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FROST DAMAGE OF CONCRETE CONSIDERING FREEZING POINT DEPRESSION OF CAPILLARY WATER IN HARDENED CEMENT PASTE

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Abstract

Frost damage of concrete was discussed considering the freezing point depression of capillary water depending on the restriction of capillary walls and on the supercooling of distributed water in small pores.

From this point of view, the basic mechanisms of frost damage to concrete may become somewhat different from that which was commonly believed. The original hydraulic pressure theory seems to explain the frost damage of concrete which has many large pores such as that of early ages or very high water-cement ratios.

1. Introduction

The basic mechanisms of frost damage of concrete have been explained by the Hydraulic Pressure Theory by T.C.Powers[1)2)]. In the original theory proposed in 1945, it is said that water in capillary at the surface of concrete freeze first and the excess water formed by the ice formation moves into the inner part, and this pressure developed by the water movement gives rise to concrete damage. In this stage the role of the size effect of the pores in hardened cement paste were not considered.

After this proposal, Powers explained in his report[3)] to the inquiry from "ACI Committee 201, Durability of Concrete" that water has different freezing points corresponding to the size of pores, and expansion and shrinkage is observed when an constant temperature is maintained. He also described the mechanism in which ice crystal absorb water from smaller pores.

From this point of view, studying pore structures of hardened cement paste is highly important to understand the mechanisms of frost damage of concrete. Moreover, it has been recognized that frost damage of porous materials has a close relation with the structure of pore, especially the volume of middle size pore[4),5),6)]. These influences of pore structure to frost damage seem to be related to the freezing of water in such materials.

In this paper, test results for water freezing in hardened cement pastes were discussed

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with the knowledge regarding pore structure. Different types of freezing deterioration of hardened cement paste were explained considering the above maintaining results in which the freezing point depression of capillary water caused by the restriction of capillary wall and by the supercooling of small size distributed water, which play an important role.

2. Measurement of the Amount of Frozen Water in Hardened Cement Paste

The amount of frozen water in hardened cement paste were measured by using specimens of $5\phi \times 20$cm. After being cast in a mould, it was rotated 6 times per minute throughout the first day of curing to cause least amount of segregation of the paste.

A kind of thermal transmission type calorimeter which was remodeled after U. Vuorinen[7] was designed for this measurement. To obtain a constant temperature change both in the freezing and in the thawing process, the calorimeter was placed in a cold chamber, with a set temperature of -90°C, and cooling and heating processes were controlled by sheet type heater in the calorimeter.

Specimens were tightly covered with stainless steel sheets, soldered together, in order to maintain a vacuum condition in order to eliminate the influence of condensation in the apparatus. The diagram of this calorimeter was shown in Fig.1.

The heat flow was measured and calculated from the temperature difference between the two copper tubes and the heat loss was calculated from the temperature change in the specimen. Vuorinen used the following equation for calculation of the amount of frozen water.

$$\alpha \Sigma \theta m \Delta t = M \Sigma \Delta T + LWf$$

where,
- α : Coefficient of heat loss (cal/ °Ch)
- θm : Mean temperature difference between the two copper tubes during the time interval Δt
- M : Heat capacity of specimen (cal/℃)
- T : Temperature change in specimen during the time interval Δt
- L : Heat of fusion of water (=79.4cal/g at 0℃)

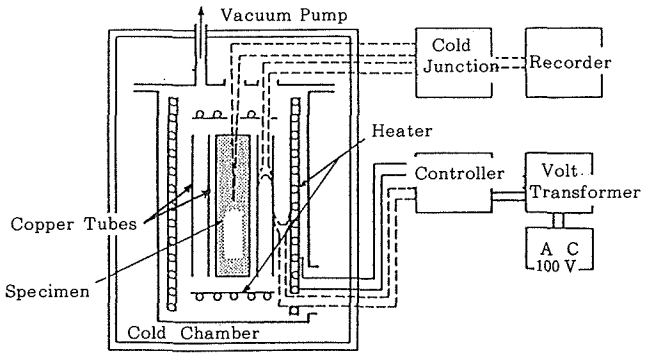


Fig. 1 System of Calorimeter

Wf : Amount of frozen water (g)

Considering the difference of specific heat between water and ice and the change of latent heat of fusion with temperature change, we calculated the amount of frozen water at every time interval Δt. In this case, the Vuorinen's equation is changed as follows ;

$$\alpha\theta m\Delta t = [\, M + (Ci - Cw)\, Wf \,]\ \Delta t + L'Wi$$

where, Ci,Cw =specific heat of ice and water

Wi =frozen water during time interval Δt

Wf $=\Sigma Wi$

L' $=f(T)$: latent heat of fusion

Since the error in calculation of heat capacity (M) of specimen which is from the extrapolation of measured data from the positive side to the negative side, gives considerable influence on the measured amount of frozen water. We calculated the value of M by the smoothed data using the method of moving averages.

Fig.2 shows the amount of frozen water in hardened cement paste during both freezing and thawing process measured by the above method. The results of frozen water corresponds with the expansion behaviour which was previously determined in the measurement of length change behaviour[8], and the volume of frozen water near 0℃ is larger when specimens are young, or the water-cement ratio are high. No frozen water was measured in hardened cement paste of 0.40 water-cement ratio when it was cured in water up to 28 days, unless the condition became far lower than −10℃. The obvious differences (hysteresis) in the volume of frozen water between freezing and thawing process were observed as they were also observed in case of the behavior of length change of concrete[8),9)].

