

A systematic review of cemented paste backfill technology for cleaner and efficient utilization of phosphogypsum in China

Guanzhao Jiang^a, Liangliang Zhao^{a,*}, Shunchuan Wu^a, Yan Li^a, Aixiang Wu^b, Yanduotai He^a, Haiyong Cheng^a, Wei Sun^a, Hong Li^a

^a Faculty of Land Resources Engineering, Kunming University of Science and Technology, Kunming 650093, China

^b School of Civil and Resource Engineering, University of Science and Technology Beijing, Beijing 100083, China

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ABSTRACT

Utilization of phosphogypsum (PG) with cleaner and efficient approach has always been a global challenge. Cemented PG backfill (CPGB) technology uses a cleaner filling material mixed with a large amount of PG to support the surrounding rock of mine goaf, which not only can efficiently solve the environmental problems during PG stacking, but also can suppress the goaf collapse. After more than 20 years of development, China has now become most popular country in CPGB technology research. This paper provided the first systematic overview of the recent research of CPGB in China in terms of cemented PG filling materials (CPGFM), environmental impacts, case studies, and challenges and prospects. Firstly, the preparation of CPGFM was introduced around the role of PG in the CPGFM, and the influencing factors and control measures of CPGFM performance were elaborated. Then, the highly anticipated environmental impacts of CPGFM were summarized based on hazardous gases emissions, phosphate and fluoride leaching and control measures. Subsequently, three engineering cases corresponding to PG utilization methods were presented. Finally, the challenges and prospects of CPGB were discussed. The results show that the use of PG as aggregate in CPGFM is an effective way to quickly reduce the stockpiles. The risk of secondary release of fluoride in various pollutants needs to be strengthened control. The existing pollutant control methods mostly use acid-base neutralization method. This comprehensive review of CPGB in China can provide valuable reference for cleaner and efficient utilization of PG worldwide.

1. Introduction

Phosphogypsum (PG) is the main industrial pollutants from wet-process phosphoric acid production (Rashad, 2017). Approximately 5 tons of PG are produced per ton phosphoric acid (Meskini et al., 2021), only a small proportion of the PG produced are utilized. The comprehensive utilization rate of PG is only 15 % worldwide, and most of the PG stockpiles are deposited on the ground without any treatment (Lu et al., 2021). Currently, the global stockpile of PG reaches 6 billion tons and is growing at a rate of roughly 300 million tons per year (Ennaciri et al., 2020; Bilal et al., 2023). The stockpiled PG has caused serious environmental problems, such as phosphorus, fluorine, and heavy metals pollution (Tayibi et al., 2009). Specifically, PG contains acidic substances such as sulfuric acid and phosphoric acid, which will volatilize in the atmosphere and eventually form acid rain. The toxic and harmful substances in PG will enter the soil, rivers or lakes through rainfall, causing soil microorganisms or aquatic organisms to die and

organize plant growth (Costa et al., 2022a). There is a large-scale desertification phenomenon around the area where PG has been accumulated for a long time (Wu, 2024). The Yangtze Sea pollution incident in China was caused by this reason (Wu, 2024).

In order to reduce the stockpile of PG, countries around the world have long begun to explore the utilization approaches of PG. PG is mainly used for the production of building materials in Japan (Murali and Azab, 2023). In India, it is used for the production of cement, bricks, fertilizer, etc. (Pappu et al., 2007). The United States and some countries usually adopt the disposal method by stockpiling (Shi, 2016). Among the many pathways of utilization, PG is widely used as a building material (gypsum products, cement) around the world (Azifa et al., 2024; Gracioli et al., 2020; Jia et al., 2021; Oubelhas et al., 2024; Sina et al., 2024). Compared with natural gypsum, PG is abundant, making it easier to obtain and cheaper. However, PG is pretreated before use to remove its own soluble phosphorus and soluble fluorine (Sina et al., 2024; Zhang et al., 2023c). The pretreatment process will undoubtedly increase the

* Corresponding author at: Faculty of Land Resources Engineering, Kunming University of Science and Technology, Kunming 650093, China.
E-mail address: 20220162@kust.edu.cn (L. Zhao).

cost of building materials. It is worth noting that countries such as Morocco, the United States, and Spain have higher levels of radionuclides in PG. Long-term human exposure to radioactive environment may lead to health problems (Fornés et al., 2021; Hull and Burnett, 1996; Qamouche et al., 2020; Tayibi et al., 2011). Therefore, PG-based building materials require strict quality control and safety measures to ensure that their environmental hazards are within acceptable limits.

As shown in Fig. 1a, the annual production of PG is huge in China, ranking first in the world. Fortunately, the comprehensive utilization rate of PG has been increasing year by year, reaching 55.6% in 2023, far exceeding the global average level (Fig. 1b). It attributed to the positive policy of "The production of phosphoric acid is determined by the consumption of PG" and "Action plan for comprehensive utilization of PG" put forward by the Chinese government. Encouraged by the authorities, various novel PG utilization technologies have emerged one after another, with cemented paste backfill (CPB) technology for cleaner and efficient utilization of PG being a prominent representative among them.

Cemented PG backfill (CPGB) is a technology of mixing PG, water and other mineral materials (cement, slag, fly ash, tailings, modifier etc.) to prepare cemented filling slurry, and then pumping the slurry into underground mine goaf through a pipeline system to effectively suppress the deformation of the surrounding rock and prevent the roof from collapsing after the consolidation of the filling slurry (Min et al., 2022; Yan et al., 2020; Cao et al., 2019). Cemented PG filling materials (CPGFM) is the core of CPGB technology. For CPGFM used in the filling field, it is necessary to ensure that it has high strength, good economy and friendly environmental protection. This technology not only can provide a safe working environment for the miners, but also efficiently solve the environmental problems during PG stacking (Belem and Benzaazoua, 2008; Shi, 2018a; Zhang et al., 2023a). The CPGB was developed in China at the beginning of the 21st century, and it has currently been adopted by dozens of large-scale mines in Guizhou, Sichuan, Yunan, Anhui, Hubei and other regions in China (Shi, 2018a; Zhou, 2023a). It has attracted a lot of interests due to solving the problems of cleaner and efficient utilization of PG and low-cost filling material acquisition, especially with the encouragement of the authorities in recent years. Simultaneously, CPGB is relatively less studied. Currently, the existing literature review mainly focuses on the application of PG in building materials, cementitious materials and road materials (DeWindt et al., 2025; Murali and Azab, 2023; Qu et al., 2025), they do not fall within the CPGB field that this paper focuses on. At the same time, a comprehensive review of PG in cemented filling is notably absent. Therefore, the purpose of this paper is to review China's CPGB to fill the above gaps.

This paper emphasizes the use of PG for filling materials. Firstly, the feasibility of using PG as filling material was analysed based on its physical and chemical properties. Then, CPGFM and its properties were

reviewed. Furthermore, the environmental impact of CPGFM was reviewed. Next, three typical cases are provided to support the industrial application of CPGFM. Finally, we discussed the urgent challenges and promising prospects of CPGB. The practice of CPGB in China can provide valuable reference for the cleaner and efficient utilization of PG and ecological treatment of mine goaf around the world.

2. Cemented PG filling materials

2.1. Characteristics of PG

2.1.1. Physical properties

Due to the different sources of phosphate rock and phosphoric acid production process, the PG color is different, usually gray-white. PG is in two forms of hemihydrate PG (HPG) and dihydrate PG (DPG), depending on the wet phosphoric acid process. Fig. 2a shows that the particle size of DPG is concentrated in 1–100 µm. Due to the high content of fine particles, DPG is not conducive to the dewatering and rapid hardening of the filling slurry. In contrast, HPG contains many coarse particles with a diameter of 50–80 µm, which is harmful to the water retention of the filling slurry. There are some differences in the particle size of PG in different countries (Table 1). The 50th percentile (D_{50}) of Brazil PG is generally smaller than that of China PG. Finer particle size can enhance the reactivity and strength development in cementitious materials, while coarser particles may lead to different setting time and strength performance (Qu et al., 2025). PG contains acidic substances such as sulfuric acid and phosphoric acid, so its pH is usually 1.5–5.5 (Zhang et al., 2023b), which belongs to acidic solid waste. The bulk density of PG is 1270–2290 kg/m³, the specific gravity is 2350–3272 kg/m³, the specific surface area is 0.13–0.45 m²/g. As shown in Fig. 2b and Fig. 2c, most HPG crystals are polygonal aggregates composed of many sheet- and plate-like crystals, but DPG crystals is usually in the form of flakes and plates.

2.1.2. Chemical properties

As illustrated in Table 2, the chemical composition of PG from different countries is roughly the same, but the content of chemical composition varies greatly. In particular, the content of SO₃ and CaO, the main components of PG, are significantly different. The contents of SO₃ and CaO in PG from China are 34.00 wt%–53.72 wt% and 28.19 wt%–40.98 wt%, respectively. This difference has been further proved in other countries. For instance, PG from Finland is notably rich in SO₃ (53.48 wt%) and CaO (38.60 wt%). Conversely, these component contents of PG from Morocco and Vietnam were relatively low. The differences in the chemical composition of PG are attributed to the nature of the phosphate ore used, the type of wet process employed, the disposal method, and the location of the stack area (Liu et al., 2024). The main component of HPG is calcium sulfate hemihydrate

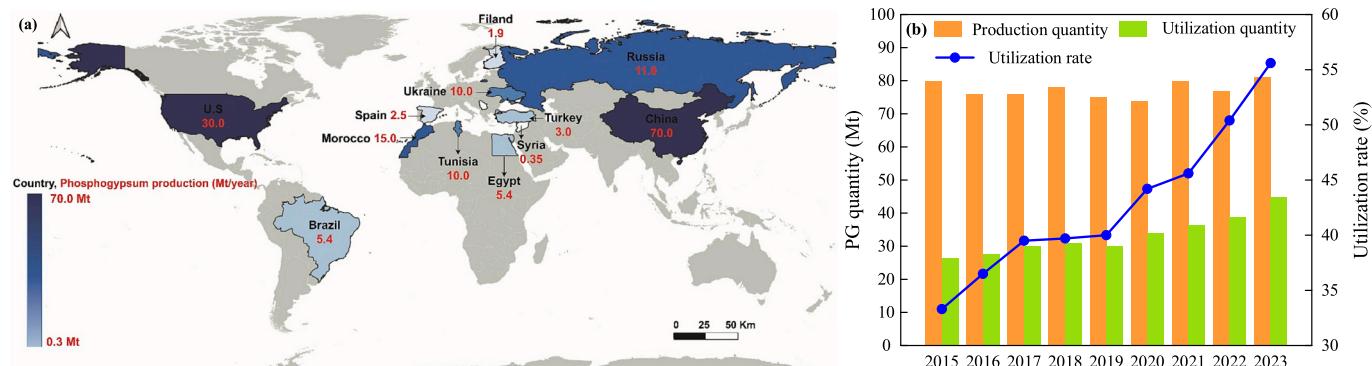


Fig. 1. Production changes of PG: (a) Repartition map of the annual volume of PG production around the world (Akfas et al., 2024); (b) Production and utilization of PG in China, 2015–2023.

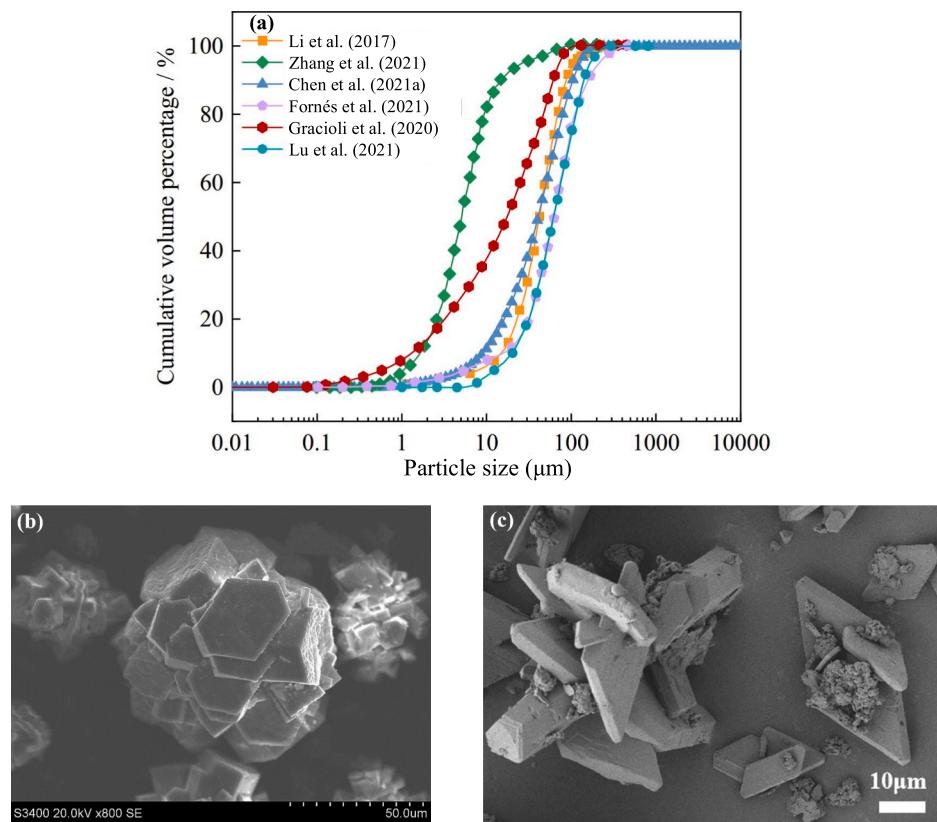


Fig. 2. Particle size distribution of DPG (a), and the micromorphology of HPG (b), and DPG (c) (Jiang et al., 2019a; Li et al., 2022; Liu et al., 2024).

Table 1
Physical properties of several typical PG from China and other typical countries.

