

Freezing resistance of high iron phoasphoaluminate cement

S X Zhang^{1,2}, L C Lu^{1,2}, S D Wang^{1,2}, P Q Zhao^{1,2} and C C Gong^{1,2}

¹ Shandong Provincial Key Lab. of Preparation and Measurement of Building Materials, University of Jinan, Jinan 250022, China

² School of Materials Science and Engineering, University of Jinan, Jinan 250022, China.

E-mail: mse_lulc@ujn.edu.cn

Abstract. The influence of freeze-thaw cycle on the mechanical properties of high iron phoasphoaluminate cement was investigated in the present study. The visual examination was conducted to evaluate the surface damage. The deterioration considering the weight loss, modulus loss of relative dynamic elastic and strength loss of mortar were also investigated. The morphology of hydration products were analysed by SEM. Compared with ordinary Portland cement and sulphoaluminate cement, the frost resistance of high iron phosphoraluminate cement is better. Hydration products of high iron phoasphoaluminate cement contain sheet crystals, and a lot of gel form a dense three-dimensional network structure, which results in a lower porosity. Different from ordinary Portland cement, the hydration product of high iron phoasphoaluminate cement does not contain $\text{Ca}(\text{OH})_2$, and low alkalinity reduces its osmotic pressure. The lower porosity and osmotic pressure are the two main reasons which causes in the higher frost resistance of high iron phoasphoaluminate cement.

Keywords: high iron phosphatealuminate cement, freeze-thaw cycles, frost resistance, mechanical properties

1. Introduction

There exists a lot freezing marine area in the north of China. In such regions, a large number of concrete structures are severely deteriorated and their service life is largely shortened mainly because of the freeze-thaw damage and erosive ions in the sea [1,2]. Thus, studying the freezing resistance of cement is necessary for the development of marine engineering. Many researchers have studied the freezing resistance of sulphoaluminate cement (SAC) and ordinary Portland cement (OPC). Due to the low durability of silicate mineral of C_2S , these two types of cement had some limit when they were used to prepare marine concrete. After the appearance of sulphoaluminate cement, phoasphoaluminate cement (PAC) is another new type of special cement, which has excellent performances [3,4]. Shiqun L. and Jiashan H. carefully researched the alumina-rich area in $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SiO}_2$ and found that the a new ternary phase formed by the addition of P_2O_5 . Electron probe microanalyser results showed that the chemical composition of new phase L was $\text{CaO} \cdot (1-X-Y)\text{Al}_2\text{O}_3 \cdot X\text{SiO}_2 \cdot Y\text{P}_2\text{O}_5$, $X=0.146\sim0.206$, $Y=0.048\sim0.081$. It's a solid solution transformed from the monocalcium aluminate ($\text{CaO} \cdot \text{Al}_2\text{O}_3$), and they named it LHss phase. The paste of that phase showed hydration performances of good early strength and increasing long-term strength. The concrete can produce a useful strength in 6h and a strength at 14 days equal to that given by Portland cement at 28 days [5,6]. Besides high early and long-term mechanical strength [7] and high temperature resistance [8], PAC had excellent corrosive



resistance [9,10]. In this paper, basic experimental research on the performance of PAC mortars subjected to freeze–thaw cycles was conducted based on the macroscopic and microscopic tests.

2. Experiment procedure

2.1. Specimen preparation

Two types of reference cement, 42.5 grade OPC and 42.5 grade SAC, were used in experiment, which came from Shanshui Corporation and Qufuzhonglian Corporation. In contrast, PAC used here was synthesized by the regents of $\text{Ca}(\text{PO}_4)_3$, Al_2O_3 , $\text{Ca}(\text{OH})_2$, Fe_2O_3 and SiO_2 in laboratory, whose physical properties was list in table 1.

2.2. Test methods

For freeze-thaw cycles test, three types of mortar specimens with size of $40 \times 40 \times 160 \text{ cm}^3$ were cast and the water–binder ratio (W/B) was 0.5. Then under the condition of temperature in $20 \pm 1^\circ\text{C}$ and the relative humidity in $90 \pm 4\%$, they were cured for different time (28 d for OPC, 14 d for SAC and PAC). After that, according to the GB [11,12], the specimens experienced different times of freeze–thaw cycles with variation temperature from -18°C to 18°C . The experiment was terminated when 300 freeze–thaw cycles were completed, the result showed that 60% loss rate of relative dynamic elasticity modulus was reached or 10% weight loss ratio was obtained.

