Reaction Mechanism Analysis of Phosphorus Slag - Fly Ash - Phosphorus Gypsum - Cement Foamed Concrete

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Abstract. In this study, phosphorous slag powder, fly ash and cement were used as composite cementing materials, and phosphogypsum was used as the activator of phosphorous slag powder and fly ash to stimulate their activity. The hydration reaction of cement, phosphorous slag powder, fly ash and phosphogypsum was studied. The results show that the hydration products of cement, cement + phosphorous slag powder, cement + phosphorous slag powder + fly ash, and cement + phosphorous slag powder + fly ash + phosphorous gypsum have the same mineral composition but different relative content. The hydration samples of cement, cement + phosphorous slag powder, cement + phosphorous slag powder + fly ash, and cement + phosphorous slag powder + fly ash + phosphogypsum have certain differences in microstructure and quantity, especially ettringite. Cement hydration can stimulate the activity of phosphorus slag powder and fly ash, in turn, the addition of phosphorus slag powder, fly ash and phosphogypsum can promote the hydration process of cement, improve the quality of hydration products, and improve the density of concrete structure.

Keywords. Foam concrete, water cement ratio, fluidity, dry density, shrinkage value, water absorption.

1. Introduction

In cement, fly ash, phosphorus slag and phosphogypsum foam concrete, the independent hydraulicity hardness of cement is the main component of matrix strength. Fly ash has pozzolanic activity, and phosphorus slag powder has potential hydraulicity, which means its strength can be enhanced by activation. Phosphogypsum is a sulfate activator that can stimulate the activity of fly ash and phosphorus slag powder [1]. When cement, phosphorus slag powder, fly ash and phosphogypsum are compounded and reacted with water, the chemical components are complementary, and the substances are mutually diffused, exchanged and reacted. The products produced by the separate reaction are different from the products formed by the composite doping. The strength is different, and the structure of the product is different [2]. This study analyzes the hydration reaction mechanism by analyzing the separate hydration reaction and composite hydration reaction between cement, fly ash, phosphorus slag powder and phosphogypsum so as to improve the understanding of the theoretical basis for improving matrix performance in cementitious materials, improving the quality of hydration products and increasing the density of concrete structures [3, 4].
2. Experimental Materials and Methods

2.1. Raw Materials

Cement: 42.5 ordinary Portland cement produced by Guizhou Conch Panjiang Cement Co., Ltd. Fly ash: Fly ash from a power plant in Guiyang. Phosphorus slag powder: Phosphorus slag powder from a yellow phosphorus plant in Guizhou. Phosphogypsum: Phosphogypsum from Guizhou Wengfu Phosphoric Acid Plant, with a pH of 4.1 and an off-white color. Foaming agent: HTQ-1 animal and vegetable protein composite foaming agent produced by Henan Huatai Building Material Co., Ltd.

2.2. Experimental Methods

2.2.1. Analysis of Raw Material Characteristics. (1) Cement: The chemical compositions have been listed in table 1 and the physical properties can be found in table 2.

| CaO   | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | Na₂O | K₂O | SO₃ | Total alkali content |
|-------|------|-------|-------|-----|------|-----|-----|---------------------|
| 55.56 | 21.70| 7.25  | 4.55  | 1.86| 0.40 | 0.70| 2.8  | 0.91                |

Table 2. Physical properties of ordinary Portland cement.

| Fineness (screenings of 80μm square-hole)/% | Standard consistency water consumption (%) | Setting Time (min) | Compressive strength (MPa) | Rupture strength (MPa) | Stability |
|---------------------------------------------|-------------------------------------------|--------------------|----------------------------|------------------------|-----------|
|                                            |                                           | initial set | final set | 3d | 28d | 3d | 28d |                       |
|                                            |                                           | 190         | 263      | 18.9 | 45.8 | 4.9 | 10.7 | Up to standard        |

(2) Phosphorus slag powders: The chemical composition of phosphorus slag powders can be found in table 3.

As can be seen from table 3, the main chemical composition of the phosphorus slag powder is CaO and SiO₂, which account for more than 80%, along with a small amount of Al₂O₃, Fe₂O₃ and MgO. It mainly exists in the amorphous forms, indicating that the phosphorus slag powder has a certain potential hydraulicity. As can be seen from figure 1, the particle size distribution of the phosphorus slag powder is relatively large, mainly concentrated in 10-60 μm.

