Proceedings of the 6th International Conference on Materials Chemistry and Environmental Engineering
DOI: 10.54254/2755-2721/2026.31094

Experimental Study on Strength and Pore Structure of Cement Mortar in Early Freezing Environment

Yongbo Yang[12], Qing Sun[3], Zhiyun Wang[3], Lishan Cui[3], Yong Ding[12*]

[1]School of Civil Engineering, Harbin Institute of Technology, Harbin, China
[2]Key Lab of Smart Prevention and Mitigation of Civil Engineering Disasters of the Ministry of Industry and Information Technology and Key Lab of Structures Dynamic Behavior and Control of the Ministry of Education, Harbin Institute of Technology, Harbin, China
[3]China Construction Third Engineering Bureau Co., Ltd., Wuhan, China
**Corresponding Author. Email: dingyong@hit.edu.cn*

Abstract. The pore structure of early freezing cement mortar was tested by mercury intrusion porosimetry. The pore size distribution and compressive strength of mortar with different water-cement ratio, curing period, age and temperature were studied. The effects of pore size distribution on the compressive strength with early freezing conditions were discussed. The results showed that both the short-term strength loss and the long-term strength loss were not serious in the negative temperature environment, and the negative temperature made the pore of 10-100nm increased, while reducing the 100-2000nm; The pore above 2000nm had little effect on the compressive strength and the pore of 10-2000nm played a major role in the effect of compressive strength, besides, the pore of 100-2000nm affected the long-term strength growth; Curing period affected the pore above 2000nm, the shorter the curing time, the higher the porosity in this range, and superplasticizer could significantly increase the pore above 2000nm.

Keywords: Early freezing, Cement mortar, Strength, Pore structure

1. Introduction

Early freezing damage of concrete can cause severe deterioration of its internal pore structure, and the pore structure characteristics of concrete strongly affect its physical properties such as impermeability and frost resistance, as well as mechanical properties such as strength and stiffness [1-4]. In recent years, scholars at home and abroad have studied concrete freezing damage from the perspective of pore structure and achieved certain results. Olivier [5] conducted a theoretical study on the mechanical properties of porous materials after freezing, and quantitatively analyzed the effects of freezing rate and pore size distribution on the freezing deformation of water-saturated porous materials. Corr et al. [6] used low-temperature scanning electron microscopy to study the morphology of ice crystals in air voids, the development of air voids in the early age stage, and the process of cement hydration at low temperatures. Dong Yangtao et al. [7] discussed the relationship between concrete pore structure, frost resistance, and mechanical properties. Han Wangyang et al. [8] studied the influence of curing period on strength under two negative temperature environments.

DOI: 10.54254/2755-2721/2026.31094

Most studies have conducted comparative research on the pore structure of concrete under standard curing and negative temperature curing, but few have detailed the changes in concrete pore structure under negative temperatures and the influence of pore size changes on mechanical properties. This paper aims to study the development of internal pore structure and strength of concrete under different conditions of low-temperature curing, explore the influence of pore size distribution changes on strength, and provide new ideas for the frost resistance and reinforcement of concrete.

2. Raw materials and test methods

2.1. Test raw materials

Cement: Swan brand P·O 42.5 ordinary Portland cement produced by Harbin Yatai Cement Plant; Fine aggregate: ISO standard sand; Admixture: Polycarboxylate superplasticizer produced by Qiangshi Admixture Factory of Harbin Institute of Technology; Water: Tap water from Harbin City.

2.2. Specimen preparation

The molding size of the mortar specimens was 40mm×40mm×160mm, with 3 specimens molded in each group. After casting and vibration, the surface of the specimens was covered with a film. After different curing periods (0h, 2h, 4h, 6h, 24h), negative temperature curing was carried out for 7d at -5℃, -10℃, and -20℃ respectively. After negative temperature curing, the specimens were taken out and immediately subjected to standard curing with curing ages of 3d, 7d, and 28d respectively. The reference group specimens after casting were directly cured in a standard curing room without negative temperature curing.

2.3. Test methods

According to GB/T17671-1999 Test Method for Strength of Cement Mortar, a 300kN cement compressive and flexural testing machine was used to determine the compressive strength of cement mortar. 3 specimens were tested for each working condition, and the average value was taken.

