Study on Preparation and Durability of Phosphogypsum Composite Cementitious Foam Concrete

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Abstract. Acid base salt solution erosion, carbonization test and freeze-thaw cycle test of cement foam concrete and phosphogypsum based foam concrete were carried out respectively. The results show that compared with cement based foam concrete, phosphogypsum based foam concrete has stronger performance of resisting acid and alkali salt attack. This is mainly due to the fact that its internal cement minerals and hydration products have less active components, and are not easy to react with acid-base salts, and have better ability to resist freeze-thaw cycles at the same time. However, the resistance to carbonation is not as good as that of cement based foam concrete. This is due to the high content of aluminum in the interior and the large volume of ettringite, which is easier to be carbonized.

1. Introduction

The massive accumulation of phosphogypsum not only takes up a lot of land resources, but also its harmful substances can threaten human health and safety through air transmission and water cycle [1-8], so it is urgent to solve the problem of phosphogypsum. As the largest building material, cement concrete has the ability to digest phosphogypsum on a large scale. The preparation of concrete from phosphogypsum is the future way out for phosphogypsum. With the development of construction industry, concrete not only needs to have higher strength, but also needs to have the properties of flame retardant, lightweight, heat insulation, sound absorption and noise reduction. Foam concrete arises at the historic moment. It is one of the trends of concrete development in the future, [9-13]. There are many factors that affect the performance of foamed concrete, such as foaming agent, cementitious material, water binder ratio, water reducing agent, other admixtures and admixtures. However, the research on the durability of foam concrete is relatively few. The existing research mainly focuses on the correlation between the density and compressive strength of foam concrete. The research shows that the compressive strength and ultimate dry density of foam concrete are one-to-one correspondence under the premise of the same composition, proportioning and preparation process. However, some durability properties of foam concrete, such as frost resistance, carbonization resistance and acid and alkali resistance, are seldom studied.
2. Raw Materials and Test Methods

2.1 Test Materials
The test raw materials are mainly phosphogypsum, produced by Sichuan Shijie environmental protection Co., Ltd.; ordinary portland cement with strength grade of 32.5mpa, produced by conch Co., Ltd.; S95 slag powder, produced by Baotian Co., Ltd.; fly ash, produced by Dawu Co., Ltd.; foaming agent, produced by BASF Co., Ltd.; water reducer, produced by subote New Material Co., Ltd.; self-made Laboratory Early strength agent and polypropylene; deionized water. The chemical composition of phosphogypsum and cement is shown in Table 1 and table 2.

| chemical composition | SiO₂ | CaO | Al₂O₃ | MgO | Fe₂O₃ | P₂O₅ | SO₃ | F | K₂O | TiO₂ | SrO |
|----------------------|------|-----|-------|-----|-------|------|-----|---|-----|------|-----|
| wt%                  | 2.41 | 34.2| 0.29  | 0.21| 0.2   | 2.34 | 51.3| 1.14| 0.04| 0.04| 0.05|

Wt: weight ratio

2.2 Test Methods

2.2.1 Preparation of foam concrete
(1) Ingredients: the total weight of raw materials is 450g. After the mix proportion is calculated according to the test requirements, each raw material is accurately weighed.

(2) preparation of foaming agent solution: mixing the foaming agent and water in proportion, making the foam with stable structure.

(3) mixing: stirring raw materials according to GB/T 17671-1999 "cement mortar strength test method (ISO method)", then mixing with the prepared foam, stir 1min[14] quickly.

(4) Molding: slowly and evenly pour the evenly stirred slurry into the test mold, spread the slurry with slight vibration, and stop foaming in the cement standard curing box.

(5) Curing: place the sample and the test mold in the cement standard curing box for 2 days, scrape the surface foaming protuberance and demould, and put the demoulded sample into the water tank with constant temperature of 20 ℃ for curing to the specified age.

In order to better observe and compare the durability of foamed concrete prepared by phosphogypsum based cementitious materials, a number of cement foam concrete with the same density and strength grade were prepared for the following experimental comparison. The target strength of the two kinds of foam concrete is 5MPa, the target dry density is 600kg/m³, and the raw material ratio of the two kinds of foam concrete is shown in Table 3.

| raw material | W/C | PCE(%) | FA | PG | MP | C | PF(%) | FSA(%) |
|--------------|-----|--------|----|----|----|---|-------|--------|
| P            | 0.2 | 1.5    | 30 | -  | -  | 70| 1.5   | 1.5    |
| G            | 0.2 | 1.5    | -  | 40 | 50 | 10| 1.5   | 1.5    |

G: phosphogypsum based foam concrete; P: cement based foam concrete
PF: polypropylene fiber; FSA: early strength agent
P: Target density; PCE: Polycarboxylate Superplasticizer
PG: phosphogypsum; MP: slag powder
2.2.2 Acid erosion study
The foamed concrete was maintained to the test age (28d), and all of them were immersed in 5%HCL solution for erosion test. The quality changes under different erosion time were tested, and the strength and the appearance were observed when eroded to 28d and 70D.

