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Preparation and properties of phosphogypsum based plastering mortar

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ABSTRACT

In order to reduce the negative impact of phosphogypsum accumulation on the environment, this paper uses phosphogypsum, magnesium slag, potassium dihydrogen phosphate, fly ash and calcium carbide slag to prepare gypsum based plaster mortar as a cementing material, and explores the optimal ratio of the composite cementing material through orthogonal experimental design. The mechanical properties of the test block were analyzed by the flexural and compressive strength of the test block, and the slurry properties were evaluated by the initial and final setting time, stability measurement, fluidity test and water resistance test. The experimental results show that when phosphogypsum: potassium magnesium phosphate: fly ash: When titanium gypsum =50:25:20:20, the strength of the composite system can reach 2.98Mpa in 60 days, and the initial setting time is 118min and the final setting time is 223min, which meets the requirements of GB/T25181-2019 building gypsum plaster mortar that the initial and final setting time is greater than 60min and less than 480min. Its fluidity is 237mm, which meets the requirement that the fluidity of GB/T25181-2019 building gypsum plaster mortar is greater than 100mm.

KEYWORDS

Phosphogypsum; Plastering mortar; Mechanical property; Slurry property

1. INTRODUCTION

phosphogypsum (PG) is an industrial solid waste produced by the wet process of phosphoric acid in the phosphate fertilizer industry. The main component is CaSO4 2H2O, and approximately 4-6 tons of phosphogypsum are produced for every 1 ton of phosphoric acid [1, 2]. At present, the annual production of phosphogypsum in the world is about 200 to 280 million tons, and the stockpile is as high as 6 billion tons. It is estimated that by 2025, the stockpile of phosphogypsum in the world will be about 7 to 8 billion tons [3, 4]. In recent years, with the rapid development of phosphate fertilizer industry, China has become the world's largest phosphate fertilizer producer and the largest phosphogypsum by-product country [5].The stockpile of phosphogypsum in China has reached 800 million tons, and about 80 million tons of phosphogypsum are added every year, but the comprehensive utilization rate of phosphogypsum is only 45% [6]. Phosphogypsum and natural gypsum are the same in composition, mainly calcium sulfate dihydrate, but the PH, solubility, particle size and dissolution performance of phosphogypsum are different from natural gypsum, resulting in phosphogypsum has the shortcomings of fast setting speed, poor water resistance and low strength. In addition, phosphogypsum also contains a small amount of phosphorus impurities, phosphorus in phosphogypsum mainly comes from the unwashed phosphoric acid in the wet phosphoric acid production process and a small part comes from the undecomposed phosphate rock, among which the soluble phosphorus mainly includes H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} [7-9]. Under the effect of ionization, a large amount of H+ will be produced to enhance the acidity of the environment, and

through the leaching and infiltration of rainwater, the surrounding surface water, groundwater and soil environment will become acidic, resulting in a large number of fish, shrimp and other aquatic organisms in the surface water will die [10]. The phosphorus element in phosphogypsum will also be washed into rivers, lakes and seas with rain, which will cause water eutrophication [11].

The mass production and stacking of phosphogypsum occupy a large amount of land resources. In addition, since more than 90% of China's phosphorus chemical industry is concentrated in areas along the Yangtze River Economic Belt with rich phosphate resources such as Yun, Guizhou, Sichuan and Hubei, a large amount of phosphogypsum is an important cause of total phosphorus pollution in the Yangtze River basin [12, 13]. According to the data released by the Ministry of Ecology and Environment, there are 97 phosphor gypsum repositories in 7 provinces and cities in the Yangtze River Basin, of which 53.61% lead to environmental problems due to inadequate management and non-standard storage [14]. Phosphogypsum dumps are mostly open-air sites. Some harmful gases, such as chlorine fluoride, will enter the atmosphere. After being washed by rain, the soluble impurities in phosphogypsum will dissolve in rain and enter the soil, and then enter the surface water and groundwater through the soil [15]. At present, there are some environmental problems around phosphogypsum storage yard, such as poor water quality, abnormal toxic gas content in the atmosphere, excessive heavy metals in the soil, which seriously endanger the living environment of human beings. The accumulation of phosphogypsum not only causes the waste of resources but also brings serious ecological environment pollution and other problems. In order to realize the sustainable and environment-friendly development of phosphorus chemical industry, rational and effective resource utilization of phosphogypsum is of far-reaching significance.

Phosphogypsum building materials is the main way of resource utilization of phosphogypsum. Phosphogypsum based plaster-mortar is made of phosphogypsum gelling material by adding admixtures. It has the advantages of light weight, high coating rate and good thermal insulation performance, and is one of the main types of phosphogypsum building materials. In this paper, phosphogypsum is used by the reaction of phosphogypsum, magnesium slag, potassium dihydrogen phosphate, fly ash and calcium carbide slag to produce gelling material. The compression and folding strength, initial and final setting time and tensile bond strength of test blocks are optimized. The optimal ratio of composite materials was determined by orthogonal test, and the influence of various factors on compressive strength was analyzed. Finally, the optimal ratio of composite materials was confirmed by experiment. It provides a new idea for the resource utilization of phosphogypsum.

