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Report:

Influence of freezing rate on cryo-damage of cementitious material*

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Abstract: We report an experimental investigation on the impact of the freezing rate on the cryo-deformation and cryo-damage of cementitious materials. Saturated, dried and air-entrained mortar specimens are subjected to laboratory freeze-thaw cycles under three freezing rates without moisture exchange with the environment. In addition to basic mechanical properties and pore distribution, the measurement is also effectuated for freezing expansion, residual deformation of the specimens in each cycle. From the results it is observed that a high freezing rate does augment the freezing expansion of material while the cryo-damage is more important for a low freezing rate. Accordingly, both the freezing rate and freezing duration should be taken into account for the cyro-damage extent of cementitious materials.

Key words: Freezing rate, Deformation, Crystallization pressure, Damage
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INTRODUCTION

The damage of cementitious materials by freeze-thaw cycles has been a concern in both material and civil engineering. Several rapid freeze-thaw tests are proposed to quantify the material freeze-thaw resistance in the laboratory (ASTM Standard C666-03, 2003; Setzer *et al*., 2004), commonly used for comparing the relative freeze-thaw resistance of different materials. However, in recent years, these test results were also exploited to serve as an index requirement for the durability design of concrete structures (CCES, 2005). Thus a rather fundamental question arises: how to justify the requirements based on these rapid-test-based indices. The answer, if it existed, would be rather complicated since evidently multiple differences exist for rapid freeze-thaw tests and in situ cases. These differences involve at least the following aspects: moisture condition, temperature variation amplitude and the freezing (thawing) rate for environmental actions; moisture content and mechanical properties of materials in their initial state.

Among these factors, moisture is investigated relatively in detail for its transport in the cementitious material during freezing-thawing (Setzer, 2001) as well as its initial saturation in pores (Fagerlund, 1975). Nowadays it is well accepted that freeze-thaw damage is basically a moisture transport event (Fagerlund, 1997). These results can help to establish the correlation between lab tests and in situ freeze-thaw actions. As for the freezing (thawing) rate, hydraulic pressure theory states that the pore pressure would be proportional to the freezing rate (Powers, 1949), and this assumption is furthermore integrated into a material tension-fatigue model (Cai and Liu, 1998). However, very few experimental data directly support this assumption, and pore pressure from hydraulic pressure theory, deduced only from the volumetric change during the water-ice phase change, is well questioned from the point of view of crystal growth (Scherer, 1999). The role of the freezing rate on the pore pressure accumulation and the subsequent material damage needs more experimental investigation.

We investigate directly the impact of the freezing rate on the cryo-deformation and cryo-damage of

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cementitious materials. To avoid the possible contribution of moisture transport, the moisture exchange between material and environment is deliberately screened.

EXPERIMENTAL METHOD

Freeze-thaw apparatus

The freeze-thaw apparatus consists of two chambers connected together. In both chambers steel containers are placed into cooling liquid, and each container can accommodate a prism specimen of 100 mm×100 mm×400 mm. A valve exists between each chamber and the feed-in pipe of cooling liquid from the refrigerator. Adjusting the position of the valve can control the cooling liquid flow into the chamber. The refrigerator has the capacity to cool a single chamber, with the valve of the other chamber completely closed, from 8 to −17 °C within 2.5 h. For this study the refrigerating and heating equipment is regulated so that the maximum and minimum temperatures are 5 and −22 °C, respectively, and different freezing rates are created by adjusting the valves of cooling liquid. In this study only one chamber is used for keeping specimens, the other one serving simply as the reservoir of cooling liquid.

