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LEACHING TOXICITY OF PHOSPHOGYPSUN-SLAG SUBGRADE MATERIALS

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Abstract: As a by-product of the phosphoric acid industry, phosphogypsum (PG) presents substantial environmental and health hazards due to residual fluorides, phosphorus compounds, and heavy metals, particularly during stockpiling or improper disposal. In this study, PG and slag were employed as primary precursors to synthesize subgrade materials, with a focus on evaluating their leaching toxicity characteristics via single-factor experimental designs. Leaching tests were conducted following the standard HJ/T 299-2007 to measure the concentrations of fluoride ion, phosphate ion, As, and Pb. Single-factor experiments were carried out to evaluate the effects of the water-to-binder ratio, hydrophobic agent dosage, and quicklime content. Results demonstrated that the optimal parameters achieved high immobilization efficiencies. Specifically, at a water-to-binder ratio of 0.32, the solidification rates for fluoride ion, phosphate ion, As, and Pb reached 98.53%, 99.12%, 76.37%, and 79.12%, respectively. Furthermore, a quicklime content of 12% and a hydrophobic agent dosage of 0.75% yielded the best comprehensive solidification performance. These findings provide crucial scientific evidence for the safe valorization of PG in subgrade engineering, contributing to the reduction of solid waste pollution and the sustainable development of the phosphorus chemical industry. It is recommended that admixture formulations be tailored to specific regional environmental conditions, accompanied by rigorous long-term monitoring of leaching toxicity.

Keywords: Phosphogypsum; Slag; Subgrade material; Leaching toxicity

1 INTRODUCTION

Phosphogypsum (PG) is a significant industrial by-product, generated as a solid waste during the wet-process production of phosphoric acid [1]. Due to the presence of residual impurities, including fluorides, phosphorus compounds, and heavy metals [2], PG poses significant risks to the surrounding ecosystem and human health during stockpiling, storage, or improper disposal [3]. Therefore, accelerating the valorization and comprehensive utilization of PG is not only a critical objective for energy conservation and emission reduction in the phosphorus chemical industry but also an imperative for the sustainable development of the phosphate fertilizer sector [4].

According to statistics from the China Phosphate and Compound Fertilizer Industry Association, China's accumulated PG stockpiles reached approximately 800 million tons in 2023. The annual generation of fresh PG is about 80 million tons, with a comprehensive utilization rate of roughly 55.6% [5]. PG offers several advantages for engineering applications, including abundant availability, low cost, stable physical properties, favorable bearing capacity and compressive strength, moderate water absorption and permeability, and relatively simple construction processes, thereby providing both economic and environmental benefits [6,7]. However, it also presents environmental and engineering concerns. Harmful constituents such as heavy metals (e.g., As, Pb) derived from phosphate ore [8], calcium fluoride, and mobile compounds (e.g., arsenates, Pb^{2+}, F^-) formed during phosphoric acid production can leach out, potentially contaminating soil and water bodies and disrupting the ecological balance [1,9]. Moreover, the high content of soluble phosphates in PG can retard cement hydration and compromise the strength of subgrade materials [7].

This study aims to investigate the leaching toxicity of PG when used as a subgrade filler in road construction. By evaluating the leaching behavior of PG-slag-based subgrade materials, this work seeks to (i) understand the associated environmental risks in practical scenarios, (ii) provide a scientific basis for establishing appropriate utilization standards, and thereby (iii) promote the application of PG in road construction, enhance its resource utilization, reduce environmental pollution, and contribute to sustainable development.

2 MATERIALS AND METHODS

2.1 Materials

All chemical reagents used in this study, including concentrated sulfuric acid, nitric acid, and hydrochloric acid, thiourea, ascorbic acid, sodium fluoride, potassium dihydrogen phosphate, potassium borohydride, and calcium hydroxide, were of analytical grade. Additionally, lead and arsenic standard stock solutions were used for analysis. The additives employed included a gypsum retarder, sodium methyl silicate as a hydrophobic agent, polycarboxylate superplasticizer, and calcium oxide (quicklime). The phosphogypsum (PG) was collected from a phosphate chemical group located in Yichang, China. The S95-grade ground granulated blast furnace slag (GGBS) was obtained from a steel manufacturing company in Wuhan, China.