2. EXPERIMENTAL PART

2.1. Raw Materials

phosphogypsum (PG) is derived from a phosphate fertilizer plant, potassium dihydrogen phosphate (KH_2PO_4, MKP), industrial grade, white crystal, purity greater than 99%, Magnesiumslag (Magnesiumslag, MS) is the solid waste of a nodulization agent production plant, carbidecalciumresidue (CCR) is obtained from Hebi Coal Chemical Co., LTD., Henan Energy and Chemical Group, and flyash (FA) is commercially available ash.

2.2. Orthogonal Experimental Design

Four-factor and three-level orthogonal design (L9(34)) was selected for the test, and the design principle is shown in Figure 1. The four factors are phosphogypsum content (A), potassium magnesium phosphate content (B), fly ash content (C) and calcium carbide slag content (D). Table 1 is the factor level table.

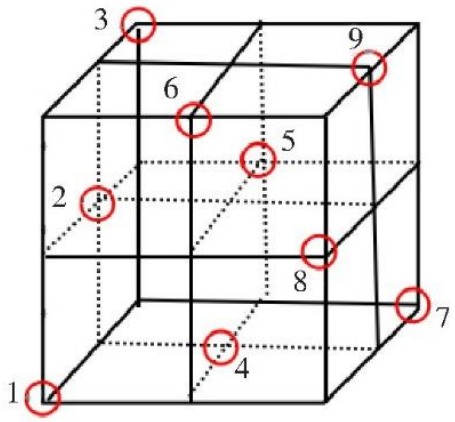

Figure 1. Three-factor, three-level orthogonal design

Table 1. Factors and levels of orthogonal test

level	The level corresponds to the value(%)			
	A	B	C	D
1	50	15	10	10
2	60	20	15	15
3	70	25	20	20

2.3. Preparation Process Of Gelling Material

The preparation process of the gelling material test block is shown in Figure 2. According to the experimental design, quantitative phosphogypsum, magnesium slag, potassium dihydrogen phosphate, fly ash and calcium carbide slag were respectively weighed and placed in a planetary mixer. The raw materials were mixed evenly at low speed without adding water at first, and then the raw materials were mixed slowly for 40s after adding quantitative water, so that the water and raw materials were fully in contact. After stirring at high speed for 120s, the net paste of the gelling material is obtained. Pour the clean pulp into a triple test mold of 40mm ×40mm ×160mm according to GB/T176712021 "Test Method for Cement mortar Strength", discharge the excess bubbles in the clean pulp on the shaking table to make the pulp mix evenly, scrape off the excess clean pulp and cover the mold with a glass plate. After 1 day of curing at room temperature, the mold is removed, and the test block is wrapped with plastic wrap to prevent water loss, and then cured at room temperature to the specified age and tested and characterized.

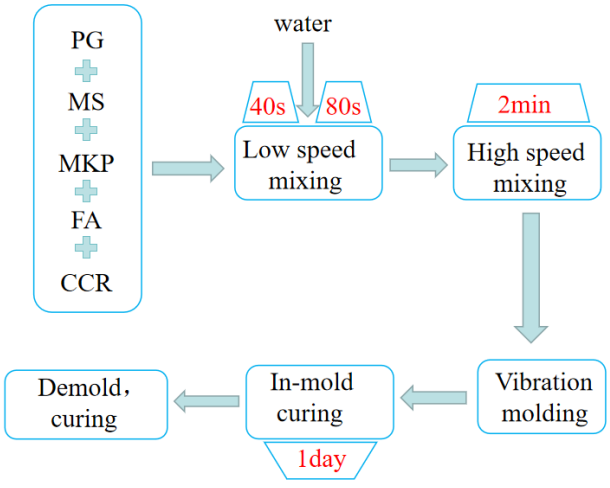

Figure 2. Experimental flow chart

2.4. Test Method

2.4.1. Mechanical properties test

According to the "Cement mortar Strength Inspection Method (ISO Method)" (GB/T17671-2021), after the test block is released and cured to the specified age, the side of the test block is placed on the DY-208JFX automatic cement pressure testing machine to test its folding strength, and the two broken half prism are used to measure the compressive strength. The arithmetic mean is taken as the final strength value.

