Effect of cement and fluidized bed combustion ashes on properties of phosphogypsum composite cementitious materials

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Abstract. The effect of fluidized bed combustion ashes (FBC) and cement by monodoping and compound doping on the mechanical properties and water resistance of phosphogypsum composite cementitious materials was studied, and the mechanism was explored by SEM. The results showed that the cement and fluidized bed combustion ashes by monodoping have a negative effect on the compressive strength of phosphogypsum, but can effectively improve its softening coefficient. When cement and fluidized bed combustion ashes mixed together, the softening coefficient increased with the increase of cement from 0 to 10%. But the softening coefficient decreased with the increase of cement from 0 to 20%, however, the compressive strength increased. Through the ANOVA analysis, the optimal dosage of cement, fluidized bed combustion ashes and phosphogypsum was obtained. Through the SEM, the hydration products covered on the surface of gypsum crystal, increased the compactness of the hardened body.

1. Introduction

The phosphogypsum is the industrial by-product of the wet production of phosphate fertilizer[1-3]. The domestic stockpile has exceeded 500 million tons, and the annual output increases by 70 million tons, which caused great pollution to the environment[4]. However, gypsum products have the advantages of light weight, fire prevention, sound insulation and heat preservation[5-7], which are widely used in the construction industry. Through the modification of phosphogypsum to prepare gypsum products, it not only effectively treats the industrial by-product phosphogypsum, but also protects green environmental and utilize the solid waste, which conforms to the overall direction of national environmental protection and circular economy industrial policies.

The β-phosphogypsum prepared from industrial by-product phosphogypsum has the problems of poor water resistance and low strength[8]. The crystal surface of β - phosphogypsum crystal is rough, containing a certain amount of phosphorus and fluorine impurities[9, 10], and cracks, resulted in the low compressive strength and softening coefficient, and high saturated water absorption rate. Thus, it is difficult to prepare high-strength and water-resistant gypsum products.

At present, there has been a lot of researches on the modification of water resistance of gypsum, mainly through surface treatment[11, 12], inorganic cementitious material modification[13-15] and adding waterproof agent[16, 17] to improve the water resistance of gypsum. The surface treatment method can not make the gypsum achieve the water resistance in the whole body. The adding waterproof agent can improve the softening coefficient of gypsum, but has a negative impact on the compressive strength.
The modification of inorganic cementitious materials can significantly improve the mechanical properties and water resistance, which is one of the effective means to modify the industrial by-product phosphogypsum. However, there is a lack of systematic research on the influence of inorganic cementitious materials on the mechanical properties and water resistance of phosphogypsum. In this paper, the effect of cement and fluidized bed combustion ashes (FBC) on the properties of phosphogypsum was systematically studied by using the mixture design, and the regression equation of the compressive strength and softening coefficient of the ternary system of cement- fluidized bed combustion ashes-gypsum in the selected range is obtained by ANOVA analysis, which formed a system mix design method based on cement, fluidized bed combustion ashes and modified β-type phosphogypsum. It has guiding significance for the practical production and application of phosphogypsum.

2. Experiment

2.1. Raw material

The calcined phosphogypsum used in this study meets the requirement of GB/T 9776-2008, produced from a company in Sichuan with a density of 2.52kg/m³. The cement is ordinary portland cement 42.5 R, produced from a cement company in Sichuan with a specific surface area of 360m²/kg. Fluidized bed combustion ashes (FBC) was the solid waste of mix coal and sulfur-fixing agent in fluidized bed boiler with high temperature. The activity index of fluidized bed combustion ashes is 78% and specific surface area is 344.6m²/kg. The treatment of fluidized bed combustion ashes included the following steps: (1) The original slag was mixed with 1~3% water to obtain powder A; (2) Added powder A to the ball mill and grinded 15~30 minutes to get powder B; (3) Powder B was dried at 90~110°C for 1~2 hours to obtain fluidized bed combustion ashes.