Country	Reference	Bulk density (kg/m^3)	Specific gravity (kg/m^3)	Specific surface area (m^2/g)	pH	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	C_u	C_c
China	Yan et al. (2023)	2290	—	0.26	—	5.20	9.53	87.19	6.93	0.97
China	Liu et al. (2019)	—	—	0.32	—	13.18	58.33	146.59	—	—
China	Xie et al. (2022)	2480	—	—	—	5.27	29.34	69.20	—	—
China	Jiang et al. (2019a)	1270	2690	—	3.4	—	—	—	3.20	1.20
China	Min et al. (2023b)	—	2350	0.27	1.68	9.89	—	—	5.90	1.06
Brazil	Costa et al. (2021)	—	3272	0.13	—	1.08	7.98	32.05	—	—
Brazil	Costa et al. (2022b)	2300	—	0.45	—	3.59	13.92	42.65	—	—
Brazil	Costa et al. (2022b)	2260	—	0.41	—	3.12	13.03	28.84	—	—
India	Mohammad and Rana (2023)	2300–2600	1470–1670	—	—	—	—	—	—	—
Turkey	Dégirmenci (2008)	1470	2890	—	—	—	—	—	—	—

Notes: D_{10} , D_{50} , and D_{90} , the particle sizes corresponding to the cumulative mass content of 10 %, 50 % and 90 % in the particle size distribution curve, respectively; C_u , uniformity coefficient; C_c , curvature coefficient.

($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), which has potential gelling activity. Adding a small amount of quicklime in HPG to remove impurities can promote the reaction of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ with water to form calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The main component of DPG is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. CaSO_4 in PG can provide abundant Ca^{2+} and SO_4^{2-} for pozzolanic reaction. Ca^{2+} and SO_4^{2-} are the main component of hydration reaction to generate ettringite (Aft) and C-S-H gel. These hydration products are conducive to the consolidation of PG filling body and have certain strength. At the same time, PG contains impurities, which may affect the hydration reaction. P may adsorb on the surface of the cementitious material to hinder the hydration process (Holanda et al., 2017). Further, the presence of P prolongs the setting time and reduces the generated amount of hydration products. On the contrary, the presence of F reduces the interaction force between the crystals and shortens the setting time (Chen et al., 2021a; Singh, 2003).

2.1.3. Toxic and harmful substances

All the toxic and harmful substances in PG originate from the original phosphate rock that mainly exists in the form of accompanying minerals stably (Wu, 2024). After digestion with sulfuric acid, the phosphate rock is converted into PG, and the toxic and harmful substances shift from a stable form to an easily releasable one within the PG system. Numerous impurities predominantly exist in the PG crystals, as well as in the interstitial and attached water of PG, posing severe pollution risks to the ecological environment (Bilal et al., 2023). The toxic and harmful substances in PG include phosphates, fluorides, heavy metals and radio-nuclides, as listed in Table 3-5. The phosphorus in PG mainly exists in three forms: soluble phosphorus, eutectic phosphorus, and insoluble phosphorus (Zhou et al., 2020). Soluble phosphorus has the greatest impact on the performance of PG, because it can combine with Ca^{2+} to form insoluble $\text{Ca}_3(\text{PO}_4)_2$ that adheres to the surface of PG, preventing the dissolution and hydration of CaSO_4 (Singh, 2003; Singh, 2005).

Table 2

Main chemical composition (wt%) of several typical PG from China and other typical countries.

Country	Reference	SO ₃	CaO	SiO ₂	Al ₂ O ₃	MgO	P ₂ O ₅	Na ₂ O	K ₂ O	F	Fe ₂ O ₃	TiO ₂	others
China	Liu et al. (2023)	49.11	36.11	5.26	3.64	0.20	1.03	—	—	0.67	1.77	—	2.21
China	Chen et al. (2023a)	47.60	39.99	7.50	0.74	0.18	1.31	0.43	—	0.51	—	0.15	1.59
China	Qin et al. (2023)	50.10	37.25	8.26	0.83	0.10	0.88	0.17	0.53	—	0.63	—	1.26
China	Chen et al. (2021b)	53.72	36.44	5.92	0.66	0.06	0.88	0.07	0.37	0.97	0.57	0.11	0.24
China	Shi et al. (2022)	45.68	35.22	4.39	0.49	0.23	3.95	0.12	0.10	0.42	0.25	0.05	0.01
China	Min et al. (2019)	50.76	35.85	1.73	0.30	0.10	1.30	0.09	0.11	—	0.33	0.06	—
China	Zou et al. (2023)	34.00	33.65	4.74	2.30	0.08	1.82	0.05	0.21	0.30	1.38	0.17	0.43
China	Zhang et al. (2022a)	36.42	28.19	12.03	0.74	0.06	0.92	0.08	—	0.32	0.14	—	—
China	Zhang et al. (2022c)	48.76	40.98	6.50	0.90	0.18	0.93	0.40	0.43	—	0.44	0.13	0.20
China	Wu et al. (2022)	39.00	40.75	15.34	1.09	0.23	1.49	0.18	0.33	0.98	—	—	0.61
Morocco	Abouloifa et al. (2023)	29.05	35.05	1.37	0.49	0.54	0.59	—	0.40	—	0.34	0.01	32.16
Tunisia	Zrelli et al. (2018)	37.50	37.18	1.03	0.06	0.07	1.11	0.05	0.03	1.66	0.13	—	21.18
Jordan	Malkaw et al. (2022)	51.22	35.56	9.14	0.26	—	1.87	0.42	0.02	0.79	0.15	—	0.57
India	Pratap et al. (2023)	42.37	38.01	7.82	5.13	0.21	1.3	0.25	—	—	0.53	—	4.38
Brazil	Costa et al. (2021)	40.43	33.02	1.10	0.11	0.02	0.73	—	—	—	0.48	0.68	24.84
Lithuanian	Vaičiukynienė et al. (2021)	53.48	38.60	0.37	0.13	0.04	0.85	—	—	0.14	0.03	—	6.36
Vietnam	Ngo et al. (2021)	38.81	26.74	10.40	0.75	0.10	0.27	0.00	0.71	1.17	0.22	0.30	20.53
Turkey	Değirmenci (2008)	44.67	32.04	3.44	0.88	—	0.50	0.13	—	0.79	0.32	—	17.23

Table 3P₂O₅ and F content (wt%) in several typical PG from China and other typical countries.

Country	Reference	Total P ₂ O ₅	Soluble P ₂ O ₅	Total F	Soluble F
China	Liu (2009)	1.63	< 0.2	—	0.18
China	Zhang et al. (2022a)	0.92	0.33	0.32	0.25
China	Yang et al. (2020)	1.17	0.87	0.52	0.12
China	Li et al. (2021b)	1.31	0.73	0.63	0.16
China	Li et al. (2021b)	0.91	0.36	0.72	0.23
Brazil	Costa et al. (2022b)	0.94	0.24	0.05	0.02
Brazil	Costa et al. (2022b)	0.87	0.00	0.11	0.01
—	Bilal et al. (2023)	1.31	0.23	0.55	0.21
—	Bilal et al. (2023)	0.52	0.37	0.45	0.31
—	Bilal et al. (2023)	0.70	0.08	0.55	0.24

Fluorine in PG is derived from phosphate ore and exists in the form of soluble fluorine, and insoluble fluorine. Soluble fluorine can shorten the setting time of PG slurry and reduce its density and strength, while insoluble fluorine exerts little effect on the properties of PG (Jiang et al., 2024). Table 3 lists the P₂O₅ and F content in several typical PG from different countries. The content of P₂O₅ is generally higher than that of F. The content of some heavy metals in the China PG solution exceeded the Chinese standard limit, but most of the heavy metals were far below the standard limit (Table 4). Conversely, the concentrations of heavy metals in PG solution from other countries are much higher than the Chinese standard limits. Most of the phosphate ores in China are phosphate massive deposits of marine sedimentation, which are distinctively characterized by particularly low radioactivity. China's PG also has low radioactive element content (Table 5). At the same time, the internal

exposure index (I_{RA}) and external exposure index (I_R) of China's PG is lower than the threshold (I < 1) of the International Commission on Radiological Protection. It is worth noting that other countries (Morocco, the United States, and Egypt, et al.) have high levels of radionuclides in PG. The pretreatment processes must be implemented to reduce the radionuclide content in PG, enabling its large-scale application while complying with safety regulations. There is no such concern about PG in China, which is really helpful for the utilization of PG from China.

2.2. Roles of PG in CPGFM

2.2.1. PG as aggregate

The inactive DPG often is used as aggregate to regulate the properties of filling materials. Liu (2009) gave two CPGFM formulations, as shown in Table 6. At this time, the normal formulation was mainly used for stable goaf, and the special formulation was mainly used in the goaf with higher strength requirements. Zhao et al. (2021) determined the optimal formulation of CPGFM as 20 % PG, 1 % lime, cement to tailings ratio of 1:6, and mass concentration of 80 %, when the strength of the backfill was 0.61 MPa for 3 days, 1.27 MPa for 7 days, and 2.57 MPa for 28 days. Pan et al. (2023) prepared a new CPGFM with a strength exceeding 22 MPa for 28 days using 65 % PG, 15 % fly ash, 5 % red mud, 10 % ordinary Portland cement, 5 % silica fume, 0.7 % superplasticizer, and a water to binder ratio of 1:5.

Chen et al. (2017) found that the ageing time of PG had a significant effect on the strength of the CPGFM in the first four days, and then it tended to stabilize. Chen et al. (2018) discovered that the strength of filling material using PG as an aggregate was not satisfactory, and adding construction demolition waste within 40 % can improve the problem. Chen et al. (2023a) and Min et al. (2021) proved that the use of ground granulated blast furnace slag instead of partial cement can

Table 4

Concentration (mg/L) of heavy metals in several typical PG solution from China and other typical countries.

Country	Reference	Cu	Zn	Pb	Co	Ni	Mn	Cr	Ba
China	Feng et al. 2023	—	0.200	—	—	—	—	0.019	0.081
China	Huang et al. (2020a)	0.348	0.089	0.025	0.030	0.005	0.495	0.049	—
China	Huang et al. (2022)	1.250	—	—	—	—	—	—	2.460
China	Li et al. (2017)	0.200	0.060	0.020	0.020	0.0100	1.600	—	—
China	GB/T 14848-2017 (2017) III	≤ 1.000	≤ 1.000	≤ 0.010	≤ 0.050	≤ 0.020	—	≤ 0.050	≤ 0.700
Morocco	Bouargane et al. (2023)	5.90 ± 1.20	3.0 ± 0.6	1.7 ± 0.3	—	1.2 ± 0.2	8 ± 8	16 ± 2	23 ± 5
Tunisia	Zrelli et al. (2018)	9.60 ± 1.37	137 ± 13.7	0.90 ± 0.09	0.30 ± 0.03	4.10 ± 0.41	< 5	13 ± 1.30	10 ± 0.67
Brazil	Sauéia et al. (2013)	12.5 ± 0.3	11.6 ± 0.3	14.0 ± 1.6	0.8 ± 0.03	9.4 ± 2.6	—	37 ± 3	—
United States	Luther et al. (1993)	27.6	60.0	5	—	9	—	—	50
United States	Rutherford et al. (1995)	3.3	11.1	—	6	24	—	—	30

Table 5

Radionuclides content (Bq/Kg) in several typical PG from China and other typical countries.

Country	Reference	^{226}Ra	^{232}Th	^{40}K	I_{Ra}	I_r
China	Chen et al. (2018b)	56.30	94.91	708.79	0.28	0.69
China	Feng et al. (2023)	86.00	4.10	109.00	0.43	0.27
China	Huang et al. (2020a)	4.24	4.06	30.47	0.02	0.03
China	Huang et al. (2022)	42.78	0.33	97.39	0.21	0.14
China	Jian et al. (2025)	58.61	13.89	72.04	0.29	0.27
China	GB 6566–2010 (2010)	< 200	< 200	< 200	≤ 1.0	≤ 1.0
Brazil	Narloch et al. (2019)	18.34 ± 0.34	17.43 ± 0.21	—	0.092	0.15 ± 0.0015
Brazil	Sauaria et al. (2005)	700 ± 38	138 ± 9	< 45	—	—
Turkey	Degirmenci (2008)	22	1.0	11	—	—
Morocco	Qamouche et al. (2020)	572.68 ± 53.64	3.74 ± 0.95	< 15.6	—	1.82
United States	Hull and Burnett (1996)	907	312	—	—	—
Egypt	El-Bahi et al. (2017)	397	11.5	785	—	1.64
Egypt	El-Bahi et al. (2017)	702	147.3	954	—	3.39
Tunisia	Tayibi et al. (2011)	188 ± 9.5	12.4 ± 1.4	< 13.5	—	—
Spain	Tayibi et al. (2011)	188 ± 9.5	8 ± 2	< 39	—	—

Table 6

Recommended formulation of CPGFM (Liu, 2009).

Formulation	Phosphor slag/%	PG/%	Activator/%	Water reducer/%	Concentration/%
Normal	20–30	65–75	5	—	60–65
Special	30–40	55–65	5	3	63–69

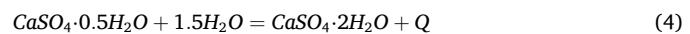
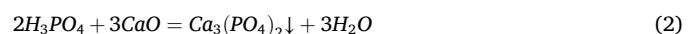
optimize the mechanical properties of the CPGFM, which was because the slag can react with sulfate in PG to produce more calcium aluminum silicate hydrate (C-A-S-H) gel and ettringite. Zhao et al. (2025) prepared the filling body with 54 % PG as aggregate, 6 % calcium carbide slag and 40 % blast furnace abrasive slag as binder, the mass concentration of the slurry was 77 %, and the strength of 0.5 % polycarboxylate superplasticizer reached 40.86 MPa.

The above work has shown the feasibility of PG as an aggregate in filling materials. When PG is used as aggregate, Portland cement is often used as binder in the initial research, which undoubtedly increases the filling cost. Researchers began to work on the development of composite cementitious materials (CCM). There are many kinds of CCM, making it difficult to form a unified standard, which is not conducive to large-scale promotion and application. Simultaneously, due to the deterioration of the impurities in PG on the hydration of the cementitious materials, the content of PG must be lower than that of the tailings in order to obtain the same strength of CPGFM as that of the cemented tailings filling material.