After the compressive strength test, several fragments of about 1cm^3 were selected and immersed in absolute ethanol to terminate hydration, dried to constant weight at 60℃, and then placed in a desiccator to cool to room temperature. Mercury intrusion porosimetry (MIP) was performed on the prepared samples to obtain their pore structure information.

3. Test results and analysis

To analyze the influence of pore sizes in different ranges on the compressive strength of cement mortar in more detail, the pore structure was independently divided into 3 pore size ranges based on the scale invariance of fractal theory: 10-100nm, 100-2000nm, and >2000nm.

3.1. Water-cement ratio

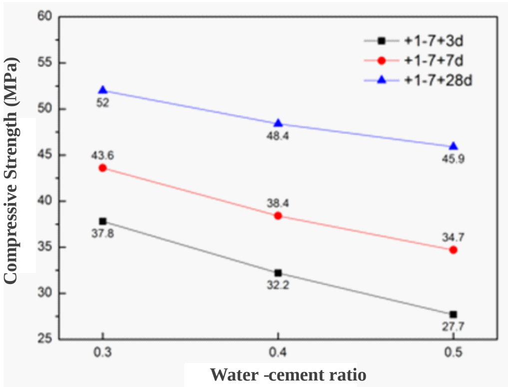

Figure 1. Compressive strength of cement mortar with different water-cement ratios

The water-cement ratios of the specimens were 0.3, 0.4, and 0.5 respectively. After curing at room temperature for 24h, they were cured at -10°C for 7d and then transferred to a standard curing room with curing ages of 3d, 7d, and 28d. It can be seen from Fig. 1 that with the increase of water-cement ratio, the compressive strength of cement mortar shows a decreasing trend.

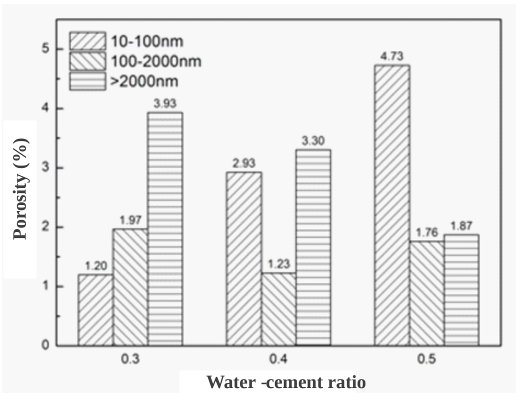

Figure 2. Fractional porosity of cement mortar with different water-cement ratios

The pore structure analysis was carried out on the cement mortar at 28d age as the test group. For the mortar with a water-cement ratio of 0.5, it can be seen from Fig. 2 that the porosity in the range of 10-100nm is much higher than that of the other two water-cement ratios, but the porosity in the range of >2000nm is much lower than that of the other two groups. It can be seen from Fig. 1 that the higher the water-cement ratio, the lower the corresponding compressive strength of cement mortar. As a porous medium material, concrete has a complex pore distribution and pore types, and its pore structure is closely related to strength. Capillary pores and other macropores will reduce the strength and elastic modulus of concrete [9-11]. Combined with the analysis of the pore size distribution diagram, the excessive porosity of the mortar with a water-cement ratio of 0.5 in the range of 10-100nm leads to its lower compressive strength than the other two groups, while its porosity in the range of >2000nm is significantly smaller than that of the other two groups. In addition to considering the influence of superplasticizer, we analyze that the mortar with a water-cement ratio of 0.5 has a higher content of liquid water than the other groups, and is most affected by freezing expansion stress during early freezing, forming many microcracks. These cracks cannot be completely repaired after being transferred to standard curing, and they are connected and do not belong to the category of pores. Therefore, the porosity in this range is much smaller than that of the other two groups. In the subsequent research, we found that the pores larger than 2000nm have little effect on the compressive strength. The analysis methods of the other two groups are similar to the above and will not be repeated.