2.4.2. Initial and final setting time and stability test

Refer to GB/ T1346-2011 "Standard Consistency Water Consumption, Setting Time, Stability test Method" to test the standard consistency water consumption, initial and final setting time and stability of the clean paste. The initial setting time was determined by Vicar test. Because the setting time is related to the hydration and initial porosity of the slurry, and the density of the cementing material of phosphogypsum based plaster-mortar is different from that of cement, the standard consistency water requirement used in the determination of setting time is not fixed. When a plunger with a diameter of 10 ± 0.05 mm penetrates the slurry at a depth of 34 ± 1 mm, the water requirement of the standard consistency is determined . The Redwood clip method was used to test the stability. The composite paste was filled with Redwood clip, cured for 24h under standard conditions, and heated at 100℃ in a water heater for 3h. After the specimen was cooled to room temperature, the distance difference between the Redwood clip tips before and after boiling was measured. The difference ≤ 5.0mm is qualified, otherwise it should be retested, if the retest result is still ≥ 5.0mm, indicating that the stability of the composite material is not up to standard.

2.4.3. Scanning electron microscopy and electron spectroscopy

Scanning electron microscope (SEM) is used to observe the microscopic morphology of raw materials and samples. The equipment model is MerlinCompact. Due to the poor electrical conductivity of the sample, it is necessary to use PECS Ⅱ 685. C type etching and coating machine to spray gold after drying, and the spraying time is 120S, so as to facilitate follow-up observation. The device is equipped with OXFOFD electron spectroscopy (EDS), which can test the chemical composition of selected areas in a sample and operates at 15KV.

2.4.4. Phase composition analysis

The phase composition of each sample was analyzed by X-ray Diffraction (RigakuUltimaIVX). The pretreatment method of the sample was consistent with that described in section 2.2.5. The X-ray map was obtained with A CuKα radiation source (λ=1.5418 A) at 40kV and 40mA, with a scanning Angle (2θ) ranging from 5° to 80°, a scanning speed of 10°/min, and a scanning step size of 0.02°.

3. RESULTS AND DISCUSSION

3.1 Orthogonal Test Results

3.1.1. Compression and folding results

According to the design in Table 1 and the preparation process shown in Section 1.3, phosphogypsum - potassium magnesium phosphate - fly ash and calcium carbide slag composite cementing test blocks were prepared, and the compressive and folding strengths of the composite materials with different ratios were measured at different ages. The test results are shown in Table 2.

Table 2. Strength test scheme and results of phosphogypsum - potassium magnesium phosphate - fly ash - calcium carbide slag composite cementification material

Serial number			dosage/%		Compressive strength/MPa			Flexural strength/MPa		
	PG	MKPC	FA	CCR	3d	7d	28d	3d	7d	28d
A1	50	10	10	10	0.78	0.86	0.98	0.37	0.72	0.72
A2	50	15	15	15	1.74	1.82	1.85	1.50	1.59	1.81
A3	50	25	20	20	1.89	2.30	2.71	1.05	1.25	1.02
A4	60	10	15	15	0.66	0.78	0.84	0.89	0.46	0.86
A5	60	15	20	20	0.63	0.75	1.27	0.66	0.78	0.65
A6	60	25	10	10	0.66	0.74	1.36	0.92	0.85	1.27
A7	70	10	20	20	0.52	0.63	0.81	0.38	0.40	0.68
A8	70	15	10	10	0.59	0.71	1.01	0.47	0.86	1.04
A9	70	25	15	15	0.60	0.63	1.04	0.72	1.05	1.04

3.1.2. Analysis of range and variance

The compressive strength data of phosphogypsum - potassium magnesium phosphate - fly ash - calcium carbide slag composite cementified material at different ages (3 days, 7 days, 28 days) were analyzed by range analysis, and the results are shown in Table 3-3. As can be seen from the table, when the curing time is 3 days, the corresponding range of each factor is 0.3967, 0.9000, 0.3967, 0.3767, respectively, indicating that the main and secondary order of the influence of each factor on the compressive strength is the content of potassium magnesium phosphate > the content of phosphogypsum > the content of fly ash > the content of calcium carbide slag. When the curing time was 7 days, the range of each factor was 0.4667, 1.0033, 0.4567 and 0.5167, respectively, indicating that the main order of influence of each factor on the 7-day bending strength was the content of potassium and magnesium phosphate > calcium carbide slag > potassium and magnesium phosphate > fly ash content. The range of the content of potassium and magnesium phosphate (B) was the largest at 3 and 7 days. The results show that the content of potassium magnesium phosphate is the most important factor affecting the early compressive strength of the composite. When the curing time was 28 days, the corresponding range of each factor was 0.4233, 0.8267, 0.4800 and 0.8933, respectively, indicating that the main order of influence of each factor on the 28-day compressive strength was calcium carbide slag content > potassium magnesium phosphate > fly ash content > phosphogypsum content. It is worth noting that, The range of calcium carbide slag content (D) is much higher than that of fly ash content (C) and phosphogypsum content (A), indicating that calcium carbide slag content is the most important factor affecting the late compressive strength of the system. According to the range analysis results, the optimal ratio of compressive strength corresponding to 3 days, 7 days and 28 days is A1B3C3D3, that is, the content of phosphogypsum: the content of potassium magnesium phosphate: the content of fly ash: the content of calcium carbide slag =50:25:20:20.