Then the influences of freeze-thaw cycles on the elasticity modulus, mass loss, flexural strength and compressive strength were test according to the GB subsequently. All the final value was the average of text result for three specimens. The weight loss was calculated by the Eq(1):

$$\Delta W_n = \left[\frac{(W_0 - W_n)}{W_0} \right] \times 100 \quad (1)$$

In the equation ΔW_n is the weight loss of specimens at every 25 freeze–thaw cycles (%), W_0 is the average weight of mortars specimens before freeze–thaw cycles (kg) and W_n is the average weight of concrete specimens at every 25 freeze–thaw cycles (kg). The dynamic modulus of elasticity loss, which was determined by Eq (2), was measured with a high-accuracy nonmetal ultrasonic analyzer as the initial value.

$$\Delta E = \left(\frac{E_{dn}}{E_{d0}} \right) \times 100 \quad (2)$$

In the equation ΔE is the dynamic modulus loss of specimens at every 25 freeze–thaw cycles (%). E_{d0} is the dynamic modulus of elasticity of concrete specimens before freeze–thaw cycles (GPa) and E_{dn} is the dynamic modulus of elasticity of concrete specimens at every 25 freeze–thaw cycles (GPa).

The following Eq (3) was used to calculate the compressive strength, where P is the compressive strength (MPa), F is the maximum load (N) and A is the area of the cube loading face (mm^2).

$$P = F/A \quad (3)$$

The test of SEM was used to observe the morphology of hydration products. The hydration of specimens was discontinued by alcohol and vacuum dried first and SEM images were acquired by Quanta FEG 250 field emission scanning electron microscope produced in FEI (American) whose resolution is smaller than 1 nm.

Table 1. Physical properties of PAC.

Cement	density g/cm^3	soundness 3h	Fineness residue /%	Setting time /min	
				Initial setting	Final setting
PAC	3.06	steadily	3.1(74 μm)	230	250

3. Results and discussion

Figure 1 showed the surface deterioration characteristic of mortars subjected to 70 freeze–thaw cycles in water. The degree of surface deteriorations for three types of mortars is obviously different. The

mortar of PAC exhibits slight attack with only a surface layer of mortar scaled. On the contrary, mortar of OPC and SAC suffers badly from the corners and edges, which shows that their damage is much worse than PAC. Visual inspection revealed that the specimens of OPC and SAC were more severely damaged than that of PAC.

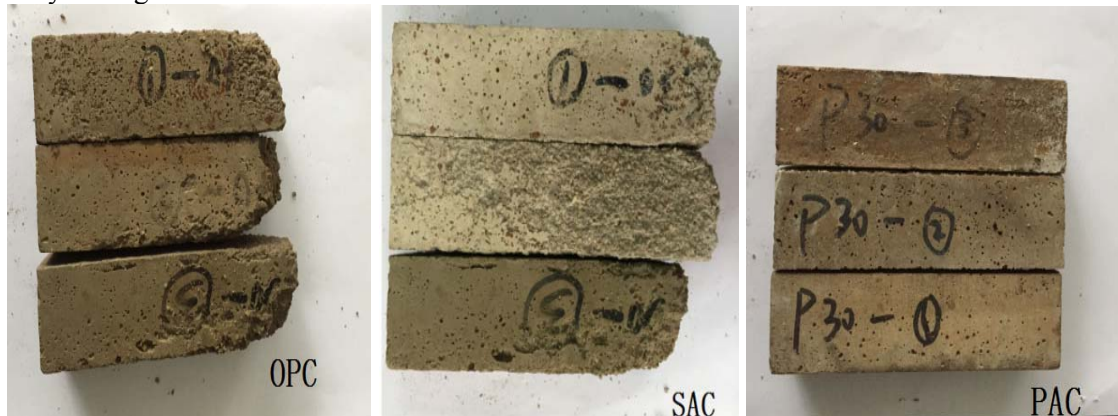


Figure 1. Surface damage characteristic of mortar subjected to 70 freeze-thaw cycles.

