Study on Mechanical Strength, Early Hydration Behavior and Hydration Mechanism of Phosphogypsum-based Cement Material

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Abstract. Nowadays, the utilization of phosphogypsum (PG) as source is a hotspot along the world. This experiment investigated the impact of varying amounts of steel slag (SS) on the initial performance of PG modified with steel slag. The mechanical property and hydrated mechanism of PG-based cementitious material were investigated through mechanical strength test, hydration heat. XRD, concentration of Soluble Phosphorus and SEM, The results indicate that the early strength of-based cement mortar modified with 5% and 10 SS was significantly enhanced. From the linear fitting curve of absorbance and phosphate ion concentration, as well as the absorbance of the original PG and modified PG extracts, it can be calculated that the phosphate ion in steel slag modified PG is 0.24 mg/L, which is much lower than the original PG (6.41 mg/L). It is concluded that the performance of PG-based cement is enhanced through SS modification.

Keywords: phosphogypsum;cementitious material; early strength; hydration heat; concentration of Soluble Phosphorus

1 Introduction

In the process of extracting phosphoric acid, after reacting with other chemicals, phosphogypsum will be generated as a byproduct [1]. It is mainly composed of gypsum, with trace amounts of organic debris, fluoride, soluble phosphorus, and other contaminants. The disposal of pesticides has the potential to contaminate nearby environments. Faced with the increasing amount of phosphogypsum, its stacking form is a form of pollution to the environment, and it is a waste of resources that cannot be fully utilized.Thus,many scholars have explored its utilization in building materials to address the application issues of PG [2].

Numerous studies [3][4] have focused on impurities removal of PG, because PG

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contains certain impurities during its generation process, and the presence of impurities can affect its practical engineering application. Impurities in PG primarily exist in three forms: soluble, hard soluble, and insoluble impurities. Soluble impurities, such as H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, F^-, and organic compounds, have adverse effect on the properties of PG. For example, when PG was used as raw material for preparing cementitious materials, soluble impurities can slow down the hydration reaction, thereby affecting early strength and limiting the practical application of PG [5]. Many scholars have employed various methods such as water washing, lime neutralization, calcination, and others to modify phosphogypsum. However, water washing may cause secondary environmental harm, calcination leads to energy loss, and lime neutralization does not completely remove impurities from phosphogypsum.

This article mainly tests the specific situation and engineering application of modified phosphogypsum in cement mortar by modifying it with steel slag. As an industrial waste, steel slag (SS) has high alkalinity and activity. We hope to improve the performance of PG by applying it to its modification, making it more suitable for the production of cement mortar. At the same time, this study will also explore the feasibility and economy of steel slag (SS) modified PG in practical engineering applications, providing strong basis for the research and application of green building materials in China.

2 Experimental program

2.1 Raw materials

The basic physical properties and composition of materials are shown in Tables 1 and 2.

Table 1. Physical properties of materials.

Material name	**P** (g/cm^3)	**SSA**(m^2/kg)
PG	2.3	346
GGBS	2.91	416
SS	3.2	585
P-II52.5R	3.1	420

Table 2. Chemical composition (wt.%).

Chemical composition	Al_2O_3	SiO_2	Fe_2O_3	CaO	K_2O	TiO_2	SO_3	P_2O_5	MgO
PG	0.47	5.05	0.38	46.01	0.04	-	43.61	1.30	0.08
GGBS	13.56	30.79	0.96	41.59	0.46	0.94	2.12	-	8.18
SS	5.65	26.9	24.15	29.6	-	-	2.64	-	5.33

2.2 Sample preparation

Initially, different proportions of SS and fixed proportions of raw materials PG were mixed in a slurry mixer (at the value of water to solid is 0.25) for 4 minutes. Subsequently, the mixture to a sealed bag and store it in a curing room (20℃, RH ≥ 95%) for 1 day. Next, the compound was dried in a broiler at sixty Celsius for 72 hours. Lastly, grinding the mixture for the future apply. The ISO standard sand was used in this study to minimize the experimental error. The mixing water used in the experiment is tap water. The mix proportions are shown in Table 3, with a water-to-cement ratio and cement-to-sand of 0.5 and 1:3, respectively.