2.2 Experimental Methods

2.2.1 Specimen preparation

Solid specimens were prepared by weighing the raw materials according to the designed mix proportions. The total mass of each solid specimen was fixed at 500 g. These materials were then homogenized in a planetary mixer. The fresh mixtures were cast into standard cement mortar molds (160 mm × 40 mm × 40 mm) and compacted. Subsequently, the specimens were cured in a standard curing chamber at 25 ± 2 °C and ≥ 80% relative humidity for 24 hours before demolding.

2.2.2 Single-factor experimental design

The dosage of hydrophobic agent, water-to-binder ratio, and quicklime content were selected as the single-factor variables. For each variable, several levels were defined. PG-slag solidified specimens were prepared accordingly, with all other conditions kept constant. The leaching test was conducted following the Chinese standard "Solid waste—Extraction procedure for leaching toxicity—Sulfuric acid & nitric acid method" (HJ/T 299-2007). The concentrations of heavy metals (e.g., As, Pb) and anions (F^-, PO_4^{3-}) in the leachates were measured. The solidification rate (or immobilization efficiency) for each target contaminant was calculated using the following formula: [*(1 - C_leachate / C_raw) × 100%*], where C_raw is the initial concentration in the raw PG as determined by pre-experiments, and C_leachate is the concentration in the leachate.

3 RESULTS AND DISCUSSION

3.1 Effect of water-to-binder ratio on leaching toxicity of PG-slag subgrade materials

As illustrated in Figs. 1 and 2, as the water-to-binder ratio increased, the solidification rates of F^-, PO_4^{3-}, As, and Pb exhibited a trend of initially increasing and subsequently decreasing, with an overall downward tendency. Specifically, the maximum solidification rate for F^- (98.79%) was achieved at a water-to-binder ratio of 0.34, whereas the peak value for PO_4^{3-} (99.28%) was observed at 0.38. For the heavy metals (As and Pb), the highest solidification rates were obtained at a water-to-binder ratio of 0.32, reaching 76.37% and 79.12%, respectively.

The water-to-binder ratio dictates the amount of free water available for the hydration of gypsum-based cementitious materials, critically affecting their workability and the resultant strength of the specimens. Typically, the strength of such materials declines as the water-to-binder ratio rises. In contrast, the softening coefficient and thermal conductivity initially increase and then decrease with an increasing ratio [10]. An appropriate increase in the water-to-binder ratio provides more water, which promotes the complete hydration of slag and PG. This process yields dense hydration products, primarily C-S-H gel and ettringite, which effectively adsorb heavy metal ions. Concurrently, the hydration of slag releases OH^- ions, raising the pH. This alkaline environment favors the immobilization of contaminants through chemical precipitation: F^- precipitates as CaF_2, PO_4^{3-} forms insoluble calcium phosphates, and As and Pb precipitate as their respective hydroxides. However, an excessively high water-to-binder ratio has adverse effects. It dilutes the concentration of reactants, hindering the solidification reactions. Moreover, the excess water increases porosity and coarsens the microstructure after evaporation, creating more pathways for the diffusion and leaching of pollutants.

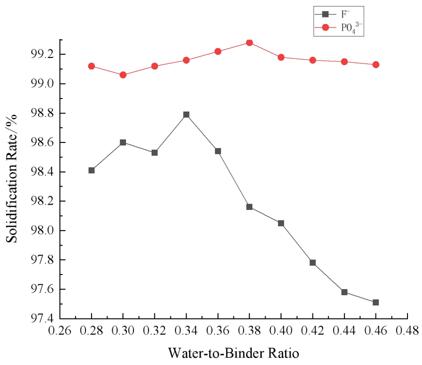

Figure 1 Effect of Water-to-binder Ratio on the Solidification Rate of Anions (F^-, PO_4^{3-}) in PG-slag Subgrade Materials