2.2.2. PG as cementitious material

HPG is produced by hemi-wet process, mainly composed of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. In theory, during the conversion from $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, HPG can show self-hardening characteristics similar to cement (Yang et al., 2014). However, the hydration reaction of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ is hindered in original HPG as soluble P_2O_5 can combine with Ca^{2+} to form an insoluble $\text{Ca}_3(\text{PO}_4)_2$ covering on the surface of HPG particle (Singh, 2003). Jiang et al. (2018) successfully developed a new HPG cementitious material (HCM) by using quicklime to modify HPG. As can be seen in Eq. (1), soluble P_2O_5 exists in the form H_3PO_4 in water. When quicklime is added, CaO can react with H_3PO_4 to produce $\text{Ca}_3(\text{PO}_4)_2$ precipitates (Eq. (2)). In this case, the HPG hydration occurs because the adsorption of H_3PO_4 on the surface of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ is prevented (Jiang, 2022). At the same time, F^- can react with CaO to form CaF_2 , so that the detrimental effect of F^- on the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ is weakened significantly (Eq. (3)) (Jiang et al., 2020). With the elimination of the harmful soluble impurities, the hydration reaction gradually proceeds as shown in Eq. (4), accompanied by the release of heat. Generally, the final setting time of HCM are less than 130 min, and the strength can basically reach the maximum value (more than 4 MPa) at

the curing time of 7 days (Jiang et al., 2018; Jiang et al., 2020). It is obvious that HCM has the advantages of fast setting and high early strength compared with ordinary Portland cement.



Jiang et al. (2022) further found that the calcium sulfate in HPG converted gradually from the hemihydrate form to dihydrate form with the extension of aging time during stacking, accompanied by a decrease in its gelling activity. When the stacking height was 1.5 m, HPG can be used to prepare the HCM within the first 137 h of aging. Thereafter, HPG had almost no gelling activity and can only be used as aggregate, as shown in Fig. 3. The stacking height of HPG may exceed 3 m, so it is necessary to further explore the effect of height on its activity change. Wang et al. (2018) found that the strengths of the CPGFM with 50 % PG by HPG mass, 1.5 % alkaline activator by HPG mass and mass concentration of 69 % were 3.0 MPa for 3 days, which can meet the needs of upward layered filling mining method.

Xue et al. (2019) prepared CPGFM with the formation of 3 % quicklime by HPG mass, 5 % cement by HPG mass, HPG to phosphorous slag ratio of 4:1, and mass concentration of 69 %. The microstructures showed that the filling material underwent complex hydration

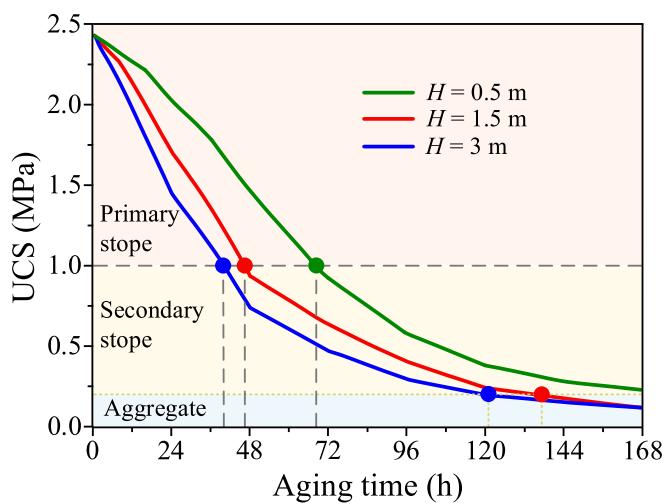
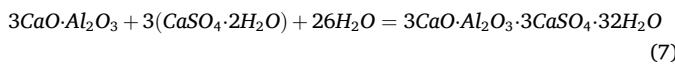
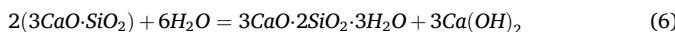
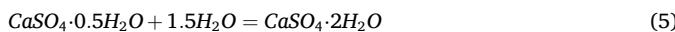


Fig. 3. Unconfined compressive strength (UCS) decay of HPG at different stacking heights (Jiang et al., 2022).

reactions, resulting in the formation of a large number of fluffy $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ whiskers, flocculent calcium silicate hydrate gel (C-S-H), and needle-like ettringite (Eqs. (5)–(7)).



The direct use of HPG as a cementitious material to replace cement completely can greatly reduce the cost of CPGM. Quicklime is a commonly used modified material for HPG. It is worth studying whether solid waste can be used as a modified material. Considering the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with slight solubility, the CPGFM with HPG used as cementitious material is very suitable for mines slightly affected by groundwater. In water-rich mines, the strength stability of the CPGFM should be considered in the design of CPGM. However, due to the difference in phosphoric acid production processes, the production quantity of HPG is relatively small. Therefore, there is still a lot of work to promote HPG as a cementitious material throughout the country.

2.2.3. PG as a component of cementitious material

Ca^{2+} and SO_4^{2-} in PG react with aluminates to produce ettringite to fill the pores between hydration products and improve the mechanical properties of filling materials. Therefore, PG is often mixed with pozzolanic blending materials as a sulfate activator to produce CCM. Li et al. (2021a) prepared the PG-slag CCM with the optimal formulation of 7 % quicklime, 30 % PG, 2 % mannite, and 61 % slag powder. At this time, the strength of this material curing for 3, 7, and 28 days exceeded 1.5, 2.5, and 5.0 MPa respectively. Qin et al. (2023) prepared a biomass fly ash-carbide slag-PG CCM using 80 % biomass fly ash, 15 % carbide slag, and 5 % PG, when the strength reached 15.36 MPa for 28 days. Li et al. (2023a) used steel slag/vanadium-titanium slag, main activators (PG and dicyandiamide waste slag), and auxiliary activators (composite phosphoric acid and cement clinker) together to prepare CCM. The CCM's UCS for 3, 7 and 28 days was 0.69, 2.47 and 5.72 MPa respectively at the optimal content of 3.6 % PG, which meet the strength requirements of GB/T 39489–2020 (2020). Zhang et al. (2021) developed a new CCM using Portland slag cement, fly ash, PG, and quicklime. They found that the addition of PG improved the mechanical performance of the CCM by lowering the porosity and increasing the formation of ettringite in the early stages. However, the impurities in PG inhibited the pozzolanic reaction of fly ash during the later curing process, resulting in a slow increase in the strength of the CCM. Ruan et al. (2023) prepared early-strength CCM by using 40 % refining slag and 30 % slag as the main raw materials, 30 % PG as the sulfate activator, and 1.5 % NaOH by total mass of other materials in CCM as the alkali activator. According to response surface methodology, NaOH had the greatest impact on strength of CCM, followed by PG and refining slag. When PG is used as a cementitious material component, the usage amount is relatively low. The influence of other components in CCM on the performance of PG should be explored.

2.3. Influencing factors of CPGFM properties

2.3.1. Phosphate

As described in Section 2.1.3, phosphate impurities in PG mainly exist in the form of soluble phosphorus, insoluble phosphorus, and eutectic phosphorus (Wu et al., 2023; Zhang et al., 2023b). For CPGFM using silicate materials such as cement and slag as binder, soluble phosphorus can hinder the normal hydration reaction of cement by adsorbing on the surface of cement particles or interfering with the formation of crystals in the early hydration stage. At this time, the mechanical performance of the hardened CPGFM deteriorates significantly due to the prolongation of setting time and the reduction of hydration

products (Holanda et al., 2017). Zhou et al. (2020) studied the effect of soluble phosphorus content on the strength of CPGFM with yellow phosphorous slag-based cementitious material. As shown in Fig. 4a, when the phosphorus content was low, the PG particles in the CPGFM filling body were surrounded by hydration products such as needle-like ettringite and flocculent C-S-H gel. On the contrary, a large number of naked PG particles were observed in the filling body with high phosphorus content (Fig. 4b). The strength of the CPGFM reduced obviously with the increasing soluble phosphorus content due to the decreasing hydration products.

Singh (2003) found that soluble phosphorus delayed the solidification and strength development of gypsum, and the performances of the gypsum depended on phosphates type. The order of influence of phosphates on the gypsum is as follows: $\text{H}_3\text{PO}_4 > \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} > \text{CaHPO}_4 \cdot 2\text{H}_2\text{O} > \text{Ca}_3(\text{PO}_4)_2$. They also thought that the combined effects of phosphates, fluorides and organic matter caused the gypsum crystals to be mostly prismatic crystals with irregular boundaries and short lengths, and strip-shaped and plate-shaped crystals, which was very detrimental to the setting and hardening of gypsum (Singh, 2005). But the added phosphate is different from the phosphate in PG, so the experimental results only have certain reference value. Jiang et al. (2018) and Jiang et al. (2020) found that in the CPGFM using HPG as cementitious material, soluble phosphorus can react with Ca^{2+} to form insoluble substances to hinder the dissolution and hydration of calcium sulfate hemihydrate crystals. Eutectic phosphorus will release from the crystal lattice to generate soluble phosphorus during the hydration of calcium sulfate hemihydrate, leading to the loose hydration products structures, the extension of setting time of CPGFM and the decreasing pH of CPGFM leachates (Wu et al., 2023).

Regardless of whether silicate materials or HPG is used as the cementitious material for CPGFM, the adverse effects of soluble phosphorus on the mechanical performance of CPGFM are more significant, followed by eutectic phosphorus, and the influence of insoluble phosphorus is not noticeable.

2.3.2. Fluoride

As described in Section 2.1.3, Fluoride exists in the forms of soluble fluorine and insoluble fluorine in PG. Li et al. (2023b) investigated the effect of fluoride content on the mechanical performance of CPGFM prepared using PG and, yellow phosphorus slag-based binder composed of yellow phosphorus slag, fly ash, cement clinker and lime. As shown in Fig. 5, the porosity of CPGFM increased with the increasing NaF content, which explained the decreasing strength of the filling body.

For the CPGFM with sulfate cementitious materials, the soluble fluorine can shorten the setting time and weaken the molecular interaction between crystals (Singh, 2003). The effect of insoluble fluorine on CPGFM is generally not considered. Singh (2003) found that the order of harmful influence of fluorides on the strength of gypsum was as follows: $\text{NaF} > \text{NaSiF}_6 > \text{Na}_3\text{AlF}_6 > \text{CaF}_2$. NaF caused the formation of anhedral prismatic and rhombus-shaped crystals of deformed boundaries. NaSiF_6 led to the formation of tabular-shaped crystals having less cohesion among themselves. Na_3AlF_6 induced to form needle-shaped crystals in abundance in association with euhedral prismatic crystals. After the addition of CaF_2 , the marginal fall in strength was due to change in crystal habit and reduction in the needle-shaped crystals. Guo et al. (2023) considered that the order of influence of the four fluorides was $\text{NaF} > \text{Na}_3\text{AlF}_6 > \text{Na}_2\text{SiF}_6 > \text{CaF}_2$. As shown in Fig. 6, CaF_2 basically did not modify the elongated needle-like crystal shape. NaSiF_6 made the crystals coarsened with decreasing overlapping points. Under the action of NaF and Na_3AlF_6 , the crystals became coarser, and plate-shaped and small rod-shaped crystals increased, leading to the significant deterioration of the pore structure of gypsum. Adding fluoride to explore the effect of fluoride on the performance of CPGFM may be different from the effect of fluoride in practical applications.

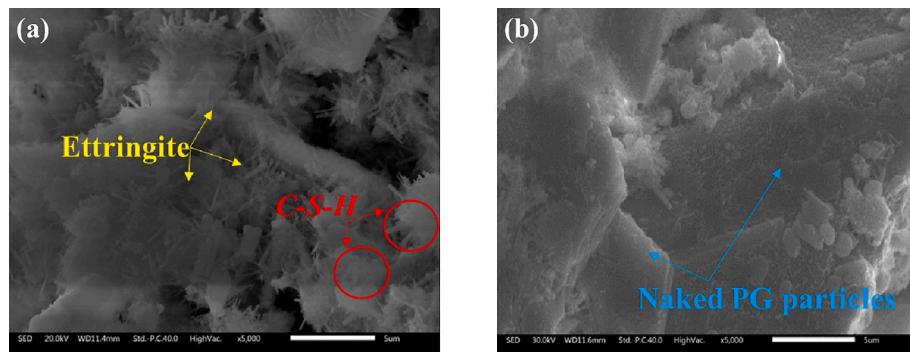


Fig. 4. Microstructures of the CPGFM filling body at a curing age of 28 days. (a) Sample with 29 mmol/kg soluble phosphorus in the original PG; (b) Sample with 377 mmol/kg soluble phosphorus in the original PG (Zhou et al., 2020).

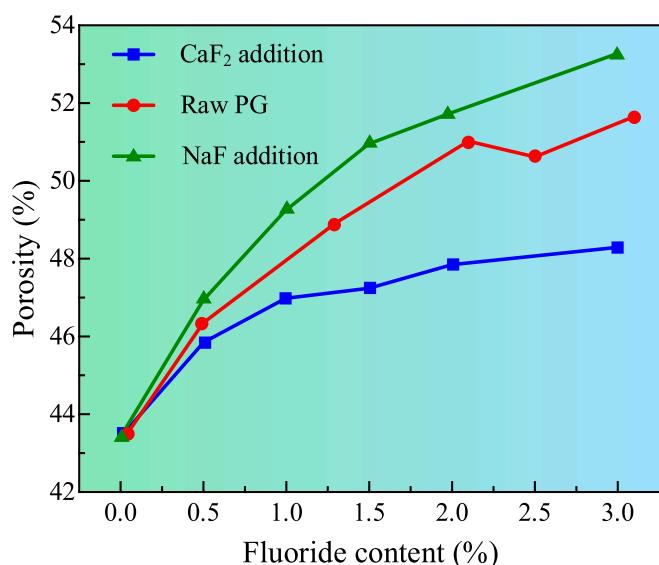


Fig. 5. Effect of fluoride addition on the porosity of the CPGFM filling body (Li et al., 2023b).