Table 3. Mix proportion

Code	PG	SS	GGBS	OPC
A0	35	0	63	2
A1	35	5	58	2
A2	35	10	53	2
A3	35	15	48	2
A4	35	20	43	2

3 Results and discussion

3.1 Mechanical strength

Through Fig. 1, as the steel slag content increases, the early strength of PG-based cement mortar shows a trend of first decreasing and then increasing, while its later strength exhibits a gradually decreasing trend.The flexural strength of A0 samples after 3 days was 0MPa, while the flexural strength of A1 and A2 samples modified with steel slag was 3.3MPa and 2.7MPa, and the 3-day compressive strength of A1 and A2 increased from 0.3MPa in A0 to 10.4MPa and 8.9MPa. From the 7-day data, it can be seen that the bending strength of A1 and A2 has increased by 39% and 24.3% respectively, and the compressive strength has increased by 52% and 22%, respectively. So, from the early strength, it can be seen that by modifying PG with an appropriate amount of SS, the early strength of PG can be improved.The reformation of incipient strength can own the remove of material (prevent hydration reactions) in PG after steel slag modification, resulting in the formation of insoluble substances, thereby increasing the rate of hydration reaction. However, with the extension of curing period, the mechanical strength of PG-based cement mortar decreases as the SS content increases [6]. This reduction in strength may own the lower hydration activity of SS compared to GGBS. This lower activity results in fewer hydration products, consequently affecting the overall strength of the mortar.

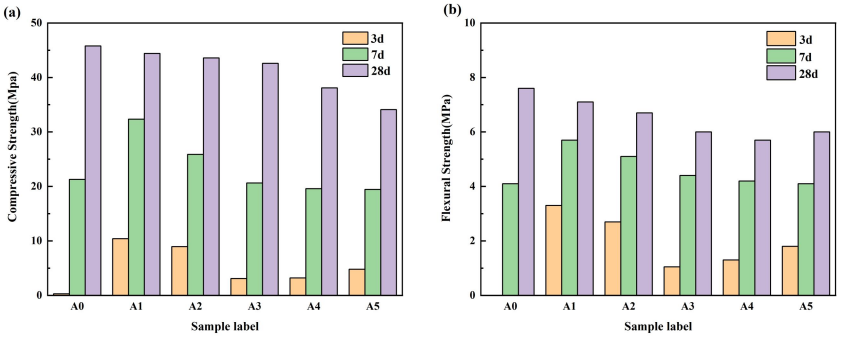

Fig. 1. The mechanical strength of the phosphogypsum-based cement mortar: (a) compressive strength; (b)flexure strength.

3.2 Hydration heat

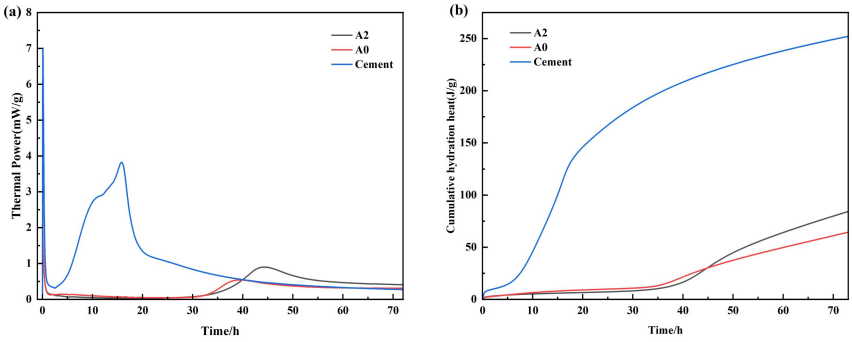

Fig. 2. (a) Heat transfer; (b) cumulative heat of PG-based cement.

From Fig. 2(a), the peaks of hydration heat of the PG-based cement show that after mixing raw materials with water, PG, GGBS, and cement dissolve in water and release heat, forming the first peak of hydration heat. As the concentration of Ca^{2+} and SO_4^{2-} in the liquid phase of the paste continues to rise to saturation, a large amount of ettringite crystals precipitate. As the alkalinity of the cement paste continues to increase, slag continuously dissolves in water, accompanied by the generation of new hydration products, releasing heat and forming the second peak of hydration heat. The hydration rate of A2 is higher than that of A0, resulting in the early strength improvement of the specimens [7].