The bending strength data of phosphogypsum - potassium magnesium phosphate - fly ash - calcium carbide slag composite cementified material at different ages (3 days, 7 days, 28 days) were analyzed by range analysis, and the results are shown in Table 3-4. As can be seen from the table, when the curing time is 3 days, the corresponding range of each factor is 0.4500, 0.4500, 0.3500, 0.3500, respectively, indicating that the main and secondary order of the influence of each factor on the compressive strength is the content of potassium magnesium phosphate > the content of phosphogypsum > the content of fly ash > the content of calcium carbide slag. When the curing time is 7 days, the corresponding range of each factor is 0.4900, 0.5500, 0.2233 and 0.0967, respectively, indicating that the main order of influence of each factor on the 7-day bending strength is the content of potassium magnesium phosphate > calcium carbide slag > potassium magnesium phosphate > fly ash content. The range of the content of potassium magnesium phosphate (B) is the largest at 3 and 7

days. The results show that the content of potassium magnesium phosphate is the most important factor affecting the early flexural strength of the composite. When the curing time was 28 days, the corresponding range of each factor was 0.2633, 0.4133, 0.4500 and 0.4533, respectively, indicating that the main order of influence of each factor on the 28-day bending strength was calcium carbide slag content > fly ash content > potassium magnesium phosphate content > phosphogypsum content, indicating that calcium carbide slag content was the main factor affecting the later strength of the system. According to the range analysis results, the optimal ratio of bending strength corresponding to 3 days, 7 days and 28 days is A1B3C2D2, that is, the content of phosphogypsum: the content of potassium and magnesium phosphate: the content of fly ash: the content of calcium carbide slag =50:25:15:20.

Table 3. Results of compressive strength range analysis

Type	Index	PG(A)	MKPC(B)	FA(C)	CCR(D)	Significance
R3d/ MPa	K1	1.4700	0.6533	0.6767	0.6700	B>A=C>D
	K2	0.6500	0.9867	1.0000	0.9733	
	K3	0.5700	1.0500	1.0133	1.0467	
	Range	0.3967	0.9000	0.3967	0.3767	
	Optimal level	A1	B3	C3	D3	
R7d/ MPa	K1	1.6600	0.7567	0.7700	0.7467	B>D>A>C
	K2	0.7567	1.0933	1.0767	1.0633	
	K3	0.6567	1.2233	1.2267	1.2633	
	Range	0.4667	1.0033	0.4567	0.5167	
	Optimal level	A1	B3	C3	D3	
R28d/ MPa	K1	1.8467	0.8767	1.1167	1.0967	D>B>C>A
	K2	1.1567	1.3767	1.2433	1.3400	
	K3	0.9533	1.7033	1.5967	1.5200	
	Range	0.4233	0.8267	0.4800	0.8933	
	Optimal level	A1	B3	C3	D3	

Table 4. Results of bending strength range analysis

Type	Index	PG(A)	MKPC(B)	FA(C)	CCR(D)	Significance
R3d/ MPa	K1	0.9733	0.5467	0.5867	0.5833	B=A>C=D
	K2	0.8233	0.8767	1.0367	0.8033	
	K3	0.5233	0.8967	0.6967	0.9333	
	Range	0.4500	0.4500	0.3500	0.3500	
	Optimal level	A1	B3	C2	D3	
R7d/ MPa	K1	1.1867	0.5267	0.8100	0.8567	B>A>C>D
	K2	0.6967	1.0500	1.0333	0.8500	
	K3	0.7700	1.0767	0.8100	0.9467	
	Range	0.4900	0.5500	0.2233	0.0967	
	Optimal level	A1	B3	C2	D3	
R28d/ MPa	K1	1.1833	0.7533	1.0100	0.8033	D>C>B>A
	K2	0.9267	1.1100	1.2367	0.9733	
	K3	0.9200	1.1667	0.7833	1.2533	
	Range	0.2633	0.4133	0.4500	0.4533	
	Optimal level	A1	B3	C2	D3	

The 3-day, 7-day and 28-day flexural strengths of the samples were analyzed by variance analysis, and the results were shown in Table 3-4. According to the results of variance analysis, the order of influence on 3-day bending strength is the content of potassium and magnesium phosphate > phosphogypsum content > fly ash content > calcium carbide slag content. The order of influence on 7-day bending strength is the content of potassium and magnesium phosphate > phosphogypsum content > fly ash content > calcium carbide slag content. The order of influence on the 28-day bending strength was calcium carbide slag content > fly ash content > potassium magnesium phosphate content > phosphogypsum content, which was consistent with the range analysis results. Therefore, according to the results of range and variance analysis, it can be seen that A1B3C2D2 is the optimal test scheme combination for 3, 7 and 28 days, that is, phosphogypsum: potassium magnesium phosphate: fly ash: calcium carbide slag =50:25:15:20