2.3.3. Chemical erosion

Chemical erosion refers to a process in which the filling body is subjected to the action of acid, alkaline, water or other chemical substances, causing the chemical components to dissolve, react, or change in structure. In this case, the strength stability and release of harmful substances are worrying. Li et al. (2023c) and Li et al. (2023d) found that in the early stage, HCl solution, NaOH solution and water promoted the formation of C-S-H and ettringite in the CPGFM filling body made of PG, cement and slag. As the erosion continued, the strength of the filling body increased in NaOH solution with the combined failure mode of tension and shear failure. In contrast, the HCl solution and water caused the strength decrease, when the CPGFM with the erosion of NaOH mainly exhibited fracture failure mode, but the CPGFM eroded by water had a shear failure. Li et al. (2019) found that acidic environments caused hydration products to dissolve to uncover the PG particles in the CPGFM filling body prepared from PG and yellow phosphorus slag-based binder. Both 5 % NaCl and 5 % Na₂SO₄ led to the expansion of microcracks and the reduction of hydration products, which was the root of the decreasing strength of the filling body. Deionized water had almost no effect on the filling body. Most of the existing studies have explored the influence of chemical erosion on the performance of CPGFM by adding acidic or alkaline solutions. However, the pH of mine water is generally lower than that of acid or alkaline solutions.

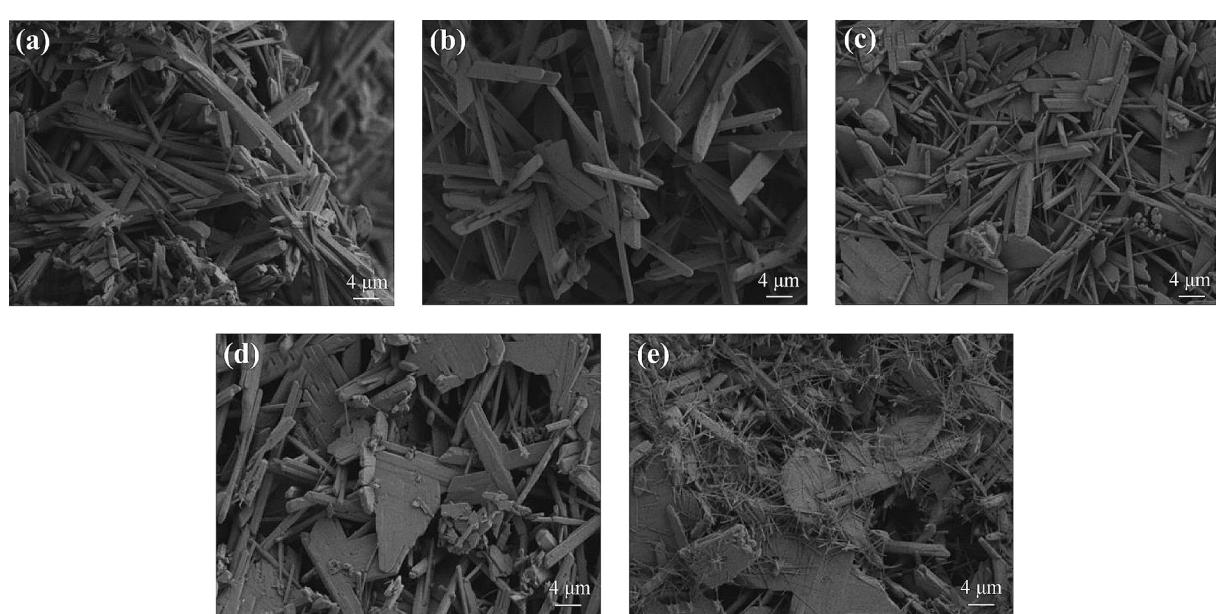


Fig. 6. SEM images of calcium sulfate dihydrate crystals under the effect of different fluorides. (a) Blank; (b) CaF₂; (c) Na₂SiF₆; (d) Na₃AlF₆; (e) NaF (Guo et al., 2023).

2.3.4. Other factors

Chen et al. (2021b) had also found that increasing temperature accelerated the cement hydration reaction and weakened the retarding effect of PG on it. As a result, the early strength of the CPGFM increased, while its later strength fluctuated slightly. He et al. (2019) considered that the flow resistance loss of the CPGFM filling slurry increased with the increasing temperature, but the relative growth rate gradually decreased. Lan et al. (2019a) thought increasing the mixing time can induce the crystal growth to be consistent, which was conducive to the formation of coarse crystal complexes with high crystal contact strength. The mixing behaviour was beneficial for the CPDFM's strength until the mixing time exceeded a certain limit. Therefore, the optimal mixing time should be determined based on the practical conditions. The agitator used in this experiment is different from the large-scale agitator used in the mine. The influence of different mixing time on the slurry performance in the actual filling of the mine should be monitored.

2.4. Control methods for CPGFM properties

2.4.1. Water washing method

Zhou et al. (2022b) revealed that the water washing treatment for PG improved significantly the strength of the CPGFM made of PG and yellow phosphorus slag-based binder, which is because water washing can effectively remove residual acids and other impurities in PG and promote the formation of hydration products (Fig. 7). Liu et al. (2019) found that water washing pretreatment can improve the strength of CPGFM by optimizing the particle size distribution of PG, and the optimal number of water washing times was 11. Moreover, their subsequent research indicated that the CPGFM filling slurry prepared by water washing PG had weaker shear thinning characteristics (Liu et al., 2022c). In the above studies, deionized water was used as the experimental water to prevent the error of the experimental results. However, tap water is mostly used in the preparation of CPGFM.

2.4.2. Modified materials addition

Modified materials, including slaked lime, CaCO_3 , carbide slag, polymeric aluminum chloride, etc., can react with the impurities in PG to improve the working performance of CPGFM. Chen et al. (2019) believed that minor slaked lime induced calcium phosphate precipitate on the surface of HPG particles, hindering the dissolution of HPG particles and the growth of gypsum to form a loose microstructure with fluffy and floccus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals (Fig. 8). Excessive slaked lime caused a tendency for calcium phosphate to precipitate on the surface of slaked lime. Accordingly, fewer calcium phosphate precipitated on the surface of gypsum and HPG particles, leading to the formation of a dense microstructure of long columnar $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals with a high degree of interlocking.

Min et al. (2023a) considered that increasing the $\text{Ca}(\text{OH})_2$ content was good for the strength evolution as a whole (Fig. 9), which was

attributed to the increasing bleeding rate of the filling body and the decreasing porosity. When the $\text{Ca}(\text{OH})_2$ content was 2.2 wt%–3.2 wt%, more water trapped in the filling body converted into pore water, resulting in a decrease in the UCS. In the early curing stages, the changes in hydration degree caused by pretreatment were the main factor that affected the UCS of the filling body. In the later curing stages, changes in structural characteristics caused by pretreatment determined the strength evolution of the filling body.

Shi et al. (2023) found that the Ca^{2+} in CaCO_3 can react with soluble impurities to form insoluble substances, which accelerated the HPG condensation process. The immobilization rate for phosphates and fluorides exceeded 90 % and 99 % respectively at the 18 % CaCO_3 content. Chen et al. (2021c) proposed that the activation effect was more satisfactory when carbide slag and K_2SO_4 were used together. In this case, the increase in the concentration of Ca^{2+} from carbide slag and SO_4^{2-} from carbide slag can produce more $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals, which can cross-link with other parts to improve the CPGFM strength. Zhang (2022b) found that polymeric aluminum chloride can solidify F in PG through its own electrostatic adsorption and ion exchange of F to weaken the retarding effect of PG and improve the strength of CPGFM filling body, but it was bad for the fluidity of the CPGFM slurry due to its adsorption on water molecules. The amount of polymeric aluminum chloride should be determined based on the user preferences. The existing research is only carried out for one kind of PG. The addition amounts of modified materials may vary with the source of PG.

2.4.3. Citric acid leaching method

Citric acid can convert phosphate and fluoride impurities into water-soluble phosphoric acid, sodium citrate, hydrofluoric acid, hydrofluorosilicate, and hydrofluoroaluminate, and ferrate (Singh, 2002), thereby reducing the inhibitory effect of these impurities on the production of hydration products. As a result, a large amount of C-S-H gel and ettringite are interlaced to form a dense network structure, further improving the mechanical performance of the CPGFM filling body. The findings of Zhou et al. supported this conclusion, and they determined that the optimal concentration of citric acid was 4 % and the number of washing was 7–8 (Zhou et al., 2023c). The specific citric acid leaching method is as follows: Dissolve PG with citric acid solution in an environment of $25 \pm 2^\circ\text{C}$, stir for 5 min, then place it on a mechanical vibrating screen to vibrate for 20 min, filter and wash 3 times with distilled water, after that dry filtered PG in an oven at $45 \pm 5^\circ\text{C}$, and then place the PG treated by citric acid in a sealed beaker for later use (Huang et al., 2020b). This method of complex treatment process makes it difficult to implement in the field of mine filling.

2.4.4. Hydrothermal method

Hydrothermal method is a technology that involves material reactions and crystal growth through in aqueous solution systems in a sealed pressure vessel (such as an autoclave) under high temperature

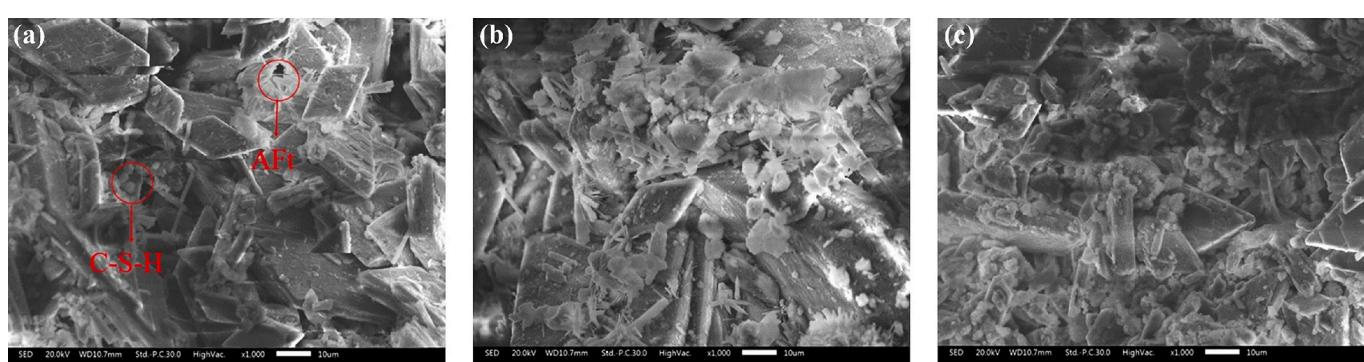


Fig. 7. SEM images of CPGFM filling body: (a) Original PG with pH value of 1.99, (b) PG washed to pH value of 3.50, (c) PG washed to pH value of 5.00 (Zhou et al., 2022b).

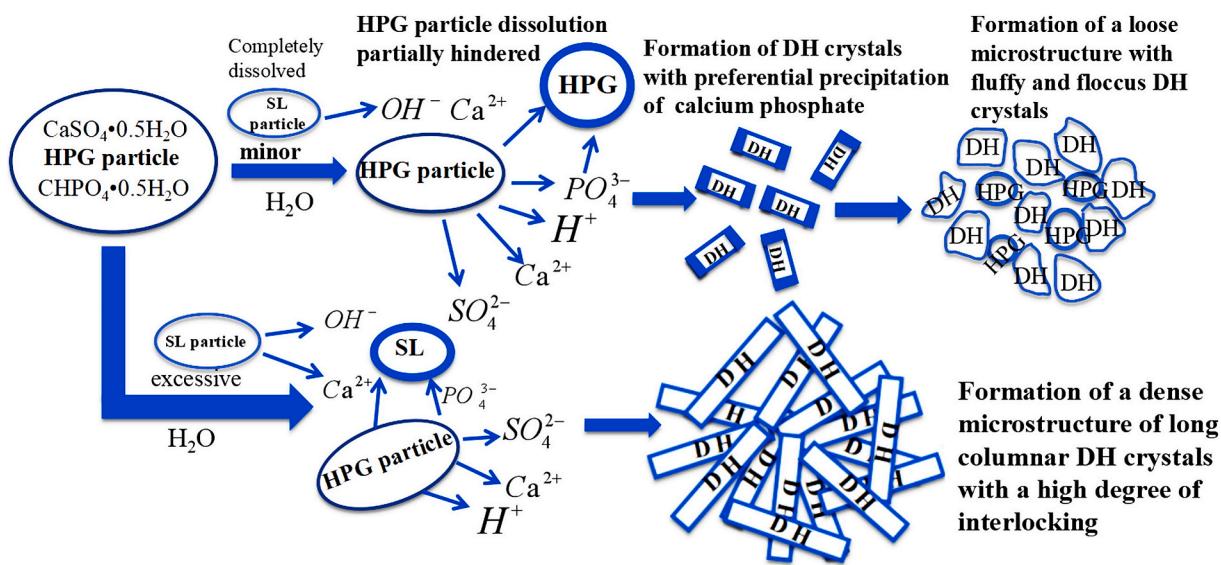


Fig. 8. The hydration mechanism of HPG with addition of slaked lime (SL). DH: CaSO₄·2H₂O (Chen et al., 2019).

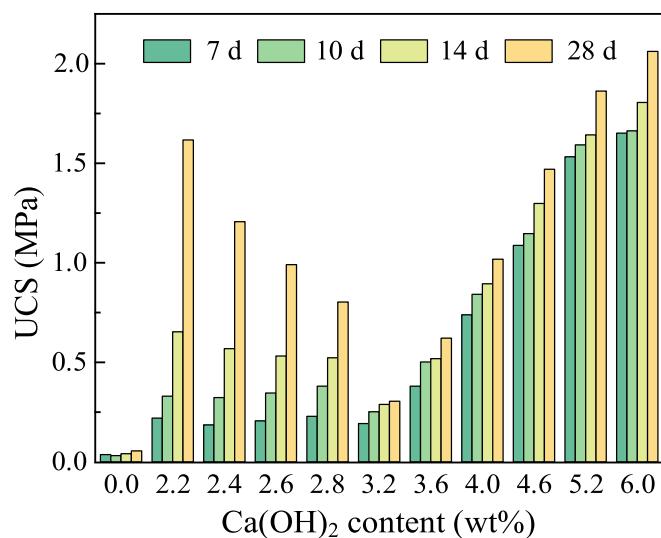


Fig. 9. Variation of UCS of the CPGFM filling body with the Ca(OH)₂ content (Min et al., 2023a).

and high-pressure conditions. The process parameters of the hydrothermal system and mineralizers determine the supersaturation and the solubility of substances in PG, thereby providing the possibility to change the growth habits of PG crystals, and accelerate the nucleation of PG crystals, promote the growth of PG crystals, and neutralize the impurities in PG (Singh and Middendorf, 2007; Yan et al., 2020; Yang, 2006).