From Fig. 2(b), the cumulative hydration heat of P•O 42.5 at 3 days was 248.5 J•g^{-1}. The hydration heat of A0 and A2 at 3 days was 65.4 J • g-1 and 82.8 J • g-1, respectively. Therefore, the reaction rate of PG modified with steel slag is improved and meets the requirements of GB/T 200-2017 for low-heat cement hydration heat [8].

3.3 XRD

The XRD patterns of PG-based cement are displayed in Fig. 3. The main components

of sample (A2) are Aft and gypsum, ettringite is the main hydration product of PG based cement, and gypsum is the unhydrated PG. From the 7-day XRD patterns, it is observed that the relative intensity of ettringite in A2 is slightly higher than in A0, which means more ettringite generated in A2, resulting higher early strength. However, this can be contributed to the modification of PG by SS, impurities in PG react with substances in steel slag, which reduces the existence of impurities that hinder the formation of C-S-H gel , promotes the formation of ettringite, leading to enhanced mechanical strength of A2 relative to A0 at 7 days. By 28 days, because the GGBS content in A2 is relatively lower compared to A0, thus, its compressive strength at 28 days is slightly lower than A0. However, the compressive strength of A2 also meets the standard of 42.5 grade cement.

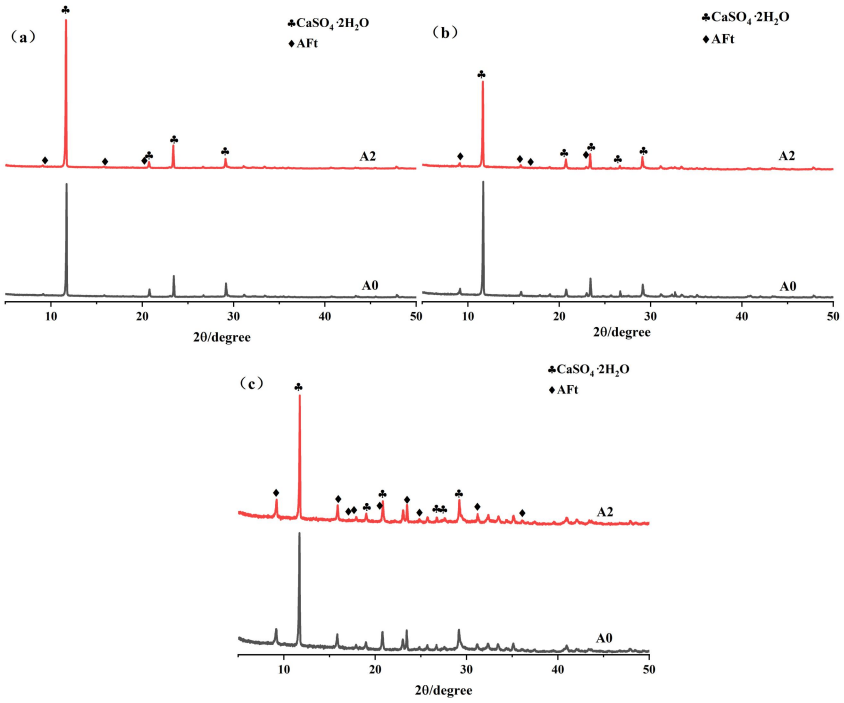

Fig. 3. XRD patterns of A0 and A2: (a) 3rd; (b) 7 th; (c) 28 th.

3.4 Concentration of Soluble Phosphorus

Soluble phosphate in PG primarily occurs in three forms: H_3PO^4, H_2PO^{4-} and HPO_4^{2-}. However, the soluble phosphate would be adsorbed and present on the outer layer of the gypsum crystals in the PG. When the raw PG rich in phosphate impurity and used in the cementitious material, the soluble phosphate would react with Ca^{2+} in the solution to form insoluble $Ca_3(PO_4)_2$, which impedes the further dissolution and hydration of gypsum, consequently significantly diminishing the early strength of the cementitious material [9].

Ammonium molybdate spectrophotometry was used to measure the phosphate ions concentration of raw PG and modified PG. In Fig .4 (a), it can be seen that the color of the colorant extraction of the raw PG is deeper than which of modified PG. In addition, from the liner fitting curve of absorbance and the phosphate ion concentration, along with the absorbance of the extraction of raw PG and modified PG. It can be calculated that the phosphate ion in the PG modified by steel slag was 0.24 mg/L, which was much lower than the raw PG (6.41 mg/L). The low concentration of phosphate ions in PG modified with steel slag is due to the reaction between CaO in SS and phosphate in PG to form Ca3 (PO4) 2 [9], which reduced the concentration of soluble phosphate.