The 3-day, 7-day, 28-day compressive strength of the sample was analyzed by variance analysis, and the results were shown in Table 3-4. According to the results of variance analysis, the main order of influence on the 3-day compressive strength is the output of potassium and magnesium phosphate > the content of phosphogypsum > the content of fly ash > the content of calcium carbide slag; the main order of influence on the 7-day compressive strength is the content of potassium and magnesium phosphate > the content of phosphogypsum > the content of calcium carbide slag > the content of fly ash. The order of influence on 28-day compressive strength is calcium carbide slag content > potassium magnesium phosphate > fly ash content > titanium gypsum content, which is consistent with the range analysis results. Therefore, according to the results of range and variance analysis, A1B3C3D3 is the optimal test scheme combination for 3, 7 and 28 days, that is, the content of phosphogypsum: the content of potassium and magnesium phosphate: the content of fly ash: the content of calcium carbide slag =50:25:20:20.

Table 5. Results of variance analysis of flexural strength

Time	Ingredients	DF	Adj SS	Adj MS	F	P	Significance
3d	PG(A)	2	0.3640	0.1875	1.30	0.434	B>A>C>D
	MKPC(B)	2	0.8486	0.4223	17.16	0.055	
	FA(C)	2	0.3302	0.1651	0.71	0.585	
	CCR(D)	2	0.1878	0.0939	0.43	0.796	
7d	PG(A)	2	0.4190	0.2095	0.02	0.586	B>A>C>D
	MKPC(B)	2	0.5770	0.2885	9.18	0.098	
	FA(C)	2	0.0997	0.0498	0.65	0.605	
	CCR(D)	2	0.1749	0.0874	0.42	0.835	
28d	PG(A)	2	0.1353	0.0676	0.32	0.975	D>C>B>A
	MKPC(B)	2	0.3013	0.1506	0.64	0.654	
	FA(C)	2	0.3083	0.1542	0.73	0.525	
	CCR(D)	2	0.6237	0.3118	15.24	0.047	

Table 6. Results of variance analysis of compressive strength

Time	Ingredients	DF	Adj SS	Adj MS	F	P	Significance
3d	PG(A)	2	0.3150	0.1575	1.43	0.332	B>A>C>D
	MKPC(B)	2	0.6425	0.3223	16.28	0.075	
	FA(C)	2	0.3002	0.1551	0.91	0.685	
	CCR(D)	2	0.2393	0.1196	0.73	0.996	
7d	PG(A)	2	0.3480	0.1740	0.65	0.605	B>D>A>C
	MKPC(B)	2	1.8327	0.9163	9.18	0.098	
	FA(C)	2	0.3251	0.1625	0.42	0.835	
	CCR(D)	2	0.4072	0.2036	0.02	0.586	
28d	PG(A)	2	0.2708	0.1354	0.87	0.254	D>B>C>A
	MKPC(B)	2	1.0401	0.5200	2.94	0.104	
	FA(C)	2	0.3713	0.1856	0.58	0.156	
	CCR(D)	2	1.3155	0.6577	7.23	0.085	

Note: DF- degrees of freedom; SS- sum of squares; MS- mean square

3.1.3 Determination of optimal interval

According to the above analysis results, the early mechanical properties of phosphogypsum - potassium magnesium phosphate-fly ash-calcium carbide slag cementing system will be significantly improved with the increase of potassium magnesium phosphate content, and the later strength of the composite cementing system will be significantly enhanced with the increase of calcium carbide slag content. Combined with the results of orthogonal experiment, the strength development of the composite in the early and late stages is considered. The content of fixed phosphogypsum is 50%, the content of potassium magnesium phosphate is 25%, the optimal range of fly ash is 15%-20%, and the content of calcium carbide slag is 20%.

3.2. Stability And Initial And Final Setting Time

According to the research, the content of sulfate is the main factor affecting the stability of the gelling system, so the stability test of C2 and C3 is carried out. Table 7 shows the stability test results of the samples. The stability of the samples is all qualified, indicating that the addition of phosphogypsum will not have a negative impact on the stability of the phosphogypsum based plaster-mortar system.