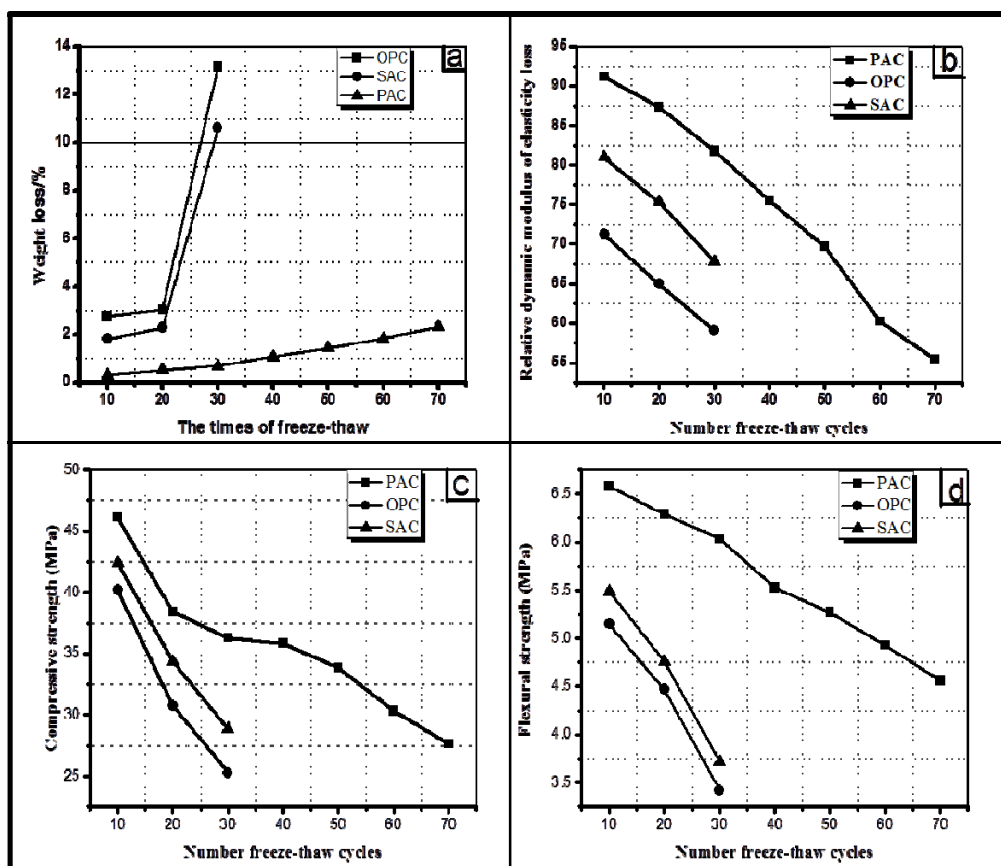


Figure 2. Results of freeze-thaw cycles.

The weight loss of OPC, SAC and PAC mortars subjected to the freeze-thaw are presented in figure 2(a). The weight loss of OPC and SAC mortars subjected to the freeze-thaw exhibited two distinct stages. In stage I, from the initial immersion to 20 freeze-thaw cycles, the weight loss increased gradually. In the stage II, from 20 to 30 freeze-thaw cycles, the weight loss of OPC mortars

increased from 2.76% to 13.16% and SAC increased from 1.81% to 10.61%. Since the weight loss exceed 10%, the freezing resistance test was stopped after 30 freeze-thaw cycles for OPC and SAC mortars. As for the specimens of PAC, from 10 to 70 freeze-thaw cycles, the weight loss increased gradually from 0.31% to 2.31%.

The modulus loss of relative dynamic elastic of mortars subjected to the freeze-thaw cycles are presented in figure 2(b). As freeze-thaw cycle increased, the relative dynamic elasticity modulus increased. The relative dynamic modulus of elasticity loss in three types of mortars presented different characteristic. For the mortars of OPC, from 10 to 20 cycles, the modulus loss of relative dynamic elastic increased gradually from 71.26% to 59.06% and it is from 81% to 67.85% for SAC. As for the specimens of PAC, from 10 to 70 cycles, the modulus loss of relative dynamic elastic increased from 91.23% to 55.43%. The results agree with the weight loss presented in figure.1.