Table 3. Chemical composition of phosphorus slag powders (wt%).

| CaO   | SiO₂  | Al₂O₃ | Fe₂O₃ | MgO | P₂O₅ | CaF  | Loss |
|-------|-------|-------|-------|-----|------|------|------|
| 43.32 | 37.53 | 3.48  | 1.69  | 1.71| 3.37 | 1.03 | 3.20 |

The compressive strength of the cement for 28 days is 46.5 MPa, and the compressive strength of the phosphorous slag powder for 28 days is 28.7 MPa. Therefore, the activity index N₂₈ of the phosphorus slag powder is 0.62.

The water demand ratio of the phosphorus slag powder is 88.8%. Since the phosphorus slag powder is relatively fine, it can be filled into the gap between the cement particles by being incorporated into the concrete to replace part of the free water.

The apparent density of cement is 3100 kg/m³, which is greater than 2850 kg/m³ of phosphorus slag powder. It is possible to reduce the weight of foam concrete by adding phosphorous slag powder to partially replace cement in foam concrete. However, there is a small amount of P₂O₅ and F in the
chemical composition of the phosphorus slag powder, which will delay the setting time. Therefore, the dosage generally cannot exceed 40%.

![Figure 1. The particle size analysis of phosphorus slag powders.](image)

(3) Fly ash: The chemical composition of fly ash, XRD mineral composition and SEM micromorphology analysis and particle size distribution are shown in table 4, figures 2a and 2b.

It can be seen from table 4 that the main chemical composition of fly ash is SiO₂, Al₂O₃ and Fe₂O₃, which account for 80% in total. As shown in XRD analysis spectrum of figure 2a, there is no obvious crystalline mineral diffraction peak, only an amorphous glass frit-shaped diffraction peak at 2θ = 20-30°, which shows that fly ash has high activity. Further, it is known from the XRD pattern that there are also crystal phases of mullite and quartz minerals of small diffraction peaks.

It can be seen from the SEM analysis pattern of fly ash in figure 2b that the fly ash mainly consists of bead-shaped particles of different sizes and some small particles are adsorbed on the large particles with smooth surface. As can be seen from figure 3, the particles are in normal distribution and the particle size is mainly concentrated in 10-60 μm.

| Table 4. Chemical composition of fly ash (wt%). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| CaO             | SiO₂            | Al₂O₃           | FeO+Fe₂O₃       | MgO             | Na₂O            | K₂O             | SO₃             | Loss            |
| 4.12            | 46.80           | 24.50           | 8.55            | 0.85            | 0.64            | 0.99            | 0.63            | 13.15           |

![Figure 2. The XRD and SEM analysis patterns of phosphorus slag powders.](image)
The compressive strength of the cement for 28 days is 46.5 MPa, and the compressive strength of the fly ash for 28 days is 32.6 MPa. Therefore, the activity index N28 of the fly ash is 0.70.

The water demand ratio of fly ash is 81.6%, because the fly ash in the form of beads acts as a ball bearing, which reduces the friction between particles and reduces the demand for water. The incorporation of fly ash can improve the fluidity of foam concrete and reduce the shrinkage and cracking of foam concrete.

The apparent density of cement is 3100 kg/m$^3$, the apparent density of phosphorus slag powder is 2850 kg/m$^3$, which is greater than that of fly ash of 2420 kg/m$^3$. The addition of fly ash to foam concrete can reduce the weight of concrete. The larger the amount of fly ash is, the more the weight of the concrete is reduced. However, if the amount is too large, the mechanical properties of the foam concrete will drop sharply and a longer curing time will be required.

(4) Phosphogypsum: Its chemical composition, XRD mineral composition and SEM micromorphology analysis and particle size distribution are shown in table 5, figures 4a and 4b.

It can be seen from table 5 that the main chemical composition of phosphogypsum is CaO and SO$_3$, with a small amount of impurities such as P$_2$O$_5$, F and organic matter. It can be seen from the XRD pattern in figure 4a that CaO, SO$_3$ and crystal water are mainly in the form of crystals of calcium sulfate dihydrate CaSO$_4$·2H$_2$O. The content of CaO, SO$_3$ and crystal water can reflect that the content of calcium sulphate dihydrate in phosphogypsum is about 90%, which meets the standard of secondary gypsum and has high utilization value. There is also a small amount of SiO$_2$, CaHPO$_4$·2H$_2$O, CaPO$_4$(OH)·2H$_2$O and AlPO$_4$·2H$_2$O in the phosphogypsum. It can be seen from the SEM analysis of the phosphogypsum of figure 4b that the phosphogypsum crystal are mostly in the shape of polygonal plate, of various sizes, with a smooth surface, and a small amount of crumb-like particles. As can be seen from figure 5, the particles are normally distributed, mainly concentrated in the range of 80-105 μm.