Fig 2 shows the test results of the initial setting time of each group of samples. It can be seen from the figure that the initial setting time of the sample changes. The early hydration is the reaction of magnesium slag and potassium dihydrogen phosphate to produce potassium magnesium phosphate cementing material, so the initial setting time of the sample decreases with the increase of the addition of potassium and magnesium phosphate. The initial setting time is an important index reflecting the early hydration process of composite materials, and the initial setting of gelling materials mainly depends on the continuous elastic solid network established by the interconnection of hydration products in the gelling system. In the later hydration process, Ca^{2+} can be combined with the $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral units released by fly ash, and is an important element in the formation of hydration products such as C-(A)-S-H gel and ettringite. The solubility constant Ksp of $Ca(OH)_2$ at 25℃ is 5.02×10^{-6}, while the Ksp of gypsum dihydrate is 5.2×10^{-3}, much higher than calcium hydroxide. Therefore, phosphogypsum can be added in large quantities content of free Ca^{2+} in flyash-calcium carbide slag system is increased to accelerate the hydration reaction and the formation of hydration products. It is worth noting that the promoting effect of phosphogypsum on flyash-calcium carbide slag system decreases with the increase of phosphogypsum content. This is due to the fact that the addition of phosphogypsum causes the dissolution equilibrium of $Ca(OH)_2$ to shift to the left, thereby reducing the dissolution rate of OH^- and active aluminosilicates.

Table 7. Stability analysis of samples

Sample	Stability
A2	Qualified
A3	Qualified

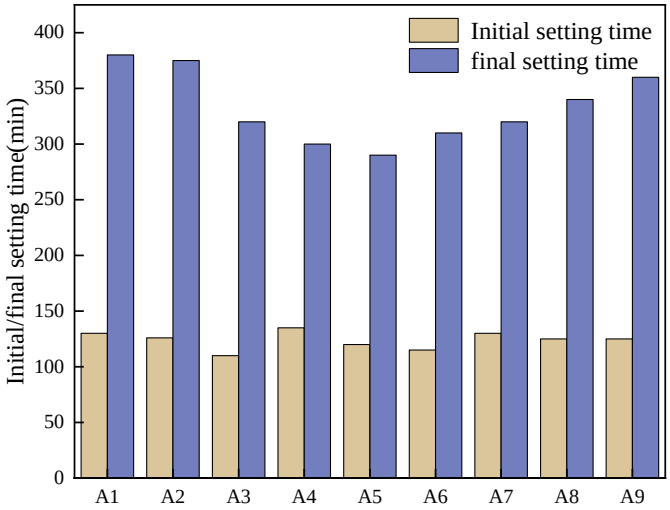

Figure 3. Initial setting time of the sample

3.3. Liquidity Analysis

The fluidity test was carried out on the samples of each group, and the mixing and fluidity of phosphogypsum based composite plaster mortar were determined according to JGJ702009, the Basic Performance test Method for Building mortar. The test results are shown in the following table.

Table 8. Fluidity measurement results of samples

Group	fluidity (mm)
C1	190
C2	188
C3	237
C4	193
C5	202
C6	234
C7	203
C8	212
C9	243

It can be seen from the table that the fluidity tends to decrease with the increase of the amount of magnesium slag. The particles of magnesium slag are relatively fine and angular, the relative dislocation resistance between the particles is large, the particles have primary cracks, and the water absorption is good. In addition, the magnesium slag itself has certain hydration activity, and the water requirement for hydration of plastering mortar will increase due to the hydration of magnesium slag, thus reducing the content of free water in plastering mortar. The fluidity of plaster mortar also decreases.

Fly ash particles are smaller than magnesium slag particles, the surface is slightly convex, the specific surface area is relatively large, the particle surface.The surface will absorb more water and has a certain lubrication ability. The fly ash particles are spherical and the phase between particles.The

resistance to dislocation is small, and the cement particles can play a physical dispersion role, so that the potassium magnesium phosphate cement wrapped.The water can be more easily dispersed, so that the water in the mortar is more evenly distributed, and the components in the mortar can be more fully wetted, and the fluidity of the plaster mortar will increase.

3.4 Water Resistance Analysis

The samples of each group after 28 days of curing were immersed in water for 7d and 28d, and their water absorption and softening coefficient were tested according to JGJ/T70-2009 Standard for Testing Methods of Basic Properties of Building Mortar.