Retarder is protein retarder, produced from Xiangqing gypsum retarder. The chemical composition of phosphogypsum, cement and fluidized bed combustion ashes are given in Table 1.

|            | SiO₂ | MgO | Al₂O₃ | Fe₂O₃ | CaO  | K₂O  | SO₃  | TiO₂ | P₂O₅ | Loss |
|------------|------|-----|-------|-------|------|------|------|------|------|------|
| gypsum     | 4.62 | 0.18| 2.90  | 1.13  | 42.67| 0.25 | 43.04| 0.21 | 2.11 | 2.89 |
| cement     | 21.39| 2.82| 5.15  | 3.86  | 61.04| 0.62 | 3.10 | 0.85 | 0.10 | 1.07 |
| FBC        | 42.71| 1.33| 21.85 | 10.25 | 14.86| 2.33 | 2.26 | 3.17 | 0.21 | 1.03 |

2.2. Mix proportions and preparation of specimens

The mix proportions for the phosphogypsum composite cementitious materials were presented in Table 2. The extreme vertex design method was used to design the mix proportion, with the dosage range of 0 ~ 20% of fluidized bed combustion ashes, 0 ~ 10% of cement, and 70% ~ 90% of phosphogypsum. The mix design model is shown in Figure 1, and the specific mix proportion is shown in Table 3.

| number | water-binder ratio | gypsum/% | FBC/% | cement/% | retarder/% |
|--------|--------------------|----------|-------|----------|------------|
| 1      | 0.60               | 100.00   | -     | 0.00     | 0.05       |
| 2      | 0.60               | 90.00    | 10.00 | 0.00     | 0.05       |
| 3      | 0.60               | 80.00    | 20.00 | 0.00     | 0.05       |
| 4      | 0.60               | 70.00    | 30.00 | 0.00     | 0.05       |
| 5      | 0.60               | 60.00    | 40.00 | 5.00     | 0.05       |

Table 2. The mix proportions for the phosphogypsum composite cementitious materials.
2.3. Test method
The compressive and flexural strength were measured by DYE-10A, according to the standard GB/T 17671-1999. The softening coefficient is the ratio of saturated compressive strength to dry compressive strength, following JC / T698-2010. The water absorption was tested according to the JCJ 70-2009. The crystal morphology of thermal insulation gypsum was observed through TECAN VEGA2.

3. Result and discussion

3.1. Effect of cement and fluidized bed combustion ashes by monodoping on properties of phosphogypsum composite cementitious material
The effects of fluidized bed combustion ashes and cement on the properties of phosphogypsum composite cementitious materials was seen from Figure 2 and Figure 3. With the addition of fluidized bed combustion ashes from 0 to 40%, the compressive strength of phosphogypsum composite cementitious material was reduced, but the softening coefficient was significantly improved. However, with the increase of fluidized bed combustion ashes from 10% to 40%, the compressive strength increased, while the growth rate of softening coefficient could slow down, when the addition of the fluidized bed combustion ashes exceeds 20%. The reason is that the hydration rate of fluidized bed combustion ashes is slow\cite{18}, which has no significant contribution to the strength of the phosphogypsum composite cementitious material. While the amount of gypsum was reduced and a weak interface transition zone between the unhydrated fluidized bed combustion ashes and gypsum

\begin{table}[h]
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\begin{tabular}{cccccc}
\hline
number & water-binder ratio & gypsum/\% & FBC/\% & cement/\% & retarder/\% \\
\hline
8 & 0.60 & 70.00 & 20.00 & 10.00 & 0.05 \\
9 & 0.60 & 90.00 & 0.00 & 10.00 & 0.05 \\
10 & 0.60 & 80.00 & 20.00 & 0.00 & 0.05 \\
11 & 0.60 & 81.25 & 16.25 & 2.50 & 0.05 \\
12 & 0.60 & 86.25 & 6.25 & 7.50 & 0.05 \\
13 & 0.60 & 86.25 & 11.25 & 2.50 & 0.05 \\
14 & 0.60 & 82.50 & 12.50 & 5.00 & 0.05 \\
15 & 0.60 & 76.25 & 16.25 & 7.50 & 0.05 \\
16 & 0.60 & 90.00 & 10.00 & 0.00 & 0.05 \\
\hline
\end{tabular}
\caption{The specific mix proportion.}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{The mix design model.}
\end{figure}
was obtained, which lead to the decrease of strength. With the increase of the fluidized bed combustion ashes, more fluidized bed combustion ashes effectively participate in the hydration reaction, and more fluidized bed combustion ashes was filled in the pores of gypsum, which increased the density of the matrix and increased the strength. When the phosphogypsum composite cementitious material was immersed in water for 24 hours, the unhydrated or not fully hydrated fluidized bed combustion ashes could continue to hydrate and generate hydrated calcium silicate, which increased the saturated water strength and softening coefficient.