3.2. Pre-curing time

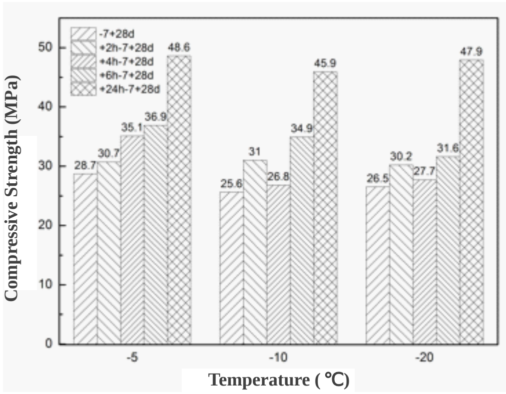

Figure 3. Compressive strength of cement mortar with different curing periods

The water-cement ratio was 0.4. After curing at room temperature for 0h, 2h, 4h, 6h, and 24h respectively, the specimens were cured at negative temperatures (-5℃, -10℃, -20℃) for 7d and then transferred to a standard curing room for 28d. It can be seen from Fig. 3 that for the cement paste at an ambient temperature of -5 ℃, its compressive strength gradually increases with the increase of curing period. For the pastes at ambient temperatures of -10℃ and -20℃, the change trends of their compressive strengths are the same but different from that at -5℃; the compressive strength of both after 4h of curing is lower than that after 2h of curing.

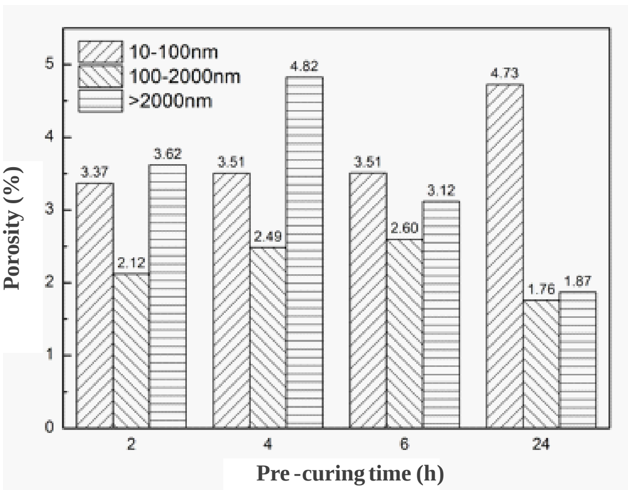

Figure 4. Fractional porosity of cement mortar with different curing periods

Based on the differences in compressive strength, the pore structure analysis was carried out on the cement mortar at 28d age with different curing periods as the test group. As shown in Fig. 4, in the range of 10-100nm, the porosity of the mortar cured for 24h is much higher than that of the other

DOI: 10.54254/2755-2721/2026.31094

three groups, and the porosities of the other three groups in this range are very close. In the range of 100-2000nm, the porosity of the mortar cured for 24h is the smallest, and the porosities of the other three groups increase with the extension of curing period. In the range of >2000nm, the porosity of the mortar cured for 4h is much higher than that of the mortar with other curing periods, and the porosity of the mortar cured for 24h is the smallest.

From the above analysis, the mortar cured for 24h has the highest porosity in the range of 10-100nm. Previous studies have shown that excessive capillary pores will lead to a decrease in compressive strength. However, it can be seen from Fig. 3 that the compressive strength of the mortar cured for 24h is much higher than that of the mortar with other curing periods. Therefore, we infer that its excessively low porosity in the ranges of 100-2000nm and >2000nm makes up for the deficiency of excessive capillary pores. Comparing the mortar cured for 2h and 4h, it is found that the porosity of the mortar cured for 4h in the range of >2000nm is much higher than that of the mortar cured for 2h, and the porosities in other regions are not much different. It is inferred that the excessively high porosity in the range of >2000nm affects the compressive strength of the mortar cured for 4h. We analyze that the shorter the curing period, the more water in the cement mortar, and the more ice crystals formed inside during freezing. These ice crystals will form many irreparable pores after melting. At the same time, the volume of liquid water expands by about 9% when it turns into solid ice. When the freezing expansion stress exceeds its tensile strength at that time, internal structural cracks will occur, which are difficult to fully recover even after being transferred to standard curing. Correspondingly, the porosity in the range of >2000nm is high, the pore structure is more fragile, and the strength is low. Comparing the mortar cured for 2h and 6h, it can still be found that the porosity in the range of >2000nm affects the compressive strength. This is contradictory to the later conclusion that "the pores larger than 2000nm have little effect on the compressive strength". We analyze that the previous conclusion was obtained based on the pore structure information of the cement mortar cured for 24h, while the above conclusion is aimed at different curing periods (<24h). We infer that the inconsistency of the prerequisites is the reason for the contradictory conclusions.