Li et al. (2022) found the removal rate of the total organic carbon increased with the increasing mineralizer concentration, temperature, and heating time. The optimal hydrothermal condition was determined by using 0.3 mol/L K₂S₂O₈ as mineralizer and heating at 120 °C for 12 h. As shown in Fig. 10., K₂S₂O₈ generated SO₄²⁻ and OH⁻ free radicals through thermal activation, which contributed to the dissipation of organic pollutants in PG. In addition, during the decomposition process of K₂S₂O₈, the phase transition of calcium sulfate from dihydrate form to anhydrous form played a leading role in the removal of phosphorus, H⁺ and SO₄²⁻. The above study using only one mineralizer is not comparable and practical.

In summary, the water washing method can effectively remove

soluble impurities and organic matter. However, this method has the disadvantages of large one-time investment, high energy consumption, and is easy to produce a large amount of sewage. Citric acid can enhance the impurity removal rate of water washing process, but also significantly increase the cost of the process. The hydrothermal method is efficient in removing impurities, but has limited PG processing capacity and high energy consumption. The modified materials can be added directly during the mixing process of filling materials, which is currently the main way to manage the performance of CPGFM due to the convenience of the process. However, more in-depth work is needed around developing cheaper and more efficient modified materials.

3. Environmental impacts

3.1. Hazardous gases

Zhou et al. (2023b) believed that the hazardous gases were generated during the mixing process of CPGFM slurry due to the reaction between the yellow phosphorus slag and acidic substances. These gases were produced in the following order: PCl₃, PH₃, NO, H₂S, NH₃, CO. CaO can be used to inhibit the gas generation by increasing the alkalinity of the slurry. When 12 % CaO by binder mass was added, the amount of the gas generation decreased by 99 %. In practice, it was necessary to ensure that the pH of the slurry was greater than 10. Li et al. (2018) found that the release of PH₃, H₂S, C₆H₆, SO₂, HF, and CO during the preparation of CPGFM slurry using yellow phosphorus slag and PG exceeded the limits of GBZ 2.1-2019 (2019). Moreover, CaCl₂ or Ca(ClO)₂ was recommended as the oxidizing agents to inhibit these reducing gases generation. Because the Fe-S and Fe-P compounds in the yellow phosphorus slag can react with the acidic substances in PG to generate hazardous PH₃, and H₂S, etc., so the mentioned studies on the hazardous gases mainly focus on the CPGFM with yellow phosphorus slag as binder. In contrast, the release of hazardous gases from the CPGFM without yellow phosphorus slag can be ignored. In practical application, the mixing of yellow phosphorus slag and PG should be avoided.

3.2. Study methods for harmful elements leaching

3.2.1. Destructive leaching test

The leaching behaviour of harmful elements is the core of evaluating the environmental impacts of CPGFM. There are various leaching testing methods as shown in the Table 7, where TCLP and SPLP are abbreviations for Toxicity Characteristic Leaching Procedure and Synthetic

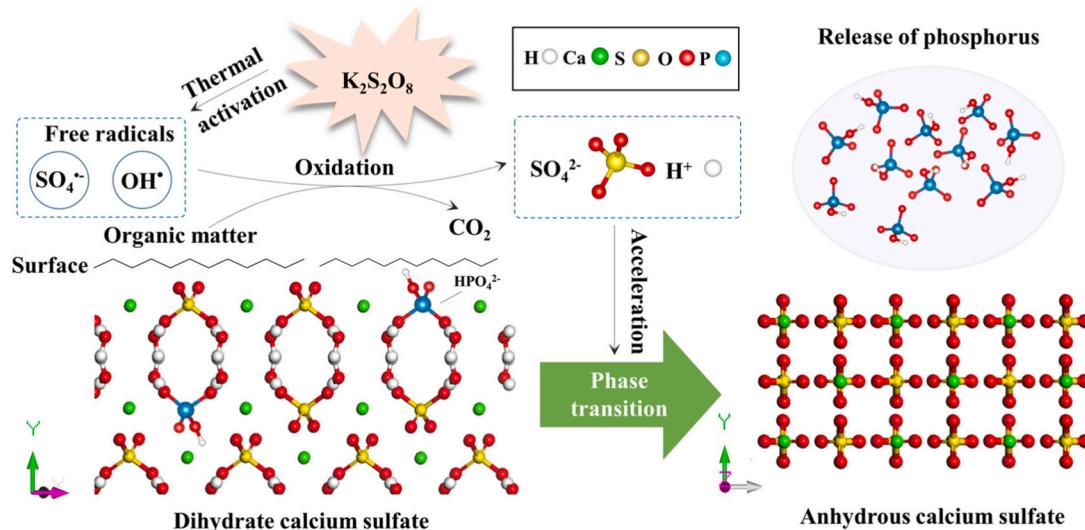


Fig. 10. Removal mechanism of organic matter and phosphorus by hydrothermal method (Li et al., 2022).

Precipitation Leaching Procedure, respectively. As listed, these methods are all destructive. In this case, the centimeter-scale filling body specimen is first broken into millimeter-scale powder, and then acidic solution or deionized water is added as a leachant to extract harmful elements compulsively from the powder in different oscillation modes. In addition, some special leaching methods are also used to evaluate the leaching performance of harmful substances in CPGFM filling bodies. Shi et al. (2018b) used the European Community Bureau of Reference (Ure et al., 1993) sequential extraction procedure to investigate the metal transfer in the CPGFM backfill. Chen et al. (2018a) used the rotary acid leaching procedure to determine the toxicity of metal elements leached from hardened CPGFM into the environment under open-air conditions. This method was revised based on HJ/T 299–2007 (2007) in terms of the use of rotating bottles and the pore size of filter membrane.

The above methods artificially destroy large-scale filling body into fine powder to accelerate the leaching of harmful substances and evaluate their ultimate leaching capabilities. However, these methods are not suitable for studying the natural leaching behaviour of CPGFM backfill under in-situ conditions.

3.2.2. Non-destructive leaching test

Non-destructive leaching tests such as column leaching tests and soaking tests are designed to investigate the leaching patterns of harmful substances in CPGFM filling bodies under in-situ condition. Chen et al. (2023c) used a column leaching instrument to study the immobilization of fluoride in CPGFM filling bodies with calcium aluminum cement as binder. As shown in Fig. 11, the test column has a length of 130 cm, an inner diameter of 10 cm, and a porous plexiglass disk at the bottom. Distilled water was used as the leachant and applied at a constant irrigation speed of 447 mm/day (approximately 2.4 mL/min). The irrigation speed was estimated from the maximum rainfall for 2020 in Tongling City China, where the raw PG was excavated. Lan et al. (2019b) conducted soaking tests to study the leaching behavior of phosphorus and fluorine in the CPGFM filling bodies prepared by HPG. In the test, the cubic specimens with the diameters of 40 cm, 70.7 cm and 150 cm were directly soaked in deionized water. Referring to HJ 557–2010 (2010), the solid-liquid ratio is set to 1:10. It was found that increasing the size of the filling body can delay the leaching of harmful substances under soaking conditions. The non-destructive leaching test can only simulate the effect of groundwater on the leaching of pollutants in the filling body, missing temperature and stress.

3.2.3. Numerical simulation

Numerical simulation can simulate the leaching process of harmful elements by building geochemical models to better understand and predict the complex dynamic characteristics of harmful elements, which avoids long and heavy experimental work. Xu et al. (2023) used chemical equilibrium simulation software Visual MINTEQ to investigate the possible composite substances formed in the PG-copper smelting slag-based filling body under different pH levels. In this case, the distribution of chemical substance morphology in the system was identified based on the leaching concentration of toxic elements. It was believed that excessively high pH was detrimental to the immobilization of harmful substances in the system. In Liu et al. (2022b) work, the United States Geological Survey program Phreeqc was used to determine the mineralogical species that dominated the PG and CPGFM leaching in different solutions. In the PG model, HF, H_3PO_4 and H_2SO_4 were introduced to represent residual acids from industrial processes. In the CPGFM model, the stabilized P and F were assumed to be in the form of $\text{Ca}_3(\text{PO}_4)_2$ and CaF_2 . Portlandite was introduced to simulate the alkalinity of the CPGFM assemblage. The Ca/Si ratio of the C-S-H matrix was assumed to be 1.5, and the dissolution reaction and equilibrium constant is from the literature (Caselles et al., 2021). Zhu et al. (2022) used the simulation software LeachXS to construct a geochemical model to analyse the chemical forms of phosphorus and fluorine elements in the HPG-based filling body. During the geochemical model calculations, the input parameters included: (a) The maximum leaching amount of major and trace elements in the CPGFM in the pH range of 1–14, which referred to the leaching test results at different pH levels. (b) Main mineral composition and chemical reaction equation, which was determined based on the physical and chemical properties of the CPGFM and related publications. Each mine is different, so the model needs to be rebuilt each time when the numerical simulation is conducted.

3.3. Leaching of harmful elements

3.3.1. Phosphorus

In water bodies, excess phosphate will cause eutrophication, which can have an adverse impact on water quality and the health of aquatic animals and plants (Shi et al., 2021). According to GB 8978–1996 (1996), the phosphate concentration should not exceed 0.5 mg/L in the Class I wastewater. The phosphate (reported as P), including PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , is determined according to GB 11893–89 (1989).

Chen et al. (2018a) studied the changes of phosphorus concentration with time in the leachates of PG, construction demolition waste (CDW),

Table 7

Descriptions of various leaching methods.

Method	Applicable conditions	Particle size /mm	Sample quality /g	Leachant	Liquid-solid ratio	Oscillation time /h	Standing time /h	Oscillation mode	Speed /(r/min)	Filter materials
GB 5086.1-1997 (1997)	Identification of leaching toxicity of inorganic pollutants in solid wastes (except cyanide, sulfide and other unstable pollutants) and, environmental impact assessment of hazardous waste storage and disposal facilities	<5	70	Deionized water or distilled water with equivalent purity	10	18	0.5	Overturning oscillation	30 ± 2	0.45 μm microporous filter membrane or medium speed blue ribbon quantitative filter paper
HJ/T 299-2007 (2007)	Identification of leaching toxicity of organic and inorganic substances in solid wastes, to simulate the leaching of hazardous components from waste into the environment under the effect of acid precipitation	<9.5	150–200	Sulphuric acid / nitric acid mixed solution (pH 3.20 ± 0.05)	10	18 ± 2	—	Overturning oscillation	30 ± 2	0.6–0.8 μm glass fiber filter membrane or microporous filter membrane
HJ/T 300-2007 (2007)	Identification of leaching toxicity of organic and inorganic substances (except cyanide) in solid waste, to simulate the leaching of hazardous components from waste into the environment under the effect of landfill leachate	<9.5	75–100	Acetate buffer solution (pH 4.93 ± 0.05)	20	18 ± 2	—	Overturning oscillation	30 ± 2	0.6–0.8 μm glass fiber filter membrane or microporous filter membrane
HJ 557-2010 (2010)	Assess the risk of leaching of inorganic pollutants (except cyanide, sulfide and other unstable pollutants) in solid waste under the action of surface water or groundwater	<3	100	Purified water	10	8	16	Horizontal oscillation	110 ± 10/ min	0.45 μm microporous filter membrane
SW-846 Test Method 1311 (1992) (TCLP)	Determination of the mobility of organic and inorganic analytes present in liquid, solid, and multiphase wastes	<9.5	100	Acetic acid solution or sodium acetate buffer solution (pH 2.88/4.93 ± 0.05)	20	18 ± 2	—	Overturning oscillation	30 ± 2	0.6–0.8 μm glass fiber filter membrane
SW-846 Test Method 1312 (1994) (SPLP)	Determination of the mobility of organic and inorganic analytes present in liquids, soils, and wastes	<10	100	Sulphuric acid / nitric acid mixed solution (pH 4.20/5.00 ± 0.05)	20	18 ± 2	—	Overturning oscillation	30 ± 2	0.6–0.8 μm glass fiber filter membrane
BS EN 12457 (2002)	Waste and sludge with high solid content (>33 % dry matter)	<4	175 ± 5	Deionized water	2 8	6 ± 0.5 18 ± 0.5	15 ± 5	Overturning oscillation	5–10 10	0.45 μm filter membrane

and PG and CDW-based backfill. As shown in Fig. 12, the CPGFM reduced the phosphorus concentration from 41.32 mg/L in PG to 0.35 mg/L, which was because Ca^{2+} can quickly react with PO_4^{3-} and HPO_4^{2-} to generate $\text{Ca}_3(\text{PO}_4)_2$ and CaHPO_4 , as shown in Eqs. (8) and (9).