![Figure 2. The effects of FBC dosages on the properties of phosphogypsum composite cementitious materials.](image1)

It can be seen from Figure 3 that in the range from 0 to 20%, the compressive strength was reduced due to the addition of cement, however, the softening coefficient was significantly improved, because of the continuous hydration of cement in water slowing down the reduction of strength. The utilization of cement modified phosphogypsum composite material has an optimal dosage, a value of 10%, and the strength and softening coefficient reach the maximum. According to the results of cement and fluidized bed combustion ashes, the addition of cement from 0 to 10% and the addition of fluidized bed combustion ashes from 0 to 20% were used to carry out the mixed test of fluidized bed combustion ashes and cement.

![Figure 3. The effects of cement dosages on the properties of phosphogypsum composite cementitious materials.](image2)

3.2. Effect of cement and fluidized bed combustion ashes by compound doping on properties of phosphogypsum composite cementitious material

The influence of cement and fluidized bed combustion ashes mixed together on the softening coefficient of phosphogypsum composite cementitious material was presented in Figure 4. The addition of cement and fluidized bed combustion ashes could significantly improve the softening coefficient and water resistance, resulted in the softening coefficient reaching above 0.7. The C-S-H gel and Ettringite in the gypsum matrix will be formed due to the presence of cement, wrapped and filled in the surface and gap of gypsum crystal, enhanced the internal structure density of hardened body and reduced the contact point between gypsum and water, thus improving the softening coefficient and water resistance. When the content of fluidized bed combustion ashes is 0-20%, the softening coefficient decreased with the increase of fluidized bed combustion ashes. This is because the unhydrated fluidized bed combustion ashes particles react with gypsum and cement to form
ettringite after hardened, destroyed the original gypsum crystal hardened body skeleton structure, resulted in the expansion and cracking of the samples\textsuperscript{[19]}. Thus, the saturated water strength and softening coefficient decreased after immersed in water. It is interesting that the more the gypsum, the lower the strength and softening coefficient due to the large solubility of dihydrate gypsum crystals and the low thermal stability of the contact point between the crystals, caused easy to dissolve and recrystallize.

Figure 4. The effects of cement and FBC mixed together on the softening coefficient of phosphogypsum composite cementitious materials.

The influence of cement and fluidized bed combustion ashes mixed together on the compressive strength of phosphogypsum composite cementitious material was presented in Figure 5. With the increase of cement content from 0 to 10\%, the compressive strength of gypsum increased first and then decreased. This is due to the excessively addition of cement resulted in the more formation of C-S-H gel and ettringite, produced local swelling internal stress inside the hardened body, which caused the expansion and crack of gypsum and destroyed the internal dense structure\textsuperscript{d}. Thus, the strength was significantly reduced. The compressive strength of gypsum increased with the increase of fluidized bed combustion ashes from 0 to 20\%. The calcium hydroxide generated by hydration of cement and calcium sulfate produced by hydration of gypsum could stimulate the potential hydraulic properties of fluidized bed combustion ashes\textsuperscript{[20]}, resulting in the formation of calcium aluminosilicate gel and ettringite.

Figure 5. The influence of cement and FBC mixed together on the compressive strength of phosphogypsum composite cementitious material.

In order to quantitatively describe the influence of cement and fluidized bed combustion ashes on the compressive strength and soften coefficient of phosphogypsum composite cementitious materials, the regression equation was obtained by ANOVA analysis of the experimental results. The results are as follows: \( y_1 = 36b + 7.7a + 0.2C + 0.4ab + 0.4bc - 0.1ac \), while \( y_2 = 0.26b - 0.06a + 0.006c - 0.002bc - 0.003ab \), where the content of fluidized bed combustion ashes is a, the content of cement is b, the content of gypsum is c, the compressive strength is \( y_1 \) and soften coefficient is \( y_2 \).

