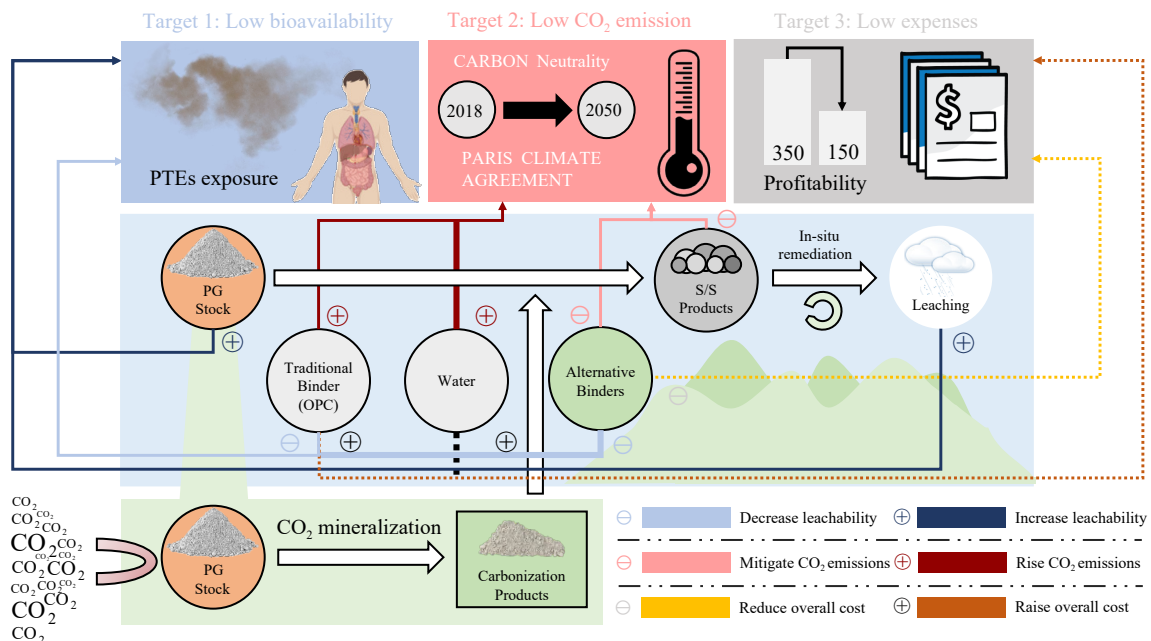
Overall, the use of CPB may contribute to technical feasibility, manufacturing scalability, and economic rationality, among other comprehensive utilization schemes. Unlike oth-

er value-added applications of PG in agriculture and REEs, which are difficult to achieve the purpose of profitably large-scale utilize PG, such a highly feasible process provides opportunities to manage the PG stockpile while simultaneously controlling the possible public health issues associated with the rising amount of PG generated. Nonetheless, there is also a need to gain more insights into the consequential impacts of PTEs release at large scales under critical environmental stresses, as well as bridge the knowledge gap referring to maximizing the socioenvironmental co-benefits, including long-term effectiveness and sustainability concerns.

#### 4. New vitalities of *in-situ* solidification/stabilization of PG toward CO<sub>2</sub> mitigation

Although PTEs retention efficiency and practical scalability are recognized as important issues plaguing the trial applications of *in-situ* solidification/stabilization of PG (Fig. 13), the most commonly discussed impact in recent years is the substantial GHG emissions related to cement production [158–159]. According to studies, approximately 1 t of CO<sub>2</sub> is produced per ton of OPC generated [160–161], with the global cement industry accounting for 36% of emissions related to construction activities and 8% of total anthropogenic emissions [160]. In the 2015 Paris Agreement, all major economic sectors worldwide committed to taking responsibility for global CO<sub>2</sub> emission, which is estimated to be halved by 2030 and reach net zero by 2050, to limit global warming to around 1.5°C [162].

In particular, China is currently the world's largest emitter of CO<sub>2</sub> [162–163], and in recognition of the importance of curbing carbon emissions in China, many policies and regulatory frameworks have been proposed [164]. Two of the best-known policies are the *Nationally Appropriate Mitigation Actions* and *Nationally Determined Contributions*, which aim to reduce CO<sub>2</sub> emissions by 45% and 60% in 2020 and 2030 compared with the CO<sub>2</sub> intensity levels of 2005, thus ushering China's "carbon neutrality economy" [159,164]. In addition, China announced to the United Nations General Assembly its commitment to peak emissions before 2030 and achieve carbon neutrality by 2060. [165]. Considering the vast amount of OPC used in the PG solidification/stabilization process, as well as limited PTEs capture capacity, there is an urgent need to focus on reducing the environmental impacts in this time period by establishing advanced strategies and schemes along with the principal targets (Fig. 13), including minimizing bioavailability, mitigating CO<sub>2</sub> emissions, and decreasing expenses. In this light, developing alternative mixture compositions offers one of the most important technologies for acquiring low-level exposure and carbon-negative emissions despite concerns regarding crucial costs, technical challenges, and actual contributions to broad communities [159,164,166]. Low-carbon supplementary cementitious materials (SCMs) and sustainable alternative binders are latent routes to mitigate the carbon footprint relative to conventional *in-situ* solidification/stabilization by partially or entirely replacing OPC content [167]. As indicated in the previous section, multiple SCMs have