Li et al. (2017) found that the total soluble phosphorus had a very high concentration in the PG leachates based on dynamic leaching tests and SPLP. After adding the cementitious material prepared by ordinary Portland cement, fly ash, yellow phosphorus waste, and lime, the concentration of total soluble phosphorus dropped rapidly to below 100 mg/L within 5 min. In this process, the soluble phosphorus precipitated as $\text{Ca}_3(\text{PO}_4)_2$ and/or $\text{Ca}(\text{HPO}_4)$. As the mixing time extended, the concentration of total soluble phosphorus gradually decreased until they reached a value of less than 2 mg/L after 8 h. Liu et al. (2022b)

considered that H_3PO_4 , H_2PO_4 , and CaH_2PO_4 were the main controlled forms of phosphorus in the leachates when pH value was less than 5. In a neutral environment, phosphate existed in the form of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. The optimal pH level for pollutant immobilization was 10–13, when $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ were the main phosphorus forms. Zhu et al. (2022) used a semi-dynamic leaching simulation test to simulate the long-term release and migration characteristics of phosphorus in the HPG-based filling bodies. It was found that the leaching concentration of phosphorus did not change significantly after the backfill experienced long-term leaching, mainly because the proportion of fluorapatite was stable found when the content of quicklime exceeded 1 % at a soluble phosphorus level of less than 0.52 %, the leaching concentration of phosphorus can be kept below 0.5 mg/L. In different in-situ groundwater leaching environments, the phosphorus concentration in the leachate was lower than 0.08 mg/L. Chen et al. (2021b) found that temperature can affect the generation and growth of hydration products, resulting in the differences in the leaching rate of

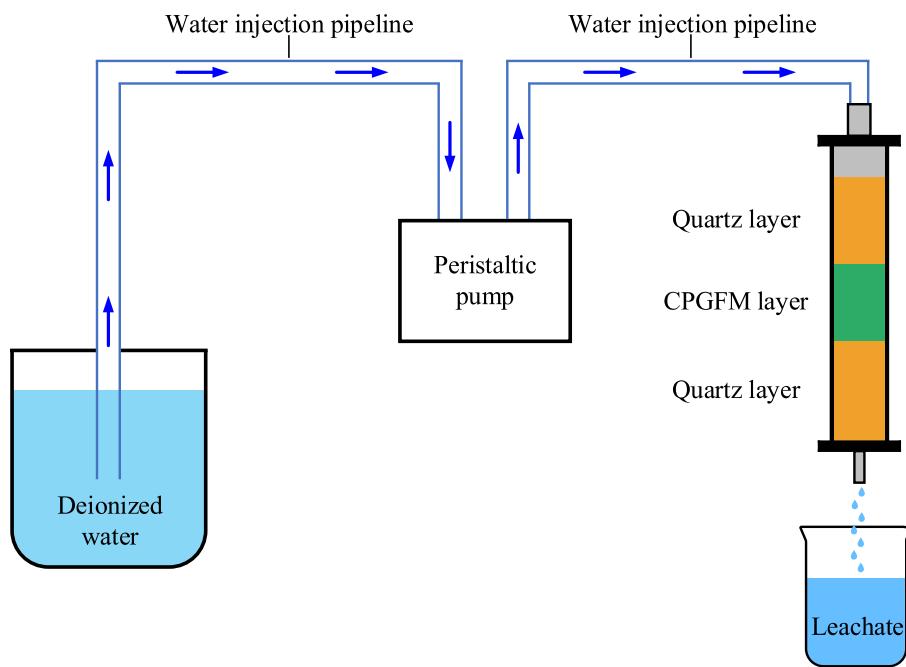


Fig. 11. The schematic diagram of the column leaching instrument (Chen et al., 2023c).

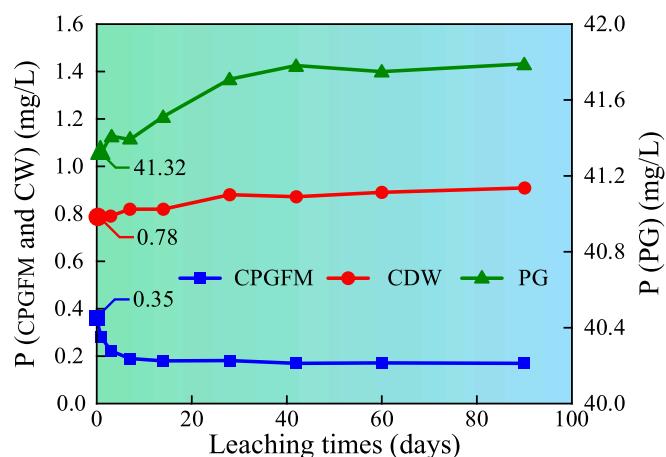


Fig. 12. Variation of P content in the leachates of PG, CDW and CPGFM with leaching time (Chen et al., 2018a).

harmful substances. The leaching amount of phosphorus first decreased and then slightly increased with the increasing curing temperature, while the leaching amount of fluoride was inversely proportional to the curing temperature. In practice, it is necessary to pay attention to the changes in ambient temperature. Zhou (2022a) gave some insights into the influence of underground environment on the dynamic leaching of phosphorus through drying-wetting cycles tests. They considered that H^+ in acidic solution promoted the release of phosphorus in the CPGFM backfill. Under high salinity conditions, the destruction of PG crystals by recrystallization only resulted in the release of trace amounts of eutectic phosphorus and had little effect on the immobilization of phosphorus. The existing research focuses on the influence of single physical field on phosphorus leaching, while the filling body is actually in the underground environment under the coupling of multiple physical fields.

3.3.2. Fluorine

Fluorine can be transferred from stacked PG to surrounding soil and water, and eventually enter the food chain, causing neurological defects,

nervous system damage, chronic poisoning and cancer in humans (Adimilla et al., 2020; Jiang et al., 2019b). Fluorine is mainly derived from fluorapatite, and most of which is volatilized in the form of HF gas. Some residual fluorine in the PG easily migrates into the surrounding environment. According to GB 8978–1996 (1996), the fluoride concentration should not exceed 10 mg/L in the Class I wastewater. The fluoride (reported as F^-) concentration was determined according to GB 7484–87 (1987).

Chen et al. (2018a) studied the variation of F^- concentration over time in the leachates of PG, CDW, and PG and CDW-based backfill. As shown in Fig. 13, the highest F^- concentration in the leachates of CPGFM backfill was 0.88 mg/L, while the F^- contents in the leachates of PG and CDW were 18.49 mg/L and 1.18 mg/L respectively at the leaching times of 7 days and 28 days. F^- can be effectively immobilized during the formation of CaF_2 precipitates in the CPGFM backfill (Eq. (10)).



Li et al. (2017) concluded that F^- concentration in the PG leachates

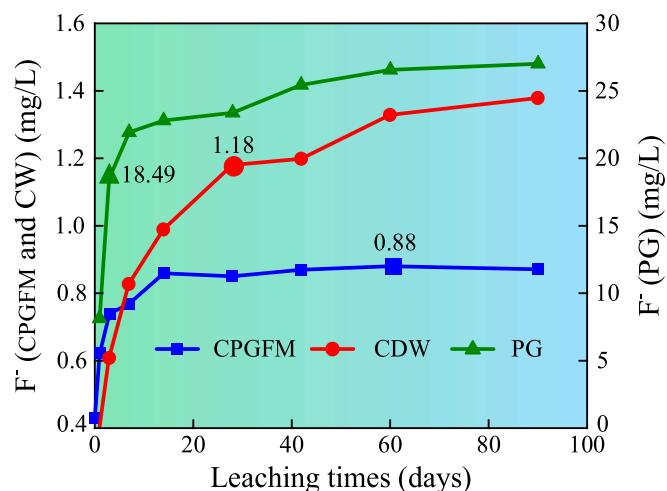


Fig. 13. Variation of F^- content in the leachates of PG, CDW and CPGFM with leaching time (Chen et al., 2018a).

was approximately 32 mg/L after leaching for more than 24 h. When PG was mixed with the cementitious material, more than 75 % of soluble fluorine was immobilized, and the F⁻ concentration in the leachates was kept below 10 mg/L. Liu et al. (2022b) considered that when the pH was less than 5, fluorine mainly existed in the form of Al-F complex. After that, fluorine was immobilized gradually in the form of CaF₂ and Ca₁₀(PO₄)₆F₂ precipitates. When the pH was more than 10, the leaching behaviour of fluorine was discussed from two aspects. On the one hand, the increasing F⁻ concentration in the leachate with pH of 11–13.5 was mainly attributed to the dissolution of Ca₁₀(PO₄)₆F₂. On the other hand, the soluble fluorine can be adsorbed onto C-S-H matrix binding sites and no ion exchange between F⁻ and OH⁻ took place, which caused the F⁻ concentration decrease. Zhu et al. (2022) thought that the leaching behaviour of F⁻ was controlled by fluorite and fluorapatite. After long-term leaching, and the proportion of fluorite decreased from 95 % to 90 %, accompanied by the increasing F⁻ concentration. Jiang et al. (2024) believed that the equilibrium concentrations of F⁻ reached 7.814 mg/L and 7.005 mg/L respectively under the closed dynamic leaching and closed static leaching conditions. The fluorine immobilization had a priority as the phosphorus immobilization was relatively easy. Li et al. (2023b) studied the immobilization of fluorine in CPGFM backfill by adding soluble NaF and insoluble CaF₂. As shown in Fig. 14, PG can only temporarily immobilize fluoride through Ca-F precipitation. Once the yellow phosphorus slag-based binder was added, the stabilized fluorine was re-released into the filling slurry with the increasing pH value. They considered that fluorine should be removed in advance or Ca-F precipitates should be replaced with other low-solubility forms when PG was used as aggregate for cemented paste backfill. The difference between the added fluoride and the fluoride in PG may lead to unreasonable results. Simultaneously, the addition of other materials in CPGFM affects the pH, which in turn affects the existence form of fluorine. There is a risk of secondary release of fluorine, which is difficult to control by the methods used in the existing research.

3.3.3. Heavy metal

The heavy metal elements in PG come from phosphate rock. Once heavy metal elements in PG enter the food chain, it can cause chronic poisoning, kidney failure, etc. in humans (Xu et al., 2018). Under the cementation of the cementing material, the heavy metal elements exist

in CPGFM filling body in different chemical forms (Li et al., 2010). When the filling body is exposed to the leaching and soaking of groundwater, these heavy metal contaminants have a risk of migrating into the water body in the filling area.

Li et al. (2017) thought that due to the immobilization of the cementitious matrix, heavy metal ions were rarely detected in the leachates of the CPGFM filling body. The leaching concentrations of heavy metal ions in the filling body with different curing ages can meet the requirements of DZ/T 0290-2015 (2015) according to the SPLP tests. Shi et al. (2018b) found that the heavy metals from PG and binder can be effectively solidified into the CPGFM backfill. The leaching concentrations of heavy metals did not change significantly with the extension of leaching time. In summary, the immobilization of toxic metal ions in the CPGFM backfill mainly roots in physical adsorption and chemical combination, as shown in Fig. 15. The physical adsorption depends on the attraction between molecules (Van der Waals force). The chemical combination attributes to the formation of stable chemical bonds between harmful ions and hydration products, which is generally related to the amount of hydration products (Yao et al., 2012). Toxic ions react with Ca²⁺, OH⁻ and other ions to form precipitates (Cd(OH)₂). Simultaneously, toxic and harmful elements enter the hydration products through ion exchange (Chen and Wu, 2025). For example, Pb²⁺, Cu²⁺ and Zn²⁺ may replace Ca²⁺ in C-S-H; Cr³⁺ may replace Si⁴⁺ in C-S-H and balance the potential with other ions; F⁻ can also replace OH⁻ in C-S-H. Chemical combination has a stronger solidification/stabilization effect than physical adsorption. In addition, the encapsulation by interlacing AFt and C-S-H gels to form a dense network structure during the solidification of the CPGFM backfill is also beneficial for the immobilization of toxic and harmful elements (Wang, 2004).

Most of the pollutants carried by PG are fixed under cementation, but some of the pollutants may be enter the groundwater under leaching/soaking of mine water. Pollutants that enter groundwater have an impact on the growth of plants and animals in water bodies. Further, polluted groundwater, plants or animals may pose a threat to human health after drinking or eating. In order to stabilize/immobilize pollutants, researchers have carried out extensive experiments to explore control measures to stabilize/immobilize pollutants.

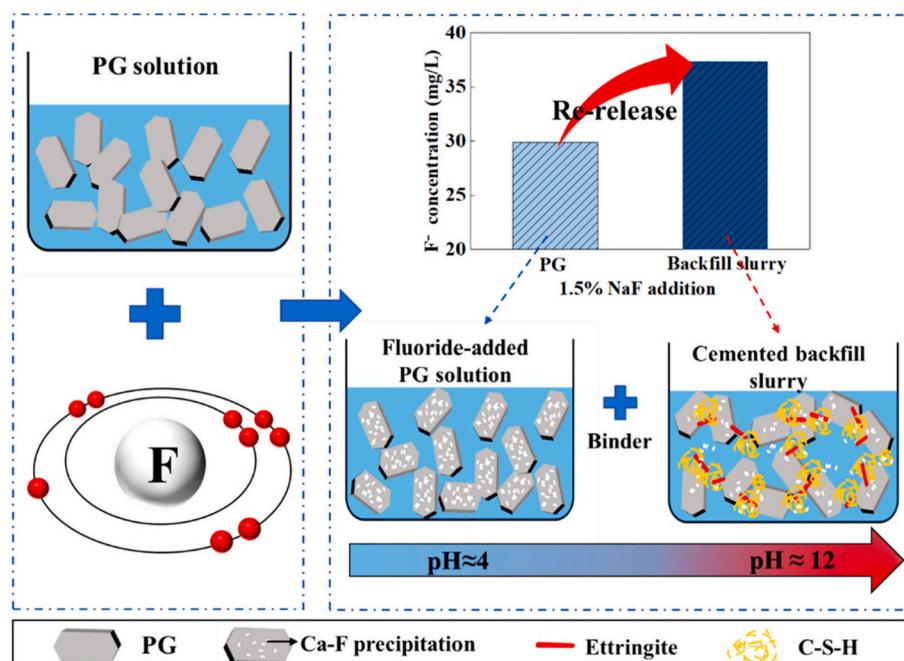


Fig. 14. Fluorine re-release in the CPGFM filling slurry (Li et al., 2023b).