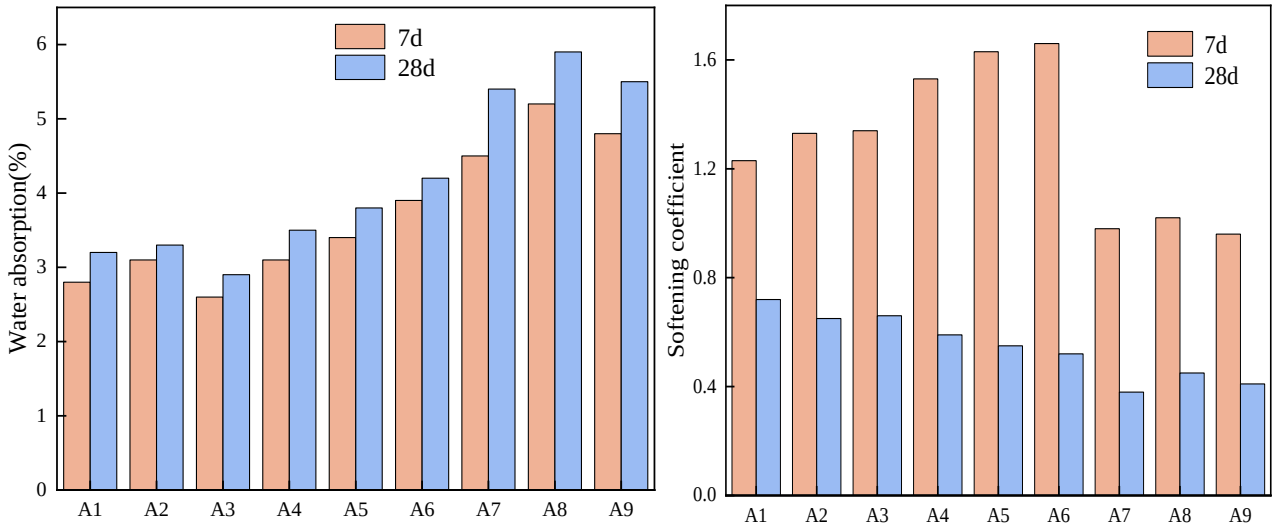

Figure 4. Water absorption of the sample (left), softening coefficient of the sample (right)

As can be seen from Figure 2, with the extension of soaking time, the water absorption rate of phosphogypsum based mortar increases, the softening coefficient decreases, and the water resistance decreases. With the increase of phosphogypsum content, the water absorption rate increases continuously, and the softening coefficient increases first and then decreases. Compared with the water absorption after soaking for 7 days, the water absorption after soaking for 28 days was improved. Compared with the softening coefficient of soaking for 7 days, the softening coefficient of soaking for 28 days decreased. With the prolonged soaking time, the specific surface area of phosphogypsum based mortar is larger, the contact points between gypsum crystals are more, the crystal structure and pore structure of the system are changed by hydrophysical and hydrochemical interactions and their mutual promotion, and the water absorption capacity of phosphogypsum based mortar is continuously enhanced. After encountering water, the water flows to the interior of the gypsum along the capillary channels, which quickly dissolves the gypsum, resulting in a continuous reduction of the softening coefficient.

3.5. Hydration Mechanism Of Phosphogypsum Based Plastering Mortar Composite System

X-ray diffraction (XRD) was used to characterize the phase changes of C2 and C3 at different curing ages.

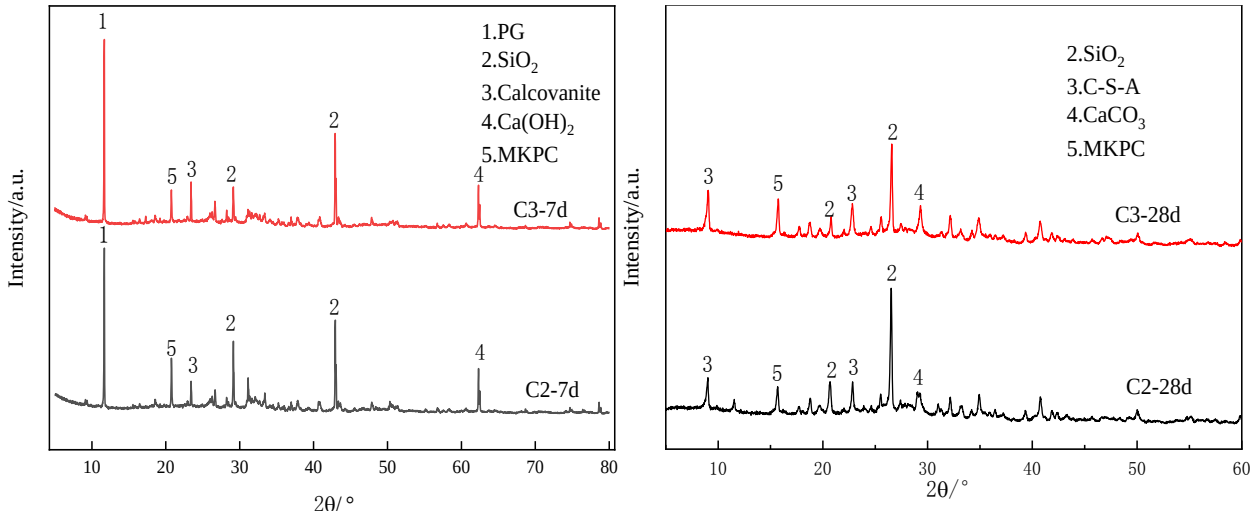

Figure 5. Phase composition analysis of samples from groups C2 and C3 in different curing periods

The gypsum component in the sample comes from phosphogypsum, silica mainly comes from fly ash particles, and $Ca(OH)_2$ comes from calcium carbide slag. Compared with C2, the diffraction peak value of calcium-vanadite contained in C3 is significantly increased, indicating that the formation of ettringite is the main reason for the improvement of the strength of the composite.