**Fig. 13.** Main goals of solidification/stabilization of PG, including minimizing the PTEs exposure, mitigating the carbon footprint, and increasing profitability. The blue route focusing on PTEs control within CPB mixtures exhibits a trade-off. While augmenting PG content accelerates PG storage consumption (+), it simultaneously heightens the risks associated with PTEs exposure, particularly in light of weathering processes (+). The red route indicates the CO<sub>2</sub> emissions related to different remediation scenarios. Although the use of traditional binder (+) and water content (+) can increase the overall carbon footprint of CPB preparation, introducing pre-CO<sub>2</sub> mineralization procedures (-), employing alternative low-carbon binders (-), as well as maximizing the sponge effect of S/S products (-) can mitigate the CO<sub>2</sub> emissions. Finally, the yellow route indicates profitability consideration, seeking to strike a balance between innovations and overall cost.

been adopted to date, including limestone [168], ground-granulated blast-furnace slag [48,169], modified quartz [51], silica fume [155], fly ash [16], metakaolin [170], and  $\gamma$ - $\text{Al}_2\text{O}_3$  [88].

Aside from minimizing PTEs bioavailability, some of them have shown advantages in curbing carbon footprint in recycling PG [88,48,169]. Fly ash and ground-granulated blast-furnace slag are both typical industrial by-products, of which the former is collected from power plants, and the latter is generated by the iron and steel industry [48,171–172]. Thus, using such by-products and/or alkaline solid wastes from other industries can effectively decrease the emissions of PG-based mixture preparation because their direct application would no longer emit additional  $\text{CO}_2$  apart from transportation [160]. However, fine limestone [160,168], a typical solid waste from construction and demolition waste that already undergoes carbonization during its service, has limited hydraulic reactivity. Therefore, it can only be used as a filler material instead of an activator or SCMs. Furthermore, although calcination can facilitate the reactivity of recycled limestone (from limestone to lime), this process has risks of increasing the overall carbon footprint [173].

Meanwhile,  $\text{CO}_2$  reduction may also be achieved via the substitution of metakaolin and  $\gamma$ - $\text{Al}_2\text{O}_3$ , which are both produced from clay minerals with different thermal treatments [88,167,170]. Metakaolin is a product from the natural clay mineral named kaolin (the main constituent in kaolin is kaolinite mineral:  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) with a thermal treatment of 600–800°C, whereas 900°C is required for  $\gamma$ - $\text{Al}_2\text{O}_3$ . It has been reported that although it amounts to approximately 60%  $\text{CO}_2$  emission of the overall production process, the calcination of kaolin would not lead to direct  $\text{CO}_2$  emission, unlike the decomposition of limestone, which is the precursor process for OPC production [88].

Further  $\text{CO}_2$  savings could be achieved by alternative binders, with many works indicating that they could act as a full alternative for conventional OPC [71,122,174–175]. To date, calcium aluminate cement [174], lime-activated fly ash [176], MgO-activated slag and bentonite mixture [156], and geopolymer [71,177] have been devoted to PG remediation, thus providing considerable benefits. Calcium aluminate cement is manufactured using limestone and bauxite rather than the limestone and clay used for OPC, thus demonstrating several environmental benefits, such as low  $\text{CO}_2$  emissions, low levels of energy consumption, and high early mechanical properties [160,174,178]. With the substitution of calcium aluminate cement, the compressive strength of the prepared PG-based CPB mixture also significantly increased due to the promoted ettringite precipitation [174]. However, biosafety issues, including the possibility of PTEs transfer, must be further investigated before introducing this solution into the environment.

The alkaline-activated binders (lime-activated fly ash [176] and MgO-activated slag and bentonite mixture [156]) are mainly based on the reaction between the alkali activator (lime and MgO) and alkaline aluminosilicates (fly ash and

bentonite), which have also shown economic and technical viability [160,167]. In addition, PTEs retention can be improved by the notably enhanced mechanical strength and anti-permeability properties [160,167]. Geopolymer is not only seen as a concept for a green society but also as a pragmatic solution for reducing  $\text{CO}_2$  emissions [167,177]. Likewise, the use of geopolymer in PG remediation requires alkaline activators, such as sodium silicate and sodium hydroxide [177,179], to promote early hydration reactions. The results indicate that due to the excess sulfate disturbing the geopolymer structure by forming ettringite, PG-geopolymer mixtures might achieve better mechanical performance at low PG content (about <5wt%) but decreased compressive strength at higher PG content (about >10wt%) [177].