As shown in Figure 6, the optimized mix proportion was presented, obtained by ANOVA analysis on the compressive strength test results. When the water cement ratio is 0.6, the cement content is 6\%, the fluidized bed combustion ashes content is 20\%, and the phosphogypsum content is 74\%, the maximum compressive strength of phosphogypsum composite cementitious material is 17MPa. Through experiments to verify the optimization results is basically consistent.
3.3. the effect of water binder ratio on the properties of phosphogypsum composite cementitious materials

In order to explore the effect of water binder ratio on the properties of phosphogypsum composite cementitious materials, the 6% content of cement, the 20% content of fluidized bed combustion ashes is 20.00% and the 74% content of gypsum were used in this experiment. The effect of water binder ratio on the compressive strength and flexural strength and softening coefficient and water absorption of phosphogypsum composite cementitious material was shown in Figure 6 and Figure 7, respectively. The compressive strength and flexural strength of phosphogypsum composite cementitious materials increased with the decrease of water binder ratio from 0.6 to 0.3, while the compressive strength of phosphogypsum composite cementitious material increased from 17MPa to 31MPa, which was increased by 97%. The softening coefficient of phosphogypsum composite cementitious materials increased with the decrease of water binder ratio from 0.6 to 0.3, the softening coefficient of phosphogypsum composite cementitious material increased from 0.74 to 0.86, which was increased by 16.2%. The reason is that the theoretical water binder ratio is far lower, and a lower water binder ratio can significantly reduce the free water in the gypsum matrix, which could reduce the porosity of the hardened body, improve the structural density, reduce the contact point of gypsum dihydrate and water, and reduce the amount of dissolution, thus, the strength and softening coefficient was significantly increased.

Figure 6. The effect of water binder ratio on the compressive strength and flexural strength of phosphogypsum composite cementitious material.

Figure 7. The effect of water binder ratio on the softening coefficient and water absorption of phosphogypsum composite cementitious material.

3.4. SEM

The SEM images of phosphogypsum composite cementitious material were shown in Figure 8. It could be obviously observed that the dihydrate gypsum is mainly a long column shape crystal with irregular distribution in the matrix and large gap between crystals. There has been lots of unhydrated fluidized bed combustion ashes and a little of indeterminate gel with the addition of 20% fluidized bed combustion ashes, causing the weak crystal overlap and little effective hydration products, While there has been little of needle ettringite crystals with the addition of 10% cement, resulting in weak overlap, which significantly improves the softening coefficient of gypsum. However, the addition of cement and fluidized bed combustion ashes makes the crystal coarse, decreased the point between crystals,
lead to a decrease in compressive strength. However, there has been lots of needle ettringite crystals and C-S-H gel covered in the surface of dihydrate gypsum crystals with the addition of 20% fluidized bed combustion ashes and 6% cement, reduced the pores between the crystals, increased the compactness of the hardened body, and the dihydrate gypsum crystals are not easy to contact with water, which significantly increased the compressive strength and softening coefficient. In addition, it can be seen that the encapsulation of the hydration products of inorganic cementitious materials on dihydrate gypsum crystals is the main reason for the improvement of the softening coefficient of gypsum products.

Figure 8. The SEM images of phosphogypsum composite cementitious material: (a) phosphogypsum, (b) phosphogypsum +20%FBC, (c) phosphogypsum +20%FBC+6%cement, (d) phosphogypsum +10%cement.

4. Conclusion
(1) The addition of fluidized bed combustion ashes and cement mixed alone has a negative impact on the compressive strength of phosphogypsum composite cementitious materials, but a positive effect on the softening coefficient.

(2) When the fluidized bed combustion ashes and cement mixed together, the addition of cement can significantly improve the softening coefficient of gypsum, and the addition of fluidized bed combustion ashes can improve the compressive strength, but has a negative impact on the softening coefficient.

(3) Through the ANOVA analysis, the optimal mix proportion of cement-fluidized bed combustion ashes-phosphogypsum was obtained, with a 6% cement, 20% fluidized bed combustion ashes and 74% phosphogypsum. Moreover, the compressive strength and soften coefficient could significantly increased with the decrease of water binder ratio.

(4) In the presence of cement and fluidized bed combustion ashes together, the hydration product could effectively cover and wrap the surface of the dihydrate gypsum crystals, increasing the compactness of the hardened body.

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