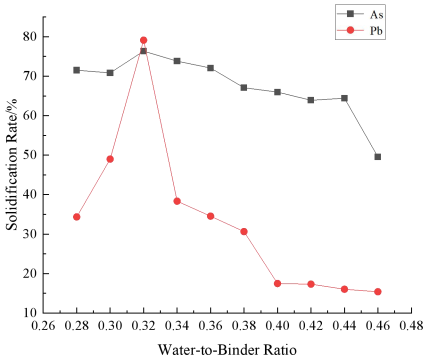

Figure 2 Effect of Water-to-binder Ratio on the Solidification Rate of Cations (As, Pb) in PG-slag Subgrade Materials

The experimental data were processed utilizing the Comprehensive Index Method. The results demonstrated that a water-to-binder ratio of 0.32 yielded the most favorable overall outcome, corresponding to the lowest composite leaching risk for the PG-slag subgrade material.

3.2 Effect of Quicklime Content on Leaching Toxicity of PG-Slag Subgrade Materials

As illustrated in Figs. 3 and 4, as the quicklime content increased, the solidification rate of PO_4^{3-} initially increased and then plateaued, exhibiting a general upward trend. The solidification rates of F^-, As, and Pb all exhibited a trend of initially increasing and subsequently decreasing. Specifically, the optimal solidification rate for F^- (98.83%) was attained at a quicklime content of 14%, while that for PO_4^{3-} (99.75%) was observed at 8%. The peak solidification rates for the heavy metals As and Pb (75.36% and 88.26%, respectively) were achieved at a quicklime content of 12%.

The hydration reaction between quicklime and slag powder facilitates the conversion of soluble P_2O_5 and F^- into insoluble precipitates, such as $Ca_3(PO_4)_2$ and CaF_2 [3]. The formation of these precipitates, combined with the encapsulation and adsorption of metal ions by C-S-H gels, mitigates the erosion of the filling matrix by metal ions, thereby promoting the strength development of the backfill [7]. However, an excessive quicklime dosage creates a highly alkaline environment, causing some calcium arsenate precipitates to redissolve and release soluble arsenic ions. Furthermore, the surplus Ca^{2+} competes with Pb^{2+} for SO_4^{2-}, which inhibits the formation of $PbSO_4$ and is detrimental to the solidification of toxic substances. The Comprehensive Index Method indicated that a quicklime content of 12% yielded the best comprehensive results for controlling leaching toxicity.

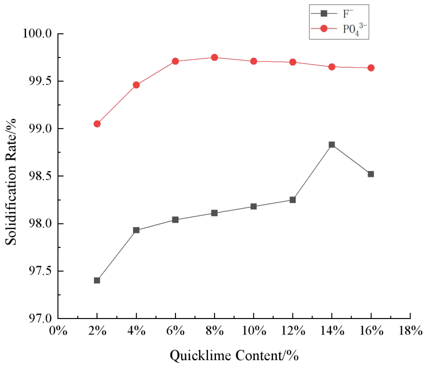

Figure 3 Effect of Quicklime Content on the Solidification Rate of Anions (F^-, PO_4^{3-}) in PG-slag Subgrade Materials

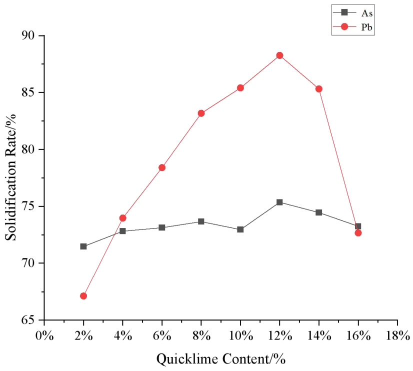

Figure 4 Effect of Quicklime Content on the Solidification Rate of Cations (As, Pb) in PG-slag Subgrade Materials

3.3 Effect of Hydrophobic Agent Dosage on Leaching Toxicity of PG-Slag Subgrade Materials

As illustrated in Figs. 5 and 6, as the hydrophobic agent dosage increased, the solidification rates of F^-, PO_4^{3-}, As, and Pb generally exhibited a trend of initially increasing and subsequently decreasing. The optimal solidification rate for F^- (98.42%) was observed at a hydrophobic agent dosage of 0.75%, while that for PO_4^{3-} (99.75%) peaked at 1.0%. The maximum solidification rates for As and Pb (68.36% and 88.94%, respectively) were recorded at hydrophobic agent dosages of 0.5% and 0.75%, respectively.