The water demand ratio of phosphogypsum is 94.4%, which is greater than 88.8% of phosphorus slag powder and 81.6% of fly ash, because the phosphogypsum particles are polygonal plate-shaped, which is not conducive to flow, and its impact on fluidity is worse than fly ash and phosphorus slag powder.

![Figure 3](image.png)

Figure 3. The particle size analysis of fly ash.

### Table 5. Chemical composition of phosphogypsum (wt/%).

|     | SiO$_2$ | Al$_2$O$_3$ | CaO  | MgO  | SO$_3$ | F    | w-P$_2$O$_5$ | t-P$_2$O$_5$ | Organics | Crystal water |
|-----|---------|-------------|------|------|--------|------|-------------|-------------|----------|-------------|
|     | 3.08    | 0.41        | 29.82| 0.11 | 41.86  | 0.41 | 0.81        | 2.35        | 0.12     | 19.11       |

Note: The moisture content of phosphogypsum is 21.61%; w-P$_2$O$_5$: water-soluble phosphorus; t-P$_2$O$_5$: total phosphorus.
The apparent density of phosphogypsum is 2500 kg/m³, which is less than 3100 kg/m³ of cement and 2850 kg/m³ of phosphorus slag powder, but greater than 2420 kg/m³ of fly ash. When it is incorporated into concrete as the sulfate activator for phosphorus slag powder and fly ash, it does not promote the hydration reaction, instead, it will prolong the setting time. Excessive incorporation of phosphogypsum will affect the performance of the concrete. Therefore, it is necessary to properly control the amount of phosphogypsum.

(5) Foaming agent: The foaming ability and stability of the HTQ-1 animal and vegetable protein composite foaming agent are shown in table 6.

As can be seen from table 6, when the foaming temperature of the HTQ-1 animal-plant protein composite foaming agent is 10 °C and the dilution ratio is 1:20, the half life of the foam is the longest and the stability is the best. When the temperature is 30 °C and the dilution ratio is 1:20, the foaming ability is the best and the foaming volume is the largest. Therefore, to realize the best foaming ability and stability, the dilution ratio should be 1:20, and the foaming temperature should be controlled at about 20 °C.

2.2.2. Performance Testing and Characterization of Foam Concrete. Apparent density: According to GB/T 208-2014 “Test method for determining cement density”, the apparent density of cement, phosphorus slag powder, fly ash and phosphogypsum are measured using the Lee’s bottle method.
Table 6. The foaming ability and stability of HTQ-1 foaming agent.

| Temperature | Property | Dilution Ratio |
|-------------|----------|----------------|
|             |          | 1:20 | 1:30 | 1:40 | 1:50 |
| 10°C        | $V_0$/ml | 331  | 300  | 261  | 241  |
|             | $t_{1/2}$/sec | 145  | 92   | 69   | 59   |
| 20°C        | $V_0$/ml | 351  | 331  | 301  | 251  |
|             | $t_{1/2}$/sec | 139  | 81   | 53   | 44   |
| 30°C        | $V_0$/ml | 362  | 321  | 312  | 269  |
|             | $t_{1/2}$/sec | 125  | 72   | 49   | 39   |
| 40°C        | $V_0$/ml | 352  | 281  | 259  | 251  |
|             | $t_{1/2}$/sec | 94   | 66   | 48   | 40   |

Water demand ratio: According to the test method for water demand in GB/T 1596-2005 “Fly ash in cement and concrete”, the water demand ratio of fly ash, phosphorus slag powder and phosphogypsum are measured.

Activity index: According to GB/T 26751-2011 “Plasticized electric furnace phosphorus slag powder used in cement and concrete”, the activity index of phosphorus slag powder and fly ash for 28 days are measured.

Particle size distribution: The phosphorus slag powder, fly ash and phosphogypsum are dried and cooled, and the particle size distribution is measured by the American Beckman Coulter LS13320M laser particle size distribution instrument.

Mineral composition analysis: The mineral composition of phosphorus slag powder, fly ash and phosphogypsum are analyzed by Siemens D5000 X-ray diffractometer.

Micromorphology analysis: After vacuum metal spraying, the morphology of phosphorus slag powder, fly ash and phosphogypsum is observed by scanning electron microscopy with German ΣSIGA field emission.

Foaming agent performance test: The foaming ability and stability of the foaming agent are detected by high-speed stirring method. 200ml of the foaming agent dilution liquid is poured into the high-speed mixer for high-speed stirring for 1 minute, and the foam volume in the mixer can be viewed as the foaming ability of the diluent for the blowing agent to be tested, the time from the stop of stirring to the time when the foam secreted 100 ml of the dilution water can be taken as the half life of the foam stability.