Material

Standard mortars with and without entrained air are retained; the material compositions are presented in Table 1 with MSa and MS standing for mortar with and without entrained air, respectively. The specimens are prisms with a dimension of 40 mm×40 mm×160 mm. The small prism is chosen to minimize the temperature gradient between the inside and the surface of the specimen, and the temperature gradient during the freeze-thaw test is controlled, being inferior to 2 °C. The specimens are demoulded at the end of one day and immersed in water for the next two weeks. After immersion of six days some specimens are taken out of the water and dried till a constant weight. At the end of two weeks, three types of specimen are prepared: immerged specimens of MS and MSa, and dried specimens of MS. Three strain gauges are attached to the three lateral side surfaces of each specimen with epoxy-based glue. After this operation all the specimens are wrapped immediately in double layers of impermeable aluminum paper and put into the steel containers of the freeze-thaw chamber. All the strain gauges are set to zero and connected to an automatic data collector. One dried specimen of MS is placed into a separate container with one thermometer inside the specimen and the other thermometer outside the specimen but near the specimen surface. The temperatures from the two thermometers are also automatically recorded. At the beginning of each freeze-thaw test, the data collection of temperature and strain is synchronized so that temperatures and strains correspond to the same time instants.

Table 1 Composition and characteristics of mortar specimens with (MSa) and without (MS) entrained air

Composition and Characteristic	Value	
	MSa	MS
Sand (kg/m^3)	1278	1360
Cement (kg/m^3)	496	528
Water (kg/m^3)	298	317
Water/cement ratio	0.60	0.60
Entrained air content (%)	6.0	−
Compressive strength at 14 d (MPa)	31.8	40.0
Rupture strength at 14 d (MPa)	5.8	6.8
Porosity by mercury intrusion (%)	−	15.9

Freeze-thaw test procedure

The freeze-thaw apparatus is regulated for three cooling rates, 2.5, 5 and 12 °C/h for the freezing phase, immediately followed by the thawing phase at a constant heating rate of 10 °C/h. For simplification the tests are noted as FT2.5, FT5 and FT12 for cooling rates of 2.5, 5 and 12 °C/h, respectively. The maximum and minimum temperatures inside the specimens are controlled to about 2 and −20 °C for the thawing phase and freezing phase, respectively. Thus for all specimens the thawing duration is about 2 h. For some technical reasons the minimum temperature is recorded as −15 °C instead of the expected −20 °C for the test FT12. For each freezing rate about ten cycles are performed. During the tests the specimen deformation and the temperature are recorded. For the first freezing cycle the specimens are put into the cooling containers and the data collection starts as the specimens are cooled to the expected maximum thawing temperature, i.e., 2 °C.

RESULTS AND DISCUSSION

Firstly some basic mechanical properties are measured for the prism specimens at 14 d and given in Table 1. The pore distribution is measured by mercury intrusion porosimetry (MIP) on two MS samples, and the measured distributions are illustrated in Fig.1 with the total capillary porosity estimated as 15.9%. From the figure, the capillary pores with a diameter ranging from 10 to 100 nm occupy an important part of the total porosity, and the pore diameter distribution is relatively centered at the order of 10 nm, implying that the difference in pore water (solution) supercooling cannot be very important during freezing and that the pore water crystallization is expected to take place during a narrow interval of decreasing temperature. In the following, the immersed specimens are considered as totally saturated while the dried specimens are assumed to contain no capillary (freezable) water.

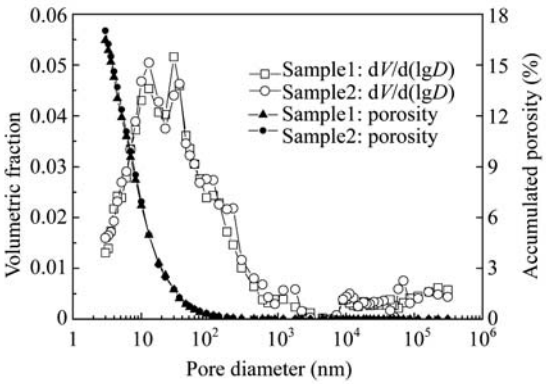

Fig.1 Capillary pore distribution and total porosity by mercury intrusion porosimetry on two MS samples