2.2.3 Alkali erosion study
The foamed concrete was maintained to the test age (28d), and all of them were immersed in 10%NaOH solution for erosion test. The quality changes under different erosion time were tested, and the strength and the appearance were observed when eroded to 28d and 70D.

2.2.4 Sulfate erosion study
The foamed concrete was maintained to the test age (28d), and all of them were immersed in 5%Na2SO4 solution for erosion test to test the quality change under different erosion time.

2.2.5 Research on frost resistance
The foam concrete was maintained to the test age (28d), and the freeze-thaw cycle test was carried out according to the standard of GBT 50082-2009 "long term performance and durability test method of ordinary concrete". The quality changes and strength changes of the specimens under different cycle numbers were tested, and the appearance damage was observed.

2.2.6 Carbonation resistance
The foam concrete was maintained to the test age (28d). Carbonization test was carried out according to GBT 50082-2009 standard for long term performance and durability test methods of common concrete, and its quality change, strength change and carbonization depth were recorded.

3. Results and Discussion

3.1 Effect of Acid Erosion on Quality and Strength of Phosphogypsum and Cement Based Foam Concrete
The effect of acid on the quality of phosphogypsum and cement based foam concrete is shown in Figure 1. As can be seen from Fig. 1, under the erosion of dilute hydrochloric acid with 5% mass concentration, the quality of 1d-7d phosphogypsum and cement based foam concrete decreased little. This is due to the carbonization of natural curing, which results in the formation of large amounts of CaCO3 on the surface, resulting in more compact surface structure, which can protect the surface and interior of concrete at the early stage of erosion, and reduce as much as possible. The effect of erosion. As time goes on, the erosion effect increases gradually. After the surface calcium carbonate structure is destroyed, the carbonized part inside the concrete is more easily eroded by hydrochloric acid solution. The quality of the foamed concrete prepared by two different cementing materials has a significant decrease. It can be seen from the diagram that the quality loss of cement foam concrete is more obvious than that of phosphogypsum based foam concrete, which is due to the large amount of cement in the cement based foam concrete, and is more susceptible to acid erosion. After 70d, the mass loss of cement based foam concrete is 8.9g, much larger than that of phosphogypsum based foam concrete 6g.
Figure 1. Effect of acid erosion on the quality of two kinds of foam concrete

The effect of acid solution on the strength of phosphogypsum and cement based foam concrete is shown in Table 4. From table 4, it can be seen that with the increase of acid corrosion time, the strength of two kinds of foam concrete decreases, and the strength of cement foam concrete decreases more than that of phosphogypsum based foam concrete, which is also related to the phenomenon of mass loss of two kinds of foam concrete in the front. coincide.

Table 4. Effect of acid erosion on compressive strength of two kinds of foam concrete

| Sample  | Erosion time(d) | 1d  | 28d  | 70d  |
|---------|----------------|-----|------|------|
| P       | strength(MPa)   | 5.0 | 4.5  | 4.1  |
| G       |                 | 5.0 | 4.7  | 4.2  |

3.2 Effect of Alkali Corrosion on Quality and Strength of Phosphogypsum and Cement Based Foam Concrete

The effect of acid on the quality of phosphogypsum and cement based foam concrete is shown in Figure 2. It can be seen from Fig. 2 that the quality of cement based and phosphogypsum based foam concrete has obviously decreased under the erosion of sodium sulfate solution of 5% mass concentration. In the early stage of erosion, the quality of the two kinds of foam concrete decreased slightly, which was mainly due to the surface carbonization of concrete resulting in low surface basicity. With the strengthening of corrosion time, the hydration products that have not been carbonized will react with the alkali solution of the corrosion solution, resulting in a series of defects, such as internal structure expansion, cracks and so on, which will accelerate the erosion of the alkali solution. As a result, the quality of the concrete will decrease considerably. As the active components in cement based foam concrete are more [15], the alkali aggregate reaction will be more prone to occur. The quality loss is also large.
Figure 2. Effect of alkali corrosion on the quality of two kinds of foam concrete

The effect of alkali solution erosion on the strength of phosphogypsum and cement based foam concrete is shown in Table 5. From Table 5, it can be seen that the strength of two kinds of foam concrete decreases with the increase of alkali solution erosion time, and the strength loss of cement foam concrete is greater than that of phosphogypsum based foam concrete, which also confirms the phenomenon of the loss of quality in former alkali solution.

Table 5. Influence of alkali corrosion on compressive strength of two kinds of foam concrete

| Sample | Carbonation time(d) | 1  | 28  | 70  |
|--------|---------------------|----|-----|-----|
|        | Strength(MPa)       |    |     |     |
| P      |                     | 5.3| 4.8 | 4.1 |
| G      |                     | 5.3| 5.0 | 4.6 |