3. Experimental Results and Analysis

3.1. XRD Analysis

The XRD analysis patterns of different hydration age samples are shown in figure 6.

As can be seen from figure 6a:

1. After hydration with 100% cement for 3 days (see sample 1 in the figure), calcium hydroxide Ca(OH)$_2$, ettringite AFT and C-S-H gels are formed. Due to the low crystallinity of C-S-H, there’s only a taro peak nearby 2θ=30° along with unhydrated cement clinker mineral tricalcium silicate (C$_3$S) and dicalcium silicate (C$_2$S).

2. After hydration with 60% cement + 40% phosphorus slag powder for 3 days (see sample 2 in the figure), calcium hydroxide Ca(OH)$_2$, ettringite AFT and low crystallinity CSH gel are formed, along with unhydrated cement. Since the intensity of the diffraction peak of sample 2 is significantly
the product formed. The phosphorus slag reacts with Ca(OH)_2 produced by cement hydration and forms C-S-H gel, while consuming a part of Ca(OH)_2.

(3) After hydration with 60% cement + 20% phosphorus slag powder + 20% fly ash for 3 days (see sample 3 in the figure), the product formed doesn’t change. Compared with sample 1 and 2, the characteristic diffraction peak intensity of Ca(OH)_2 is lowered, but the characteristic diffraction peak intensity of AFt is high. It can be seen that fly ash reacts with Ca(OH)_2 at a high speed, and the generated products include C-S-H gel and AFt.

(4) After hydration with 60% cement + 20% phosphorus slag powder + 20% fly ash + 10% phosphogypsum (adding) for 3 days (see sample 4 in the figure), the products are identical, and the characteristic diffraction peak intensity of Ca(OH)_2 doesn’t change much, but the intensity of the characteristic diffraction peak of AFt is rising, which indicates that AFt is the main product of phosphogypsum after reaction [5].

It can be seen from figures 6a-6c that the characteristic diffraction peak intensity of tricalcium silicate (C_3S) and dicalcium silicate (C_2S) in pure cement gets lower with the extension of hydration age (see picture 1 in each figure), indicating that the hydration process of cement is gradually deepening, but it is not complete. When the hydration reaction reaches 28d and 56d (see (b), (c)), the peak sizes of Ca(OH)_2 and AFt of sample 2 and 3, 4 are close, which indicates that the hydration reaction of the later stage of phosphorus slag powder is increasing. The T-head of the C-S-H gel is larger than that of sample 1 and it becomes more pronounced at 56 days.
3.2. Phosphorus Slag - Fly Ash - Phosphogypsum - Cement Foam Concrete Sample
The mix ratio of foam concrete in this study is: cement 60%, phosphorus slag powder 20%, fly ash 20%, phosphogypsum 10%, 65% foam volume (density grade A06). The foam concrete sample can be found in figure 7.

(a) Density grade A06 Foam concrete  
(b) A06 foam concrete section  
(c) SEM micrograph of 65% foam and foam concrete

Figure 7. Foam concrete samples.

3.3. SEM Analysis
The SEM analysis patterns of 28 days hydration samples are shown in figure 8.
   It can be seen from figure 8a that there are many hexagonal plate-like Ca(OH)$_2$ crystals in the hydrated sample of 100% cement 28d, and AFt whiskers are grown in areas with large void, interspersed in gelled C-S-H.
   It can be seen from figure 8b that after the cement and the phosphorus slag powder are hydrated for 28 days, corroded pores and grooves can be found on the surface of the phosphorus slag powder particles, covered with short cylindrical AFt whiskers and a layer of fish scale C-S-H gel. The aspect ratio of AFt whiskers is significantly smaller than that formed by 100% cement hydration.
   It can be seen from figure 8c that in the samples of cement, phosphorus slag powder and fly ash hydrated for 28 days, the surface of the fly ash and phosphogypsum particles is covered with a thick layer of C-S-H gel, and a large amount of AFt whiskers can be found on the surface of the fly ash particles, and the C-S-H gel and AFt whiskers are interpenetrated into each other, forming a complex and dense network structure.
   It can be seen from figure 8d that after the phosphogypsum is added to the cement, phosphorus slag powder and fly ash system, the corrosion of the surface of the phosphorus slag particles is intensified, and the internal reaction has occurred. The fly ash is also wrapped with a thick layer of hydration products the same way as the phosphorus slag particles. Cement, phosphorus slag powder, fly ash and phosphogypsum particles are wrapped in C-S-H gel, AFt whiskers are interspersed in the C-S-H gel system, and the whiskers are overlapped with each other in the pores to make the whole structure intact.