When the curing time is 7 days, unreacted gypsum dihydrate and $Ca(OH)_2$ can be observed in samples C2 and C3, and the formation of potassium magnesium phosphate and ettringite can be observed. This can be attributed to the fact that magnesium slag and potassium dihydrogen phosphate are very water-soluble and can be fully in contact with other raw materials and quickly dissolved in the slurry. After the magnesium slag dissolved quickly and participated in the hydration reaction, the potassium magnesium phosphate cementing material was formed, which was the extraction of the cementing system provided early strength.

When the curing time is 28 days, the strength of ettringite in groups C2 and C3 is significantly higher than that in 7 days, which conforms to the phase change law of phosphogypsum - magnesium slag - potassium dihydrogen phosphate - fly ash - calcium carbide slag. The slow excitation of $Ca(OH)_2$ and the low activity of fly ash enable long-term pozzolanic reaction in the flyash-titanium-gypsum - calcium carbide slag system. In this process, the OH^- of calcium carbide slag continuously depolymerizes the fly ash particles, releases the active silicoaluminate in the fly ash, and combines with calcium ions and sulfate ions in the slurry to produce cross-linked C-(A)-S-H and ettringite, which makes the strength of the composite material increase rapidly in the later stage of hydration.

4. CONCLUSION

In this paper, phosphogypsum-magnesium slag-potassium dihydrogen phosphate-fly ash-calcium carbide slag was used as raw materials to prepare phosphogypsum based plaster mortar. The optimal range of composite material ratio was determined through orthogonal test, and the influence of various factors on the compressive and flexural strength of the sample was analyzed and determined. The initial and final coagulation time, fluidity, water resistance, XRD of different samples were tested, the macro and micro properties of the samples were characterized and compared, and the basic performance evaluation and hydration mechanism of phosphogypsum based plastering mortar were obtained. The conclusions are as follows:

(1) The ratio between phosphogypsum, magnesium slag, potassium dihydrogen phosphate, fly ash and calcium carbide slag was determined by orthogonal experiment, and the mechanical properties of each group of samples were obtained. The increase of the content of potassium and magnesium phosphate had the greatest effect on the early mechanical properties of the composite system, and the

excessive addition of fly ash was not conducive to the development of the early mechanical properties of the system, but was conducive to the improvement of the mechanical strength in the later period. The biggest factor to improve the mechanical properties of the composite system in the later period is the calcium carbide slag content.

(2) Through comparison, it can be seen that phosphogypsum can effectively shorten the initial setting time and improve the compressive and folding strength of phosphogypsum-magnesium slag-potassium dihydrogen phosphate-fly ash-calcium carbide slag within a certain range, but too much phosphogypsum will lead to a decline in the later strength. When phosphogypsum: potassium magnesium phosphate: fly ash: titanium gypsum=50:25:20:20, the strength of the composite system can reach 2.98MPa in 60 days.

(3) When phosphogypsum: potassium magnesium phosphate: fly ash: When titanium gypsum =50:25:20:20, that is C3, the initial and final coagulation time can be obtained by testing, and the initial and final coagulation time is 118min and the final coagulation time is 223min, which meets the requirements of GB/T25181-2019 architectural gypsum plaster mortar that the initial and final coagulation time is greater than 60min and less than 480min. Its fluidity is 237mm, which meets the requirement that the fluidity of GB/T25181-2019 building gypsum plaster mortar is greater than 100mm.

(4) The water absorption of 7d in group C3 was less than 28d, and the softening coefficient of 7d was greater than 28d. With the extension of soaking time, the specific surface area of phosphogypsum based mortar is larger, the contact points between gypsum crystals are more, the crystal structure and pore structure of the system are changed by hydrophysical and hydrochemical interactions and their mutual promotion, and the water absorption capacity of phosphogypsum based mortar is continuously enhanced. After water is encountered, water flows along the capillary channels to the interior of the gypsum, which quickly dissolves the gypsum, resulting in a continuous reduction of the softening coefficient.

(5) The main hydration products of phosphogypsum based plastering mortar composite cementitious material are ettringite and C-(A)-SH gel. The addition of phosphogypsum resulted in the formation of ettringite in the system, and the content of Si and Al in C-(A)-S-H gel was increased, and the overall hydration degree of the material was improved. With the increase of curing time, the content of hydration products in the composite system increased significantly, the crystallinity of ettringite and the polymerization degree of C-(A)-S-H gel increased continuously, and C-(A)-SH gel was filled in the crystal skeleton of Ettringite, and the two were closely connected to provide strength for the composite gelling system.

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