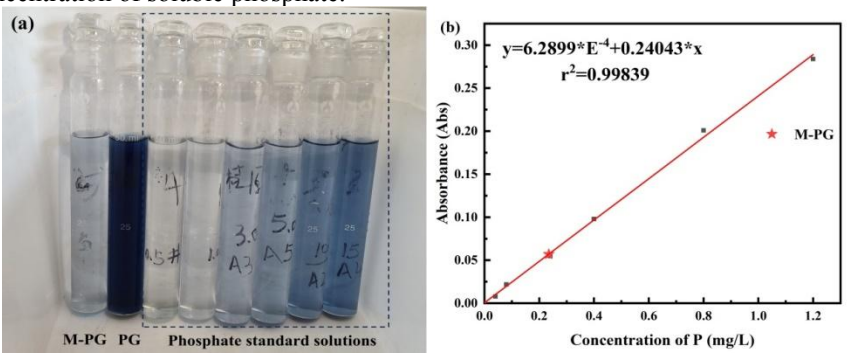

Fig. 4. The concentration test of phosphate: (a) coloration; (b) fitting curve of absorbance with concentration of phosphate.

3.5 SEM

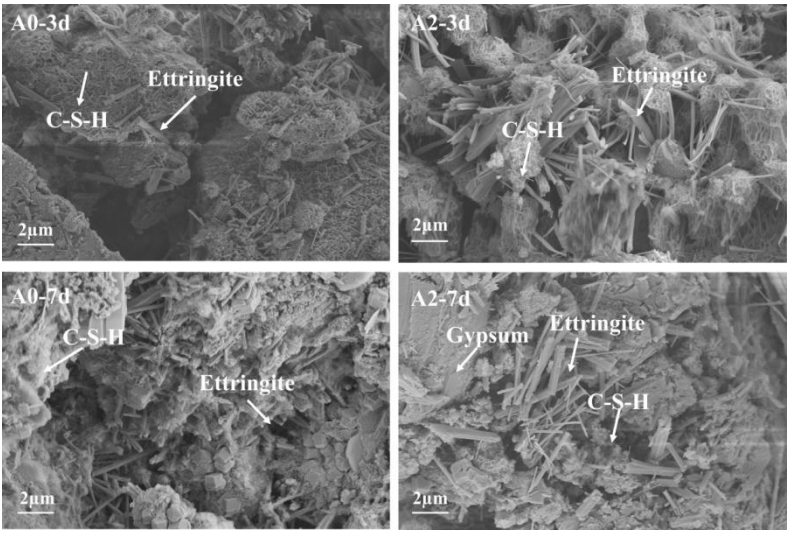

Fig. 5. SEM images of the PG-based cementitious material.

From the microscopic morphology of PG-based cement at 3 and 7 days, A2 has more ettringite than A0, A2's C-S-H gel is more compact than A0's, and A0's SEM pores on the 3rd day are more and larger than A2's [10]. Combined with results of hydration heat, XRD, concentration of soluble phosphorus and SEM, steel slag can react with impurities in PG (which hinder PG reaction), thereby eliminating the adverse factors of PG based cement.

Conclusion

This article investigates the basic testing of PG before and after steel slag modification, XRD and SEM were used to analyze the phase composition and microstructure morphology, aiming to understand the hydration mechanism. Based on the results, the following conclusion can be drawn:

(1)The introduction of 10% steel slag into PG-based cementations mortars results in a notable improvement of strengths. Specifically, after 3 days, the flexural strength increases by 2.8 MPa, while the compressive strength gains 8.9 MPa.

(2)PG-based cement modified with 10% steel slag exhibited higher hydration heat compared to unmodified PG-based cement. Therefore, it can be inferred that the modified PG can increase the reaction rate of PG-based cement.

(3)Analysis using XRD and SEM indicates that PG-based cement modified with 10% steel slag exhibits higher quantities of ettringite and C-S-H gel compared to unmodified PG-based cement.

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