3.3. Curing age

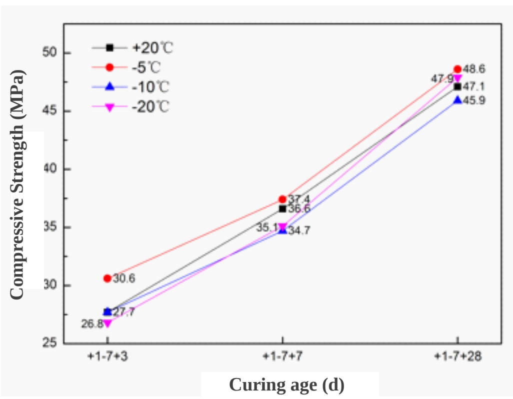

Figure 5. Compressive strength of cement mortar at different ages

The water-cement ratio was 0.5. After curing at room temperature for 24h, the specimens were cured at different temperatures (+20°C, -5°C, -10°C, -20°C) for 7d and then transferred to a standard curing room. Among them, +20°C was the positive temperature control group. As shown in Fig. 5, the strength of cement mortar at each temperature continuously increases with the increase of curing age.

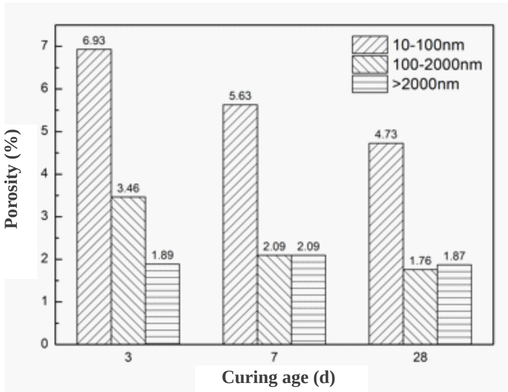

Figure 6. Fractional porosity of cement mortar at different ages

The pore structure analysis was carried out on the cement mortar cured at -10℃ for 28d as the test group. It can be seen from Fig. 6 that with the increase of the age of cement mortar, the porosity in the range of 10-100nm gradually decreases; the porosity in the range of 100-2000nm decreases significantly in the early stage, but the decrease is not obvious in the later stage; the porosity in the range of >2000nm does not change significantly in both the early and later stages. From the macro-mechanical properties, with the increase of age, the compressive strength of the test group's cement mortar is continuously increasing, indicating that the pores larger than 2000nm have little effect on the compressive strength, and the pores in the range of 10-2000nm play a major role. It can also be found from Fig. 5 that the lower the porosity in the range of 10-2000nm, the higher the corresponding compressive strength of the cement mortar. The early strength increase rate of the test group's cement mortar is 34%, and the later strength increase rate is 23%. From Fig. 6, we can see that the decrease range of porosity in the range of 10-100nm is approximately the same, while the decrease range of porosity in the range of 100-2000nm is very significant in the early stage and not obvious in the later stage. We infer that this is the main reason for the decrease in the later strength increase rate.