Pengfei et al. reported that as the dosage of organosilicon hydrophobic agent increased, the compressive and flexural strengths of PG initially increased and then decreased, whereas the surface contact angle and softening coefficient showed significant improvement [6]. Notably, when the hydrophobic agent was combined with Portland cement, the water absorption rate dropped significantly from 16.0% to 0.8%. This is attributed to the fact that under high-alkalinity conditions, hydrophobic organic molecules undergo polymerization, promoting the formation of a hydrophobic membrane that blocks water penetration channels and inhibits ion diffusion. However, an excessive dosage of hydrophobic agent encapsulates slag particles, hindering their contact with water. This results in incomplete hydration and a reduced generation of C-S-H gels, which is detrimental to metal ion adsorption. Additionally, non-uniform mixing may lead to the formation of microcracks in areas with a high concentration of hydrophobic agent, thereby compromising the solidification efficiency of toxic substances. Based on the Comprehensive Index Method, a hydrophobic agent dosage of 0.75% was determined to yield the optimal comprehensive performance in controlling leaching toxicity.

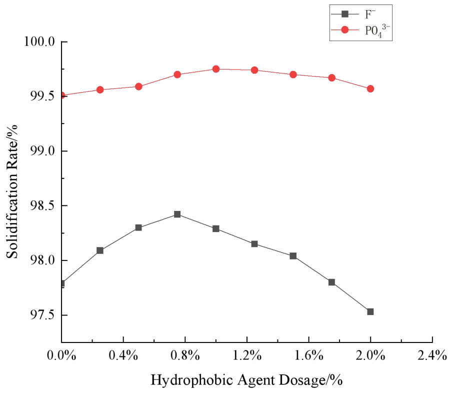

Figure 5 Effect of Hydrophobic Agent Dosage on the Solidification Rate of Anions (F^-, PO_4^{3-}) in PG-slag Subgrade Materials

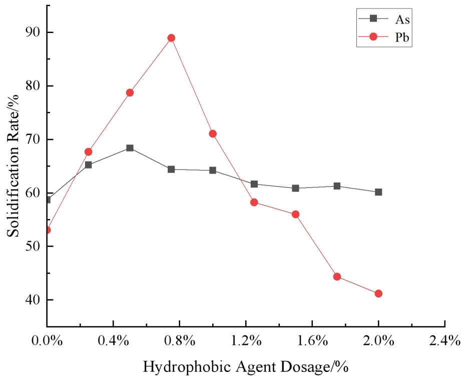

Figure 6 Effect of Hydrophobic Agent Dosage on the Solidification Rate of Cations (As, Pb) in PG-slag Subgrade Materials

4 CONCLUSIONS

(1) The optimal comprehensive solidification performance for F^-, PO_4^{3-}, As, and Pb was achieved at a water-to-binder ratio of 0.32, with corresponding solidification rates of 98.53%, 99.12%, 76.37%, and 79.12%, respectively.

(2) A quicklime content of 12% yielded the best comprehensive solidification efficiency for F^-, PO_4^{3-}, As, and Pb, achieving solidification rates of 98.25%, 99.70%, 75.36%, and 88.26%, respectively.

(3) The comprehensive solidification of F^-, PO_4^{3-}, As, and Pb was maximized at a hydrophobic agent dosage of 0.75%, with solidification rates reaching 98.42%, 99.70%, 64.39%, and 88.94%, respectively.

(4) Future Perspectives: This study primarily investigated the leaching toxicity characteristics of PG-slag subgrade materials. However, due to time and experimental constraints, certain aspects warrant further investigation. Specifically,

this work focused on the effects of water-to-binder ratio, quicklime content, hydrophobic agent dosage, and PG content, while other potential influencing factors were not considered. Future research should address these limitations to provide a more comprehensive assessment of long-term environmental safety.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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