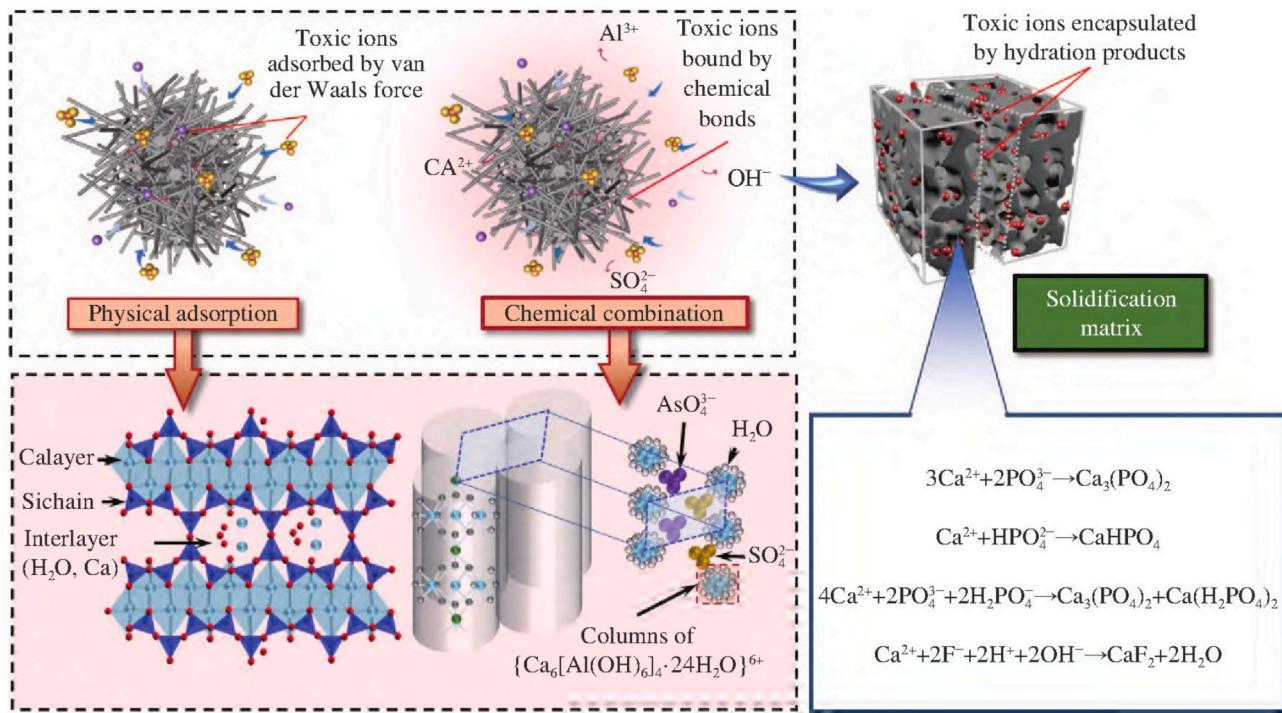
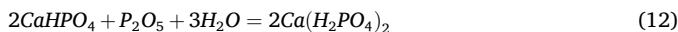


Fig. 15. Schematic diagram of immobilization of toxic metal ions by the CPGFM backfill (Chen and Wu, 2025).

3.4. Control measures

3.4.1. Alkali treatment

Quicklime, slaked lime, calcium hydroxide, sodium hydroxide and other alkaline additives are often used to control the migration of phosphorus. When quicklime is used as a modifier, the forms of reactants depend on the contents of quicklime and P₂O₅. When CaO and P₂O₅ react completely, the reactant exists as insoluble Ca₃(PO₄)₂ with excellent phosphorus immobilization (Eq. (2)). When P₂O₅ is excessive, the reactant is in the form of CaHPO₄ with increasing solubility (Eq. (11)). As P₂O₅ continues to increase, the insoluble reactants gradually transform into the soluble Ca(H₂PO₄)₂ (Eq. (12)). Jiang et al. (2020) calculated the theoretical amount of quicklime required to eliminate soluble P₂O₅ and F⁻ based on Eqs. (13)–(14).



$$w'_{\text{P}_2\text{O}_5} = 168w_{\text{P}_2\text{O}_5}/142w_a \quad (13)$$

$$w'_{\text{F}^-} = 56w_{\text{F}^-}/38w_a \quad (14)$$

where: $w_{\text{P}_2\text{O}_5}$, w_{F^-} , w_a are soluble P₂O₅ content, F⁻ content and effective calcium content of quicklime, respectively.

Zhang et al. (2023c) used calcium hydroxide to immobilize soluble phosphorus impurities in PG. The immobilization rates of soluble phosphorus were 0 %, 66 %, 67 %, and 68 % respectively at the mass fractions of calcium hydroxide solution of 0 %, 0.05 %, 0.10 %, and 0.15 %. The optimal concentration of the calcium hydroxide solution was determined to be 0.05 %. Chen et al. (2023b) found that NaOH can weaken the inhibition of phosphate and fluoride on the early hydration of binders due to the formation of Ca₃(PO₄)₂ and CaF₂. They believed that Ca₃(PO₄)₂ was relatively stable under alkaline conditions, but when the pH value exceeded 10, the stability of CaF₂ decreased and more F⁻ was released. That is to say, alkali treatment is good for managing the phosphate pollution, but its role in the fluorine immobilization is

limited.

3.4.2. Aluminate materials

Considering the limited immobilization of alkaline materials on fluorine, the addition of aluminate materials is an alternative solution to the fluorine pollution. The common aluminate materials include calcium aluminate cement, γ -Al₂O₃, polymeric aluminum chloride, etc. Chen et al. (2023c) revealed the immobilization of fluorine by calcium aluminate cement under torrential rainfall conditions. As shown in Fig. 16, fluoride retention in hardened CPGFM mixtures can mainly be attributed to the formation of Ca/Al-F complexes and their adsorption onto the surfaces of amorphous aluminates and calcium aluminate hydrates. Liu et al. (2022a) concluded the incorporation of γ -Al₂O₃ promoted the precipitation of AFt and induced the formation of aluminum-containing amorphous phases. The addition of γ -Al₂O₃ increased the fluorine retention capacity, but it was less dominant in phosphorus immobilization. In addition, using γ -Al₂O₃ to partially replace cement can reduce total CO₂ emissions by about 35 %. Polymeric aluminum chloride was an alternative additive to the fluorine immobilization due to its excellent electrostatic adsorption, and can promote the generation of C-S-H gels. The fluorine immobilization was attributed to the ion exchange between OH⁻ and F⁻ (Chen et al., 2022; Zhang, 2022b). When the concentration of polymeric aluminum chloride increased to 2.0 g/L, the F⁻ concentration in the leachates of CPGFM specimens decreased by 23.64 %. The addition of aluminate materials with poor immobilization on phosphate in CPGFM increases the filling cost obviously.

3.4.3. Incorporated mineral materials

Incorporating iron tailings or modified quartz sand into CPGFM can hinder the migration of phosphorus by monolayer chemical adsorption (Shi et al., 2021; Shi et al., 2022). When the iron tailings were incorporated into the CPGFM, it took 15 min to ensure the phosphate concentration in bleeding water below 0.5 mg/L, while the duration in the CPGFM with the addition of modified quartz sand was 20 min. The balance between phosphorus immobilization and additional expenditures required further discussion when the two mentioned materials were added. Scholars have explored the use of granulated blast furnace

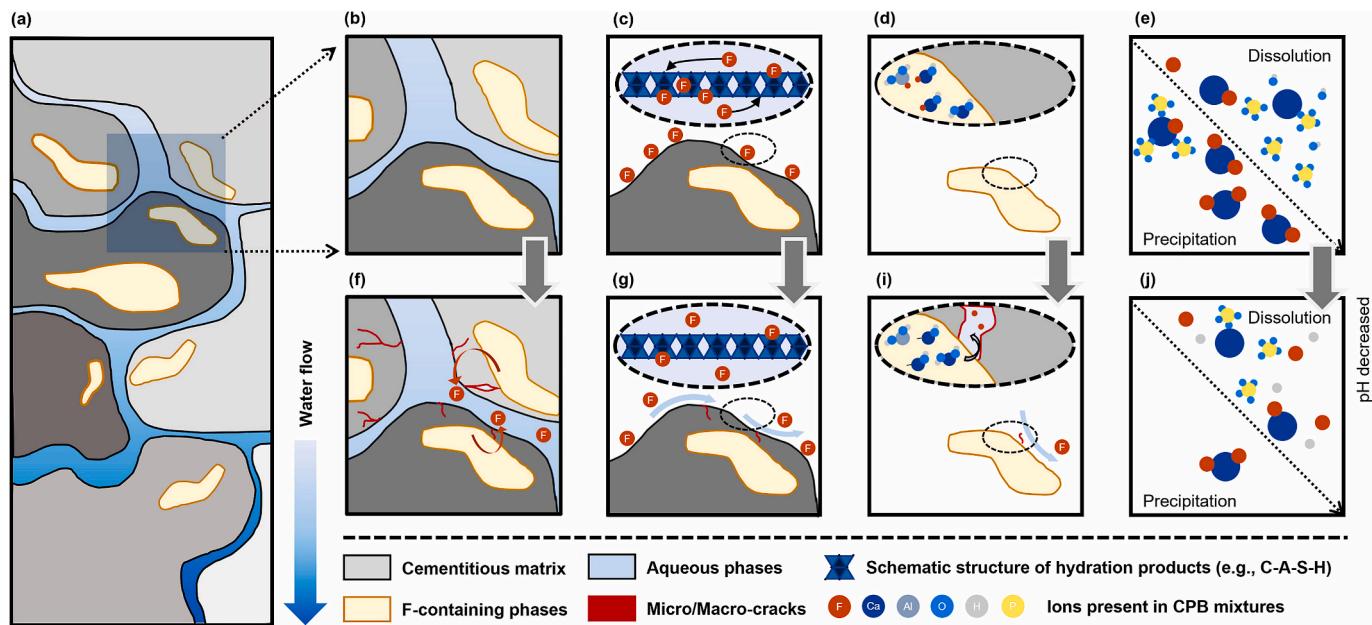


Fig. 16. Fluoride retention and release mechanisms in CPGFM mixtures. (a) the porous structure of hardened CPGFM mixtures, (b) the physical encapsulation of fluoride-bearing phases, (c) the adsorption of fluoride onto the surface of hydration products, (d) the co-precipitation of fluoride with other phases and/or incorporation of fluoride into their crystal structures, (e) the precipitation-dissolution equilibrium of fluoride minerals, (f-j) the changes of correlated fluoride immobilization mechanisms after the column leaching (Chen et al., 2023c).

slag to replace part/all of ordinary Portland cement to control phosphate and fluoride pollution (Chen et al., 2023b; Oguz, 2004). After the addition of ground granulated blast furnace slag, more hydration products were generated, and a new amorphous phase (C-A-S-H) was identified. C-A-S-H gel can effectively immobilize phosphorus and

fluorine through adsorption, incorporation, or encapsulation (Chen et al., 2023b). There are many kinds of mineral materials, but finding universal solid waste is crucial.

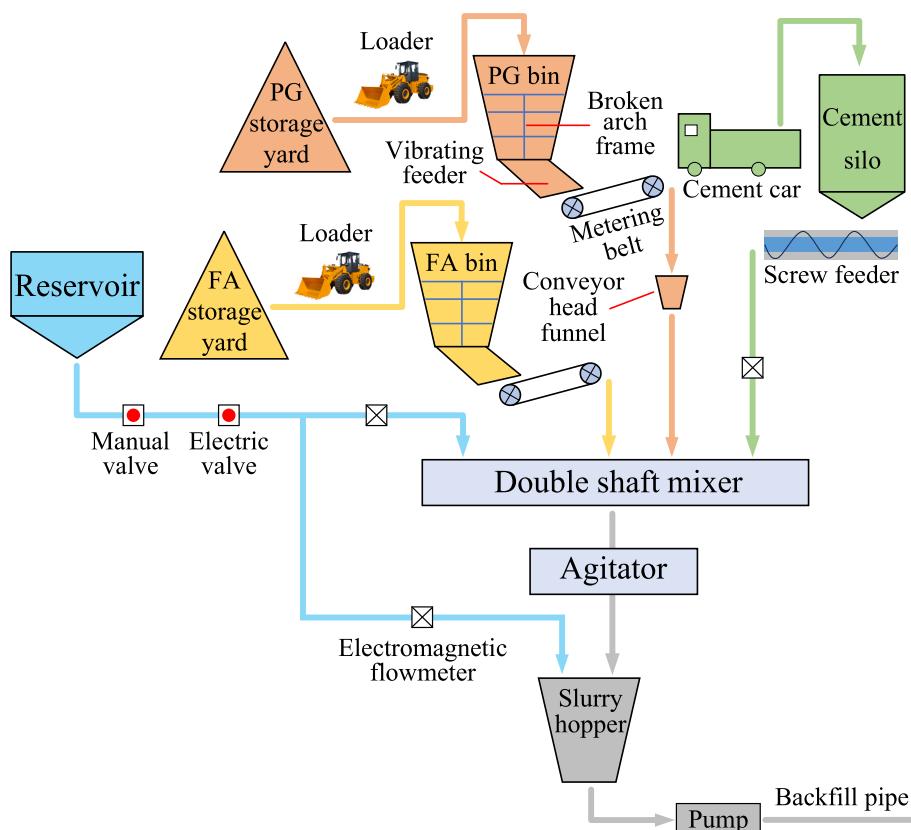


Fig. 17. Schematic diagram of CPGB process in Kaiyang Phosphate Mine (Li et al., 2018).

4. Cases for cemented PG backfill

4.1. CPGB in Kaiyang phosphate mine

Phosphorus chemical plants affiliated to the Guizhou Kailin Group in China produce up to 3.4 million tons of PG and other phosphorus waste annually, which are stored directly on land with a management cost of 12.5 CNY/m³ per year (Dang et al., 2013; Shi et al., 2018b). In the face of environmental and economic issues, Kailin Group attempted to use CPGB technology to treat the goafs in Kaiyang Phosphate Mine affiliated to this company. The CPGFM was prepared by cement, fly ash and PG with 1:1: (4–8) of cement: fly ash: PG and 60 wt%–63 wt% of concentration. In this case, the bleeding rate of the CPGFM slurry is 5.45 %, and the UCS of hardened CPGFM can reach 1.5–2.0 MPa after curing for 14 days (Li et al., 2018; Yao, 2009). The mechanical properties of the filling body were determined by sampling with a core drilling equipment at the curing time of 6 years, when the UCS reached 7 MPa, and the tensile strength was 0.778 MPa (Li et al., 2018).