3.4. Analysis of Hydration Mechanism
From the above XRD and SEM analysis, the hydration mechanism of the cement composite phosphorus slag powder, fly ash and phosphogypsum is
   (1) Pure cement rapidly reacts with water to form hydrated products such as Ca/Si high-alkalinity C-S-H gel, free Ca(OH)$_2$ and AFt.
Figure 8. The SEM analysis patterns of 28 days hydration samples: (a) 100% cement, (b) 60% cement + 40% phosphorus slag powders, (c) 60% cement + 20% phosphorus slag powders + 20% fly ash, (d) 60% cement + 20% phosphorus slag powders + 20% fly ash + 10% phosphogypsum (adding).
(2) After the addition of 40% phosphorus slag powder, under the activation of OH- in the cement product Ca(OH)2, the phosphorus slag powder breaks the chemical bond such as Si-O-Si, Al-O-Al and Si-O-Al in the vitreous and release the SiO2 and AlO3. The hydration reaction of SiO2 and AlO3 with Ca(OH)2, overbased C-S-H gel and gypsum in cement produces low-alkalin CSH gel (Ca/Si small) with stronger strength and better stability and hydrated calcium sulphoaluminate AFt whiskers. During the hydration reaction, soluble P and F in the phosphorus slag powder also react with Ca(OH)2, forming poorly soluble calcium phosphate and calcium fluoride [5], and partially cover the cement and phosphorus slag powder particles to prevent further hydration of the cement and phosphorus slag powder particles, so that the crystals which have already nucleated can grow sufficiently. Therefore, the AFt whiskers formed by the cement and the phosphorus slag are coarser.

(3) After the addition of phosphorus slag powder and fly ash, phosphorus slag powder and fly ash are simultaneously affected by Ca(OH)2, the Si-O bond and Al-O bond are broken and reacts with C-S-H, Ca(OH)2 and gypsum in the pozzolanic reaction, forming the hydration products C-S-H gels and AFt whiskers. Since the content of Al2O3 in the fly ash network intermediate is higher than that of the phosphorus slag powder, the activity of the vitreous structure is large, and the Si-O and Al-O bonds are more likely to be broken, so the fly ash reacts faster than the phosphorus slag.

(4) After the addition of phosphorus slag powder, fly ash and phosphogypsum, apart from the reaction with Ca(OH)2, AlO3 in the phosphorus slag powder and fly ash also reacts with Ca2+, SO42- dissolved from phosphogypsum and C-S-H gels, forming AFt. SO42- is adsorbed on the activation point of Al3+ network intermediate on the surface of the vitreous of phosphorous slag powder and fly ash, disconnecting Si-O-Al bond, and continuously stimulating the activity of phosphorus slag powder and fly ash. SO42- also reacts with the cement product Ca(OH)2 forming CaSO4, which further reacts with phosphorus slag powder and fly ash [5].

The addition of phosphorus slag powder, fly ash and phosphogypsum to the cement will delay the hydration of the cement and reduce the early strength, but it can reduce the free Ca(OH)2, improve the quality of the C-S-H gel, increase the amount of hydration products and promote the long-term strength.

4. Conclusion
(1) In the four cementitious materials system of Cement, cement + phosphorus slag powder, cement + phosphorus slag powder + fly ash, cement + phosphorus slag powder + fly ash + phosphogypsum, the mineral composition of the hydration products is the same, but with different relative content.

(2) Quantity and microscopic morphology of hydrated samples in four cementitious materials systems of cement, cement + phosphorus slag powder, cement + phosphorus slag powder + fly ash, cement + phosphorus slag powder + fly ash + phosphogypsum are different, especially in terms of ettringite.

(3) Cement hydration products can stimulate the activity of phosphorus slag powder and fly ash. In turn, the incorporation of phosphorus slag powder, fly ash and phosphogypsum can also promote cement hydration, improve the quality of hydration products, and improve the density of concrete structure.

Reference
[1] Sheng G 2004 The Mechanism of the Activation of Phosphorus Slag Activity and the Retardation of Portland Cement Nanjing: Nanjing University of Technology
[2] Pu X and Wang Y 2002 High-performance active mineral admixture and high performance of concrete (continued) Concrete (3) 3-6
[3] Jiang D 2003 New progress in the application of foam concrete China Cement (3) 46-48
[4] Wei W 2013 Analysis and application of foam concrete Concrete (2) 136-138
[5] Tsuyuki N and Koizumi K 2004 Granularity and surface structure of ground granulated blast-furnace slags Journal of the American Ceramic Society 82 (8) 2188-2192
[6] Liu X 2014 Effect of activator on the properties of brick powder foam concrete Concrete (1) 76-78