DOI: 10.54254/2755-2721/2026.31094

3.4. Temperature

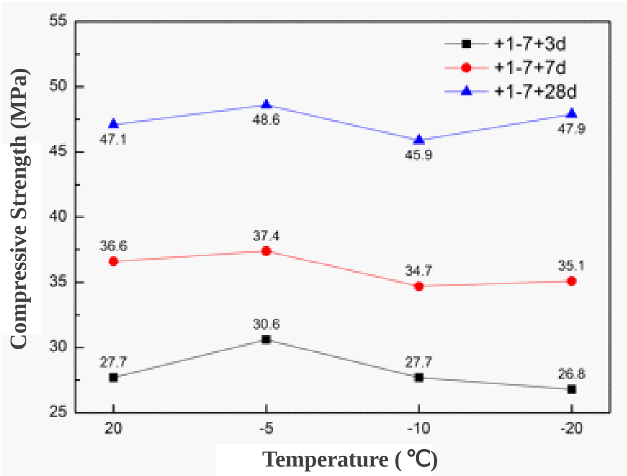

Figure 7. Compressive strength of cement mortar at different temperatures

The water-cement ratio was 0.5. After curing at room temperature for 24h, the specimens were cured at different negative temperatures (+20°C, -5°C, -10°C, -20°C) for 7d and then transferred to a standard curing room. It can be seen from Fig. 7 that for the cement mortar with three ages and different freezing temperatures, only the compressive strength of the mortar at 3d age decreases with the decrease of temperature, indicating that the degree of cement hydration is greatly affected by temperature in the early stage; the lower the temperature, the slower the hydration process, the fewer the hydration products, resulting in lower compressive strength. The compressive strength of the mortar at 7d and 28d ages reaches the lowest at -10°C.

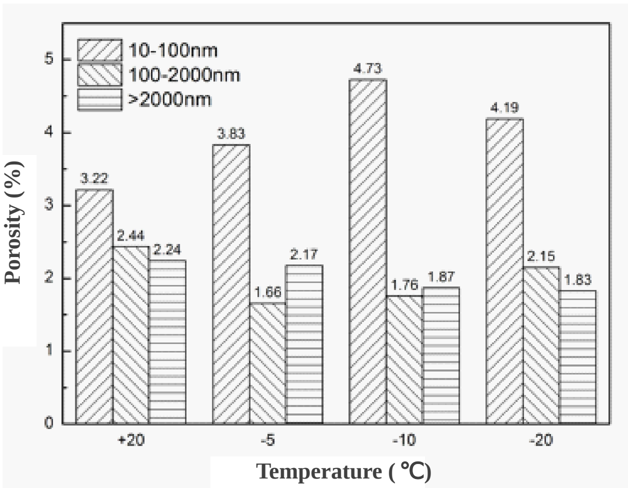

Figure 8. Fractional porosity of cement mortar at different temperatures

The pore structure analysis was carried out on the cement mortar at 28d age. It can be seen from Fig. 8 that the negative temperature environment increases the pores of the cement mortar in the range of 10-100nm and reduces those in the range of 100-2000nm. From the above research, it is known that capillary pores and other macropores have a great influence on the compressive strength. It can be found from Fig. 8 that in the range of 10-100nm, the porosity at -10°C is the highest, and this region belongs to capillary pores. The excessively high porosity leads to the lowest compressive

DOI: 10.54254/2755-2721/2026.31094

strength. For the phenomenon that the porosity at -10℃ is the highest in the range of 10-100nm, we infer that this region belongs to capillary pores. According to the Gibbs-Thomson equation [12], the smaller the pore size, the lower the freezing point. Therefore, although cement hydration is inhibited at -5℃, it can still proceed. However, the degree of hydration at -10℃ is smaller than that at -5℃. -20℃ is an extreme environmental condition where liquid water freezes rapidly in a short time, and the degree of cement hydration is almost zero. The mortars under the three environments will form larger pores due to the freezing expansion of water, but the mortar at -5℃ has more hydration products that can fill and repair the macropores. After being transferred to positive temperature, the mortar at -20℃ will also hydrate normally, and the pore structure will form and develop normally. However, the mortar at -10℃ cannot produce more hydration products to make up for the damage while being affected by freezing expansion, thus resulting in the above phenomenon.

In addition, we also found that the strength of the cement mortar at -5℃ is the highest and higher than that of the reference group, which is different from that of cement paste. For this phenomenon, according to the "early structure" viewpoint proposed by Ba Hengjing [13] in his paper Formation and Hydration of Early Structure of Concrete at Negative Temperature, it is inferred that the mortar cured for 1d has formed an early structure at -5℃. Under negative temperature conditions, the early structure is formed, the pore structure is good, which can provide good thermodynamic conditions for hydration, and the strength of the mortar continues to increase at negative temperature, so it is higher than that of the reference group. Through pore structure analysis, we can also see that although the porosity of the mortar at -5℃ in the range of 10-100nm is higher than that of the mortar at +20℃, its porosity in the range of 100-2000nm is much lower than that of the mortar at +20℃. We infer that the excessively high porosity in the range of 100-2000nm affects the compressive strength of the mortar at +20℃, making it lower than that of the mortar at -5℃.