The schematic diagram of the CPGB process is shown in Fig. 17. PG and fly ash are first transported to the PG/fly ash yard by truck, then shoveled into the intermediate bin by a loader. Then, the PG/fly ash is broken up by the arch frame, and transported into a double-shaft horizontal mixer by the vibrating feeder and the belt conveyor. At the same time, the cement purchased from the market is transported into the silo through compressed air. The weighed PG, cement, fly ash and water are mixed in the mixer and an agitator to form the CPGFM filling slurry. Finally, the slurry is transported to the underground goaf by gravity (Li et al., 2018). Due to the high proportion of PG in the CPGFM, the CPGB technology can utilize the PG in a large-scale and green way. The CPGB has long been applied to all ore blocks affiliated to Kaiyang Phosphate Mine, including Maluping Ore Block, Yongshaba Ore Block and Qing-caichong Ore Block. This technology has increased the recovery rate of ore from 70 % to 90 % with an annual increase in profits of 200 million yuan per year (Dang et al., 2013; Shi, 2018a; Zhou, 2022a). In addition, it has saved 5000 million yuan per year in expenses for land acquisition, dam construction, anti-seepage treatment and waste management (Dang et al., 2013). Nevertheless, this technology still uses a large amount of cement, and the filling cost is high. It is necessary to develop new

cementing materials as soon as possible.

4.2. Combined goaf backfill and open-pit restoration by HPG in Fulin phosphate mine

Guizhou Chanheng Group produces 1.5 million tons of HPG and 500,000 tons of phosphorus tailings every year. In this case, the existing PG storage yard will reach its maximum capacity in 2021. To protect land resources, authorities no longer approve new PG storage yards. Moreover, the local government has issued the policy that the production capacity of phosphoric acid depends on the consumption of PG to force phosphorus chemical plants to improve the utilization rate of PG. In the face of the increasingly prominent environmental regulations, Chanheng began to develop CPGFM with HPG used as binder in 2015. After years of efforts, the combined goaf backfill and open-pit restoration based on HPG has been established around the preparation of CPGFM, HPG conversion control, design of special equipment for HPG filling, and has been successfully applied to the Fulin Phosphate Mine (Jiang et al., 2025). This technology prepares the CPGFM slurry with 40 %–62 % HPG, 1 %–3 % alkaline agent, 0 %–30 % phosphorus tailing, 0.3 %–0.9 % admixture, and 28 %–35 % water at the preparation station. As shown in Fig. 18, the CPGFM with a UCS of more than 0.2 MPa is used for underground goaf backfill, otherwise it is used for the ecological restoration of open pit. Even considering the transportation of HPG, the purchase of alkaline agent and admixtures, the cost of the CPGFM is still 20 % to 50 % cheaper than that of cement-based filling materials with the same 3-day strength. The mine can consume more than 60 % of the annual production of PG by Chanheng, providing a satisfactory solution for the efficient utilization of PG. However, only a few phosphating chemical plants produce HPG, which has caused greater obstacles to the promotion and utilization of HPG nationwide.

4.3. Utilization of CPGFM in Qingping phosphate mine

The Qingping Phosphate Mine is a large-scale phosphate ore base in Sichuan Province, China. The ammonium phosphate plant affiliated to Qingping Phosphate Mine produces about 500,000 tons of PG annually (Shi, 2018a). To extend the life of the PG yard, Qingping Phosphate

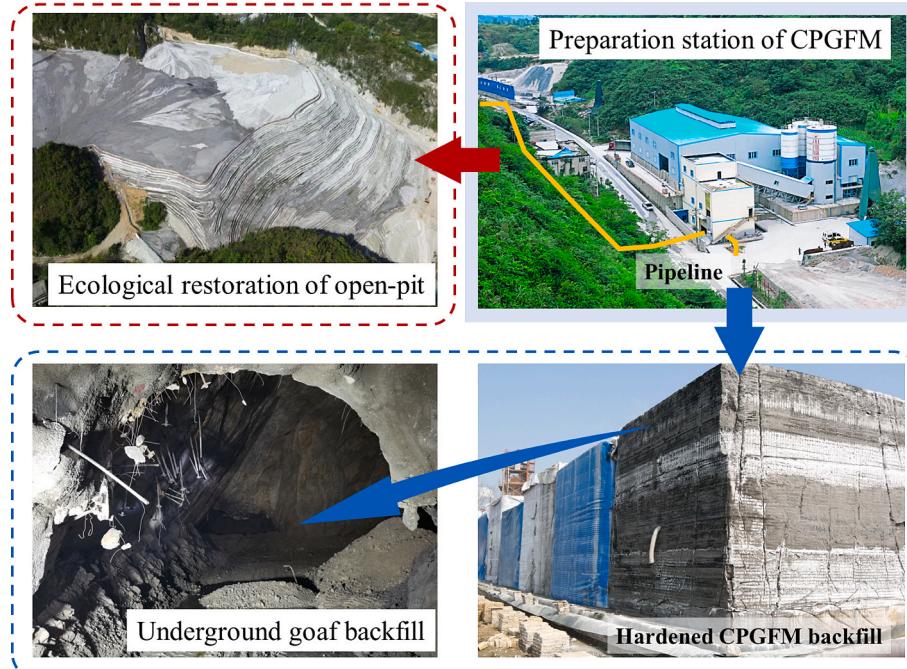


Fig. 18. Schematic diagram of combined goaf backfill and open-pit restoration technology by HPG.

Mine attempts to use PG for underground goaf backfill. The strength of CPGFM with 35 % fly ash, 10 % cement, 4 % lime, and 51 % PG is more than 1.5 MPa for 7 days, 2.5 MPa for 14 days. At this time, the slurry concentration is 60 wt% with a fluidity of 21.3 cm. Compared with original cement-based filling materials, the CPGFM has better economic and technical benefits (Liu et al., 2022d). In practice, PG is stored temporarily in the stacking yard, then fed by a loader to the crushing equipment. After that, the scattered PG is discharged to the feeding belt by a vibrating machine, and transported to a mixer after being weighed. Cement, quicklime, and fly ash are stored in the silo, and then are mixed with PG and water to prepare a CPGFM slurry according to the designed formulation. A gravity conveying pipeline is designed to avoid excessive energy consumption. The usage of PG in the filling of Qingping Phosphate Mine is relatively low. New CPGFM should be developed to accelerate the utilization of PG.

5. The development trend of CPGB in China

5.1. Challenges

5.1.1. PG quality management

Due to differences in ore sources, production process parameters, and storage time, the quality of PG varies with its origins and batches. Therefore, strict quality management standards for PG must be established to ensure that the PG can meet filling requirements. In most cases, PG is produced by phosphate chemical plants, but applied to the phosphate mine. The management of PG quality depends on whether the plant and the mine can establish an effective two-way communication mechanism, which is often troublesome for managers.

5.1.2. Cost control

In order to compensate for the deterioration of the impurities on CPGFM and control potential environmental pollution, it is often necessary to incorporate more cementitious materials or modified materials, and pre-treat PG, resulting in an obvious increase in the cost of CPGFM. In general, phosphorus chemical plants and phosphate mines are located separately, the transport cost is also an important consideration in the economic analysis of CPGFM at this time.

5.1.3. Durability studies

The good durability of CPGFM filling body is the basis for long-term prevention of deformation and failure of goaf surrounding rock and ensuring the safety of underground operations. PG is mainly composed of slightly soluble calcium sulfate dihydrate. The strength evolution of the CPGFM filling body has not been uncovered validly under the coupling effect of cementitious material hydration and groundwater seepage. In this case, the durability of the filling body is unpredictable, leading to serious safety hazards in underground mining activities.

5.1.4. Fluorine immobilization

Because F has a strong non-metallic property and easily combines with metal cations such as Na^+ and K^+ to form water-soluble NaF , KF , etc., it is more difficult to immobilize F than P. When attempting to immobilize F using alkaline materials, the surface of $\text{Ca}(\text{OH})_2$ particles is easily wrapped by the generated CaF_2 precipitates, resulting in the inability of $\text{Ca}(\text{OH})_2$ to fully react with F. Aluminate materials or other mineral materials can immobilize F effectively, but there is still a lot of work to be done in terms of balancing the increasing materials cost and the immobilization rate of F.

5.1.5. PG supply

In the process of transporting and feeding PG with wheeled equipment, many uncertainties, such as untimely PG scheduling, unskilled workers, and equipment failures, can easily break down the continuous and efficient supply of raw materials. The increasing difficulty in discharging PG with high humidity has also a significant adverse effect on

the filling efficiency. In addition, the management of PG production tends to be extensive, when rocks, steel bars or other large-sized debris are often mixed into the PG. The filling process must be interrupted to remove these debris.

5.2. Prospects

5.2.1. PG quality evaluation and control methods

The current study ignores the effect of PG quality (chemical composition and gelling activity) fluctuations on the performance of CPGFM, reducing the generalizability of the research results. PG with stable quality is an important prerequisite for the promotion of CPGFM. Therefore, it is necessary to establish a PG quality evaluation and control method for the whole process from ore quality to phosphoric acid production to PG transportation.

5.2.2. New CPGFM development

The hot topic in the development of CPGFM has been cost reduction and performance improvement. New CPGFM with the advantages of high early strength, low filling costs and high PG utilization rate will be prepared by selecting appropriate mineral admixtures and modifiers, and accurately designing the formulation of filling material. At the same time, it is considered to introduce amorphous phase water-condensing agent, vapor phase introducer and surface water repellent agent to improve the durability of the CPGFM backfill.

5.2.3. Efficient fluorine immobilization methods

Addition of modifiers is usually used to immobilize the harmful elements in the CPGFM backfill. However, the method is not very effective in controlling fluoride, and may also cause fluorine to be released into the environment again due to changes in the environment. The development of new efficient fluorine immobilization methods, such as ion exchange resins, coagulation and sedimentation, and biological methods, is a promising trend for CPGB technology.

5.2.4. PG continuous feeding technology

PG continuous feeding is an important concern for the development of CPGB technology. On the one hand, it is necessary to develop special feeding equipment to solve the problem of high humidity PG discharge. On the other hand, the intelligent control technology should be developed to avoid operation errors, when a PG transportation scheduling program is designed to realize real-time monitoring and intelligent adjustment of PG transportation and feeding parameters.

5.2.5. CPGFM formula optimization based on machine learning

The CPGFM formula must be designed based on the specific conditions of the mine due to its non-replicability. It is time-consuming and labor-intensive to optimize the CPGFM formula by manual operation. Machine learning uses algorithms to learn laws, patterns, and trends from a given dataset and make predictions or decisions based on them. In the future, machine learning technology can find out the key variables affecting the CPGFM performance faster and more accurately, and dynamically adjust the CPGFM formula to achieve the goals of reducing costs and environmental protection.

5.2.6. Integrated mine and chemical plant production mode

The “integrated mine and chemical plant” production mode is a circular economy mode that closely integrates mining, ore dressing, smelting, and chemical production to maximize the use of resources and minimize environmental pollution. In this case, mines and chemical plants are not only built adjacent to each other, but also deeply coupled in terms of industrial chain, resource utilization, and environmental protection treatment. As a result, the problems of continuous PG feeding, economic PG transportation, and PG quality control will be addressed properly. This mode can create greater economic benefits and social value for enterprises, and promote the transformation of the

industry towards sustainable development mode.

5.2.7. CO₂ mineralization and storage

With the rapid development of the economy, the emission of greenhouse gas CO₂ has increased sharply. The greenhouse effect caused by excessive CO₂ emissions seriously threatens the human living environment. The use of CPGFM to mineralize and physically store CO₂ is a positive exploration of new PG utilization ways, and can make a beneficial contribution to reducing carbon emissions.

6. Conclusion

The environmental problems caused by the large-scale storage of PG has always been troubling. The CPGB technology can achieve efficient PG utilization and effective goaf treatment. At present, the CPGB technology has been applied in dozens of mines in China. In view of this, this paper reviews the preparation, performance control, environmental impact and application status of CPGFM, while looking forward to the thorny technical challenges and the potential development directions.

In view of the rich reserves and the appropriate properties, PG can be used as aggregates, cementitious materials, and cementitious material components for the mass production of CPGFM. However, phosphates, fluorides, and other components in PG as well as external chemical corrosion issue have a harmful impact on the CPGFM performance. The CPGFM performance can be improved through water washing, modified materials addition, citric acid leaching, and hydrothermal methods. Harmful elements such as phosphorus, fluorine, and heavy metals will be released under the action of groundwater. In this regard, the control measures such as alkali treatment, aluminate system and mineral materials addition are discussed to reduce the leaching of harmful elements and ensure environmental safety. Representative cases such as Kaiyang Phosphate Mine, Fulin Phosphate Mine and Qingping Phosphate Mine are introduced to demonstrate the different filling paths of PG in China.

CPGM contains various solid wastes including PG. The performance of the filling bodies prepared by these materials from a wide range of sources are also very different. In the process of groundwater leaching, the pollutants carried by PG have the risk of release, especially the fluoride with the risk of secondary release is difficult to solidify. In the future, machine learning and other technologies should be used to establish a solid waste evaluation standard system, intelligently control the formula of CPGFM, ultimately prepare filling body with high strength and no pollution. Research on CO₂ mineralization and storage by CPGFM will be carried out to contribute to the early realization of the goals of carbon peak and carbon neutrality. The purpose of CPGB is to realize the efficient, environmentally friendly and economical utilization of PG through scientific methods and advanced technical means. The successful experience of CPGB in China can provide a good reference for PG utilization around the world.

CRediT authorship contribution statement

Guanzhao Jiang: Writing – original draft, Visualization, Funding acquisition. **Liangliang Zhao:** Writing – review & editing, Visualization, Methodology. **Shunchuan Wu:** Methodology, Data curation, Conceptualization. **Yan Li:** Methodology, Investigation, Data curation. **Aixiang Wu:** Methodology, Data curation, Conceptualization. **Yanduotai He:** Writing – original draft, Investigation, Formal analysis. **Haiyong Cheng:** Supervision, Methodology, Funding acquisition. **Wei Sun:** Validation, Supervision, Investigation. **Hong Li:** Writing – review & editing, Data curation, Conceptualization.

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.

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Data availability

Data will be made available on request.

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