3.3 Effect of Sulfate Attack on Quality and Strength of Phosphogypsum and Cement Based Foam Concrete

The effect of sulfate solution on the quality of phosphogypsum and cement based foam concrete is shown in Figure 3. It can be seen from Fig. 3 that the quality of cement based and phosphogypsum based foamed concrete increases significantly under the erosion of sodium sulfate solution of 5% mass concentration. This is because SO42- in sulfate reacts with calcium hydroxide and calcium aluminate hydrate in cement stone to form calcium sulphot aluminate (ettringite), which will increase the quality of concrete and expand and crack. At the same time, the internal stress generated in the growth process of ettringite will further intensify the expansion. Therefore, in the former 63d of sulfate attack, cement base and phosphogypsum based foam concrete showed an increase in mass. However, after 63d, the quality of cement based foam concrete began to decrease significantly, which was caused by the expansion and cracking of internal structure leading to the rapid destruction of external structure [16], compared with cement based foam concrete, phosphogypsum based foam concrete showed. A more excellent sulfate attack resistance is due to the fact that phosphogypsum based foam concrete contains less cement stone minerals, which is less responsive to SO42- in sulphate, thus reflecting a more excellent resistance to sulfate attack.
3.4 Effect of Freeze-thaw Cycles on Quality and Strength of Phosphogypsum and Cement Based Foam Concrete

The effect of freeze-thaw cycles on the quality and strength of phosphogypsum and cement based foam concrete is shown in Table 6. From table 6, we can see that after 30 cycles of freeze-thaw cycles, the quality of cement based and phosphogypsum based foam concrete is due to volume expansion of foam concrete due to water absorption at the initial stage of freeze-thaw cycles, which further increases porosity, increases water absorption and ultimately leads to foam. The quality of concrete has increased. However, as the number of freeze-thaw cycles increases, the structure of foam concrete is destroyed, resulting in a rapid decline in quality and strength. In comparison, the quality and strength loss of cement based foam concrete are more serious. This is because the cement and fly ash mix lead to a larger gap in the internal structure, which will be more susceptible to freeze-thaw cycles.

**Table 6.** Effect of freeze-thaw cycles on the quality and strength of two kinds of foam concrete

| Carbonation times | Weight after water absorption (g) | Strength change(MPa) | Weight after drying (g) |
|-------------------|----------------------------------|----------------------|------------------------|
| 0                 | 0                                | 0                    | before 0               |
|                   | 10                               | 10                   | 10                     |
|                   | 20                               | 20                   | 20                     |
|                   | 30                               | 30                   | 30                     |
|                   | 0                                | 0                    | 0                      |
|                   | 10                               | 10                   | 10                     |
|                   | 20                               | 20                   | 20                     |
|                   | 30                               | 30                   | 30                     |
| P                 | 450                              | 462                  | 438                    |
|                   | 420                              | 5.0                  | 4.0                    |
|                   | 2.8                              | 1.0                  | 230                    |
|                   | 215                              | 200                  | 176                    |
| G                 | 453                              | 460                  | 441                    |
|                   | 433                              | 5.0                  | 4.3                    |
|                   | 3.5                              | 2.6                  | 233                    |
|                   | 220                              | 202                  | 171                    |

3.5 Effect of Carbonization on Degradation of Phosphogypsum and Cement Based Foam Concrete

The effect of carbonization on the deterioration of phosphogypsum and cement based foam concrete is shown in Table 7 and table 8. For example, the two table shows that as the carbonization process proceeds, cement based and phosphogypsum based foam concrete shows obvious carbonation resistance. To compare, the carbonation resistance of phosphogypsum based foam concrete is far behind the carbon resistance of cement based foam concrete. This is because phosphogypsum based foam concrete has higher aluminum content than cement based foam concrete, which makes the
amount of ettringite in its system more, while ettringite is more easily decomposed after carbonization, thus carbonization corrosion will become more serious.

Table 7. carbonation depth test of two kinds of foam concrete

| Sample | carbonation time(d) | 1  | 3  | 7  | 14 | 17 | carbonation completed |
|--------|---------------------|----|----|----|----|----|-----------------------|
| P      | carbonation depth(cm)| 1.3| 3.0| 5.2| 6.4|    | carbonation completed |
| G      | 1.5                 | 3.3| 6.0|    |    |    |                       |

Table 8. Effect of carbonization on deterioration of two kinds of foam concrete

| Sample | Weight(g) | Strength(MPa) |
|--------|-----------|---------------|
|        | before carbonization | carbonation completed | before carbonization | carbonation completed |
| P      | 230       | 232.2         | 5.0                 | 5.21                |
| G      | 230       | 233.1         | 5.0                 | 4.89                |

4. Conclusion
(1) The carbonation resistance of phosphogypsum based foam concrete system is significantly weaker than that of cement based foam concrete system. This is because phosphogypsum based foam concrete has higher aluminum content than cement based foam concrete, which will increase the content of ettringite in the system and make it easier to carbonization.

(2) The phosphogypsum based foam concrete has better freeze-thaw resistance than cement based foam concrete. This is because the mixing of cement and fly ash in cement based foam concrete will lead to the discontinuity of gradation, resulting in the formation of internal pores, which is more likely to be affected by freeze-thaw cycles.

(3) Phosphogypsum based foam concrete performs better than cement based foam concrete in the presence of acid base salt solution. This is because cement based foam concrete contains more cement minerals, and hydrated products contain more active minerals, which are more susceptible to erosion by acid base salt solution.

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