4. Conclusions

This chapter mainly discusses the influences of water-cement ratio, age, curing period, and temperature on the compressive strength of cement paste and mortar subjected to early freezing. At the same time, these influencing factors also change the internal pore structure of the material. Through the analysis of the above results, the following conclusions are obtained:

(1) Water-cement ratio: With the increase of water-cement ratio, the compressive strength of cement mortar gradually decreases. Excessive porosity in the range of 10-100nm is the main reason for the low compressive strength. In addition, it is found that superplasticizer can significantly increase the pore size in the range of >2000nm.

(2) Curing period: For the cement paste at an ambient temperature of -5℃, its compressive strength gradually increases with the increase of curing period. For the pastes at ambient temperatures of -10℃ and -20℃, the change trends are quite different, indicating that excessively low ambient temperature will cause irregular changes in pore size distribution. In addition, the shorter the curing period, the more water in the cement mortar, and the more macropores and cracks generated during freezing. After being transferred to standard curing, it is difficult to fully recover, resulting in many macropores and microcracks, and correspondingly, the porosity in the range of >2000nm is high.

(3) Age: The compressive strength of cement mortar gradually increases with the increase of age. The pores larger than 2000nm have little effect on the compressive strength, and the pores in the range of 10-2000nm play a major role. Moreover, the pores in the range of 100-2000nm are the main reason affecting the later strength increase rate.

DOI: 10.54254/2755-2721/2026.31094

(4) Temperature: Both the early and later strength losses of cement mortar caused by negative temperature are not significant. The negative temperature environment increases the pores of cement mortar in the range of 10-100nm while reducing those in the range of 100-2000nm.

References

[1] Ge, X. L., Ke, M. Y., Liu, W. B., & et al. (2024). The evolution law of freezing stress under concrete freeze-thaw action and its influence on frost resistance. Materials Reports, 38(12), 111-115.

[2] Liu, R. Q. (2011). A study on the critical frost resistance strength of concrete at low temperatures under multiple factors [Master's thesis]. Dalian University of Technology.

[3] Xue, J., Tang, M. S., & Lou, Z. H. (1985). Proceedings of the 7th International Congress on the Chemistry of Cement. China Architecture & Building Press.

[4] Şahin, Y., Akkaya, Y., & Taşdemir, M. A. (2021). Effects of freezing conditions on the frost resistance and microstructure of concrete. Construction and Building Materials, 270, 121458.

[5] Olivier, C. (2005). Poromechanics of freezing materials. Journal of the Mechanics and Physics of Solids, 53(8), 1689-1718.

[6] Corr, D. J., Juenger, M. C. G., Monteiro, P. J. M., & et al. (2004). Investigating entrained air voids and Portland cement hydration with low-temperature scanning electron microscopy. Cement and Concrete Research, 26(8), 1007-1012.

[7] Dong, Y. T., Meng, L., Lan, L., & et al. (2016). Study on the influence of concrete pore structure on frost resistance and mechanical properties under variable temperature curing. Railway Engineering, (3), 157-160.

[8] Han, W. Y., Zhu, W., Liu, M. L., & et al. (2016). A study on the strength development of cement at negative temperatures. Cement Engineering, (2), 12-14.

[9] Lin, W. G., Liu, L., Ye, H., & et al. (2025). Analyzing the influence of pore structure and vibration on clogging in pervious concrete. Journal of Cleaner Production, 495, 145065.

[10] Yang, J. H., Yuan, D. D., Huang, D. W., & et al. (2022). Effects of aggregate types and softening effect on multiaxial mechanical properties of lightweight aggregate concrete. Construction and Building Materials, 353, 128832.

[11] Du, X. L., & Jin, L. (2012). Study on the macro-mechanical properties of concrete considering the influence of pores and microcracks. Engineering Mechanics, 29(8), 101-107.

[12] Wang, Z. P., & Wang, T. (2013). A brief introduction to the principle and application of nuclear magnetic resonance freezing pore measurement method. Materials Reports, 27(1), 129-133.

[13] Ba, H. J., & He, Z. M. (1991). Formation and hydration of early structure of concrete at negative temperatures. Low Temperature Architecture Technology, (2), 46-48.