The cryo-deformations of saturated (immersed) specimens, dried specimens as well as air-entrained and saturated specimens are presented in Fig.2 for the first cycle of the FT2.5 test. The saturated specimens contract less compared to the dried ones, due to the internal crystallization pressure, while the relaxation effect of entrained air is evident and contributes more and more to the specimen contraction with the freezing time. Two concepts are introduced in Fig.2: freezing expansion and residual strain. The freezing expansion is equal to the difference between the deformation of saturated specimens and that of dried ones. It can be attributed to the effects of the phase change of pore water during freezing, including mainly a new ice-liquid interface formation, volumetric change from water to ice as well as different thermal expansion coefficients of ice and water (Coussy, 2005). From Fig.2, the freezing expansion has a maximal value, which corresponds to the freezing of an important quantity of pore water, and can be referred to a pore distribution of 10~100 nm. The residual strain stands for the irreversible deformation of saturated specimens at the end of thawing. It records the progressive damage induced by the pore pressure during each cycle.

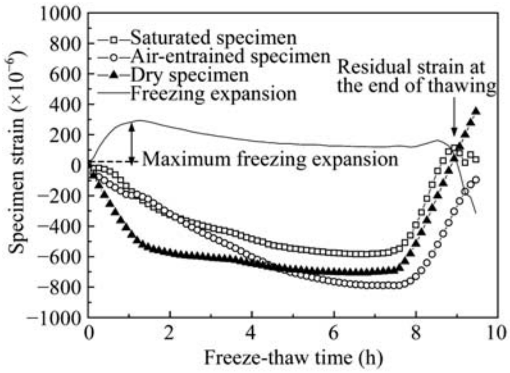

Fig.2 Cryo-deformation of saturated, dried and air-entrained specimens during the first freeze-thaw cycle of test FT2.5

The cryo-deformations of saturated specimens are presented in Fig.3a for three freezing rates during the first cycle, and the corresponding freezing expansions are presented in Fig.3b. From the freezing expansions it can be seen that the freezing rate does have an impact on the amplitude of pore pressure. The maximum freezing expansion of FT12 is obviously more important than those of FT5 and FT2.5; however, the amplitude of freezing expansion is not at all proportional to the freezing rate as indicated by the hydraulic pressure theory. From the available research results (Coussy, 2005), the pore pressure during freezing can be attributed mainly to two mechanisms: crystallization pressure of ice formation and the liquid water (solution) flow induced by phase change, if the former is assumed not to depend on the freezing rate while the latter can be freezing rate-dependent. The higher freezing expansion of FT12 can be attributed to a more important viscous flow of pore liquid water from the crystallization site to smaller pores, which is demonstrated by a viscous flow think model (Coussy and Fen-Chong, 2005).

With the cycles, progressive damage is observed for the saturated specimens. The specimen damage, represented by residual strain, is illustrated in Fig.4a for three freezing rates. The specimen damage in FT2.5 evolves with a rate much more important than those in FT5 and FT12, despite the fact that higher pore pressure is created in the first cycle of FT12. This can only be explained by the longer freezing period, about 8 h for FT2.5 compared to about 2 h for FT12. During test FT2.5, even with a lower pore pressure, more damage is created by a longer loading period. In fact a similar phenomenon exists in the compressive strength test of cementitious materials: measured strength increases with loading rate. Accordingly, the viscosity of solid matrix of mortar intervenes in the damage creation process in Fig.4a. Meanwhile the maximum value of the freezing expansion evolves with the cycles, as presented in Fig.4b. On account of the progressive damage in Fig.4a and due to the fact that the external water intake is screened in all the tests, the increase in maximum freezing expansion can only be attributed to the progressive softening of the material solid matrix by damage and not to increasing pore pressure.