However, the technical limitations, challenges associated with the availability of raw materials, and the overall cost of implying such new technologies may mean that these schemes might be unrealistic. For example, although fly ash and ground-granulated blast-furnace slag have been proven to facilitate PG remediation, almost all their sources have been used in cement production and/or additives in concrete [61,160]. Similarly, the lack of high-alumina raw materials (bauxite) limits the large-scale application of calcium aluminate cement and  $\gamma$ - $\text{Al}_2\text{O}_3$  [88]. In addition, the most critical issue in engineering is cost, which means that alternative binders and SCMs should be highly scalable and cost-effective [160]. However, due to their rarity, the preparation costs of aluminum-rich mixtures are much higher than those using OPC [88]. Thus, it is also important to systematically check the long-term performance of the introduced alternative binders and SCMs, which is now insufficient.

Meanwhile, techniques for  $\text{CO}_2$  curing and direct atmospheric carbon capture may highlight a picture of the zero-emission target (Fig. 13, marked in green), which can simultaneously achieve the ambitious goals of carbo-negative and value-added resource utilization of PG. Generally, PG has high calcium ion content (e.g., gypsum, bassanite, anhydrate, and sulfuric acid) that is able to react with the  $\text{CO}_2$  present in the atmosphere and permanently store the captured  $\text{CO}_2$  in the form of stable calcite. Such carbonation-based  $\text{CO}_2$  mineralization using PG as the raw material for carbon capture and storage has been rapidly developed in recent years and is considered one of the promising technologies for combating global warming [180]. Although several scholars have conducted laboratory investigations on fixing  $\text{CO}_2$  through other alkaline solid wastes (e.g., demolished construction wastes, steel slags, lime mud, and fly ash) [173,180], its applications in PG remediation should be strengthened, especially the implements related to the massive industrial application. The primary obstacle arises from the intricate nature of PG. This means that the contents and compositions of impurities remaining in PG may be diverse due to changes in phosphoric acid production processes or changes in regional legislation. Furthermore, stored Pb may present more complex feedstocks because of the weathering process, which induces interactions between PG and storage sites. The variability in



PG waste contributes to the formation of impure carbonation products, thereby constraining their potential for subsequent industrial utilization (e.g., construction materials, paper industry, and chemical production) [181].

## 5. Summary and future perspectives

Over the past decades, the challenges related to PG stocks have curbed the sustained phosphorus supply for the agricultural sector. This has led to adverse effects on soil ecosystems and the surrounding flora and fauna, including the excessive uptake of bio-accumulative fluoride in plants, water eutrophication, and potential hazards to mammals. Various advanced technologies for PG recovery, including REE recovery, construction material utilization, agricultural abatement, and *in-situ* CPB solidification/stabilization, have been employed to mitigate the accumulation of PG. Among these, the integration of PG into the *in-situ* remediation pathway is considered a promising imperative methodology with the advantages of technical feasibility, manufacturing scalability, and economic rationality. However, the prevalent use of OPC in formulating PG-based CPB mixtures is presently confronted with various challenges, including concerns related to GHG emissions and sensitive durability. To effectively implement this sustainable and highly scalable remediation approach as a feasible pathway in PG management, ongoing technological advancements must ensure the enduring sustainability of PTEs retention in accordance with the climate goal of achieving zero-carbon practices.

Further developments can be pursued with regard to the components of PG-based CPB mixtures, such as using SCMs, alternative binders, pre-CO<sub>2</sub> mineralization on PG and/or post-CO<sub>2</sub> curing on hardened samples, which, if developed commercially in the coming decades, will have a significant impact on the mitigation of CO<sub>2</sub> emissions. Furthermore, while decarbonization of the technology can be achieved through advanced low-carbon CPB components, it can also be attained by low-carbon mixture designs. Thus, given that most of the current standards are primarily based on technical or economic performance, with little regard for their environmental characteristics, shifting the current mix design standard toward a more environmentally friendly perspective could provide a basis for realizing climate gains. Efforts from stakeholders and policymakers, such as the implementation of carbon criteria and carbon tax, can effectively accelerate the decarbonization of this strategy. There is also an urgent need to achieve further progress in standardized techno-economic analysis and life cycle assessment of these advanced technologies, which could shed light on the overall socioenvironmental cost involved and, therefore, help avoid potential market failures.

Finally, a comprehensive understanding of PTEs immobilization mechanisms and accurate prediction of PTEs release also play key roles in convincing the market of the long-term performance of PG-incorporated materials. A combination of multiple experimental techniques and simu-

lations would allow for a more consistent description of the interactions among the CPB mixtures, soil, water, and weathering processes.

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## Conflict of Interest

Qiusong Chen is an editorial board member for this journal and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests

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