Figure 2(c) and figure (d) show the results of compressive strength and flexural strength tests for the mortar samples subjected to freeze-thaw cycles. It can be seen from figure2(c) that after 30 freeze-thaw cycles, the compressive strength loss ratios of mortars for PAC, SAC and OPC are 0.7%, 10.61% and 13.16%, respectively. As for PAC mortar, after 70 freeze-thaw cycles, the compressive strength loss is 2.31%. It can be seen from the figure 2(d) that the flexural strength loss of OPC and SAC developed rapidly, while for PAC mortar the flexural strength loss developed gradually. The results agree with the compressive strength loss presented in figure 2(c).

Figure 3, figure 4 and figure 5 present the microstructure of mortars subjected to freeze-thaw cycles. As shown from figure 4, needle-like crystals can be observed in the pores for SAC mortar, which are ettringite crystals. The main production of PAC hydration is sheet crystals, which connect each other and many gels filled in the gap. The sheet crystals and gels could form a more compact mortar structure.

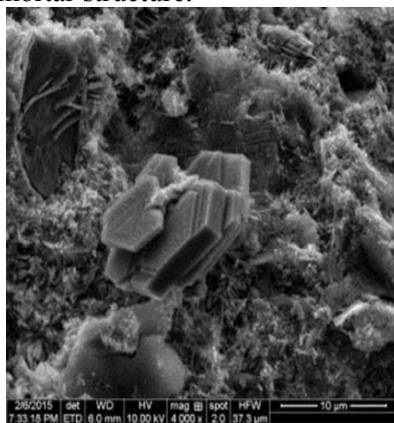


Figure 3. SEM image of OPC cement mortar.

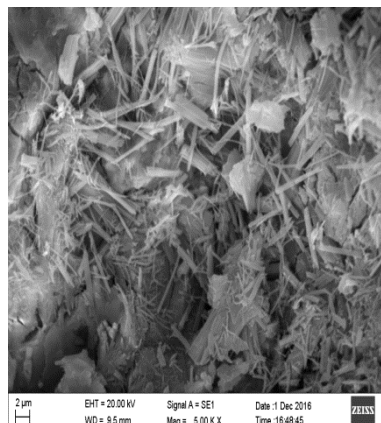


Figure 4. SEM image of SAC cement mortar.

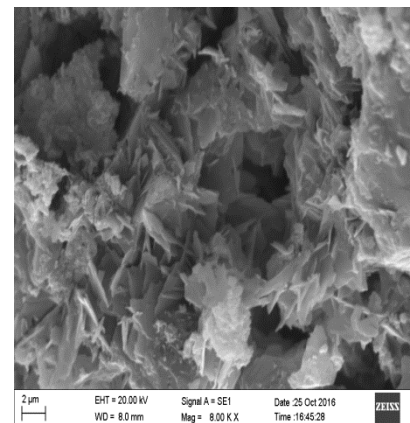


Figure 5. SEM image of PAC cement mortar.

Table 2. Physical properties of PAC.

CEMENT	alkali content	PH
OPC	0.77	12.9
SAC	0.59	12.1
PAC	<0.4	10.9

Table 2 shows the alkali content and PH of three types of mortar. The PH of OPC, SAC and PAC is 12.9, 12.1 and 10.9, respectively. Since $\text{Ca}(\text{OH})_2$ is not the production of PAC hydration, the alkali content of PAC cement is much lower than OPC and SAC. The lower alkali content may have positive effects on the mortar subjected to freeze-thaw cycles. The positive effect could be that the lower ion concentration result in small permeation pressure during the freeze-thaw cycles. The small permeation

pressure cannot break the three- dimensional structure network which can maintain the compressive strength of PAC. The effect of lowing permeation results in cement mortar damaged lightly when exposed to freeze–thaw cycles.

4. Conclusions

In this paper, the freezing resistance of high iron phoasphoaluminate cement was analyzed by comparing the OPC and SAC. The following conclusions can be drawn.

The experimental result of weight loss, compressive strength loss and flexural strength loss show that the freezing resistance of PAC is better than SAC and OPC. The test of SEM indicates that the production of sheet crystals and gels of PAC form a more compact cement mortar structure and may result in a lower porosity, which could maintain the compressive strength. The alkali content and PH can result in small permeation pressure during the freeze-thaw cycles. The small permeation pressure cannot break the three-dimensional structure network, which can maintain the compressive strength of PAC. The lower porosity and osmotic pressure are the two main reasons which causes in the higher frost resistance.

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