CONCLUSION

It is well accepted that the material damage by freeze-thaw cycles is due to the pore pressure accumulated during the crystallization of the interstitial solution in the porous network. A realistic estimation of the pore pressure level is of utmost importance for predicting the resistance of engineering cementitious materials to environmental freeze-thaw actions. From the present work the following conclusions can be drawn:

(1) The freezing rate alone does have an impact on the pore crystallization pressure. More important pore pressure can be created by a higher freezing rate, which can be explained by the liquid viscous flow from the crystallization site to smaller pores. But the impact extent is rather limited, an increase of 40%

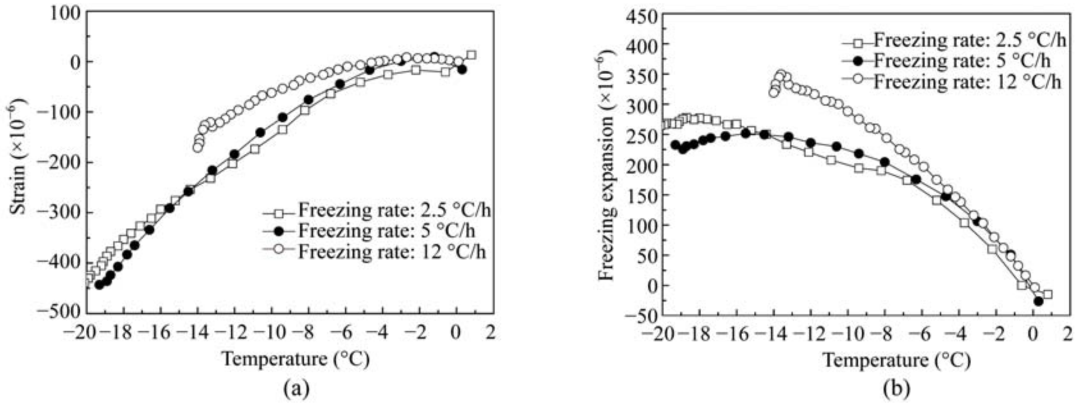

Fig.3 Cryo-deformation (a) and freezing expansion (b) of saturated specimens at different freezing rates

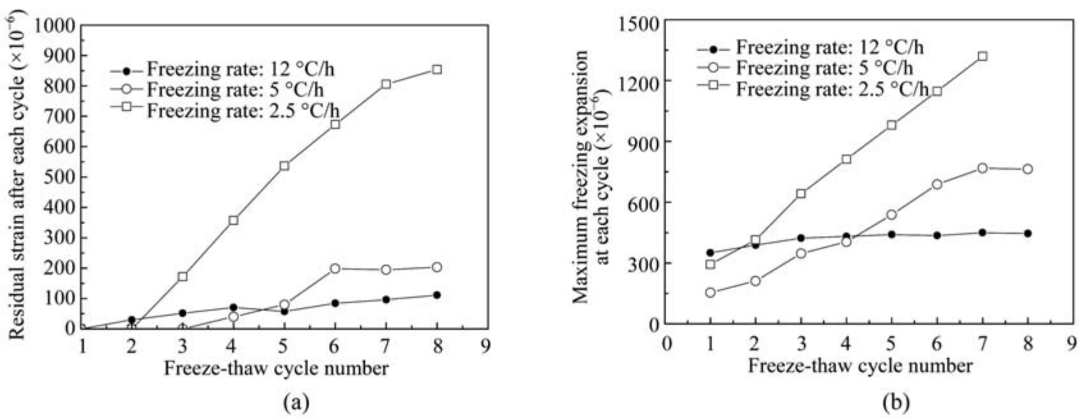

Fig.4 Residual strain (damage) after each thawing (a) and maximum freezing expansion (b) of saturated specimens at different freezing rates

from FT2.5 to FT12 deduced from the freezing expansion amplitude, far from the prediction of hydraulic pressure theory.

(2) The freezing rate has an impact on the specimen damage caused by the freezing duration. The longer the freezing duration, the more the damage can be created. The impact of the freezing rate on the pore pressure level is just secondary and the viscosity of the material solid matrix dominates the damage process.

(3) The present study implies that to predict the freeze-thaw resistance of cementitious materials one should consider, besides moisture conditions, the freezing extent (minimum temperature), the freezing rate as well as the freezing period. The viscosity of the material solid matrix plays a vital role in the damage evolution process.

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