On the assumption that the difference of the amount of the frozen water in freezing and thawing process is caused by supercooling mechanism, and seeding which R. H. Helmuth[10)] pointed out is essential to start the process of freezing, freezing and thawing of water in an ink bottle pore model will be shown in Fig.3 (Here T1, T2 are freezing and melting points which correspond to the radius R1, R2, Va, Vb, Vc that are the volume of pores sized radius R1, R2, R1).

Based on the above assumption, differences of frozen water at the same temperature of the freezing and thawing process can be explained by the lack of uniformity of pore sizes. In actual condition of frost damage, the melting point of the thawing process is not important, but the freezing temperature which becomes difficult to change by supercooling must be considered to be important in the mechanisms of frost damage of concrete.

Fig.4 shows the increases of frozen water volume of hardened cement paste in the freezing process compared with the length change behaviors measured in another specimen. The beginning of freezing causes expansion and shrinking behavior in the process and it also corresponds to the beginning of the shrinking behavior accurately (Fig.5). There is little doubt that water freezing in hardened cement paste causes the behavior of expansion and shrinkage. The shrinking behavior seems to indicate that there must be a function to diffuse the water.

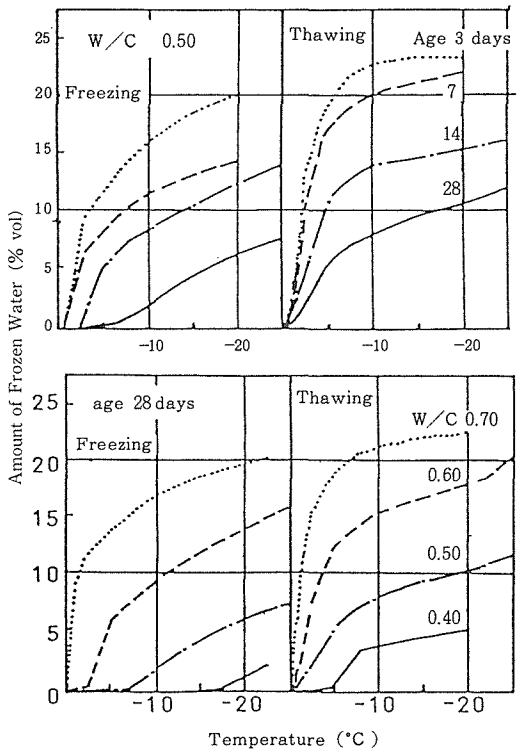


Fig. 2 Amount of Frozen Water in freezing and in thawing process

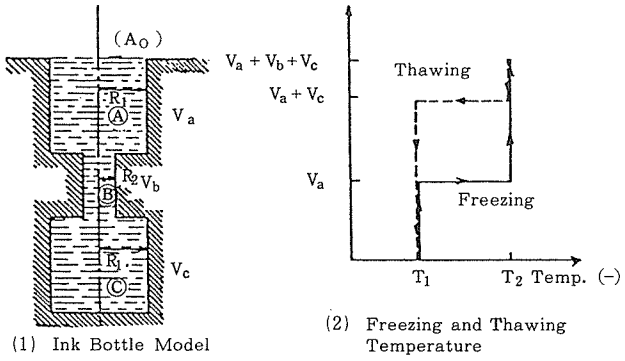


Fig. 3 Freezing and Thawing of Water in Ink Bottle Pore Model

In another test series[8] carried out by maintaining constant temperature in the process of freezing and thawing, it was found that in only the damaged specimens which had expanded more than 0.5×10^{-3} during the process of temperature fall showed expansion in the process of maintaining constant temperature. Though time used in maintaining the temperature in this test was limited to 24 hours, the effect of diffusion may not be so important for the frost damage of concrete.

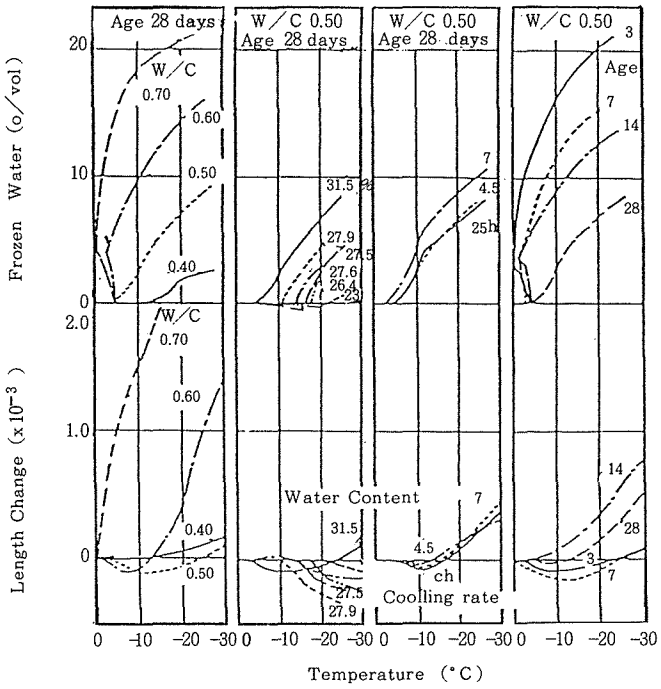


Fig. 4 Comparison between Frozen Water and Length Change Behaviour

3. Influence of Pore Structures on Water Freezing in Hardened Cement Paste

To study the freezing temperature of the water in hardened cement paste, pore size distribution was measured by using a sample of the same batch in frozen water measurement. For radius over 32 Å, mercury porosimeter was used, and for under 32 Å, pore volume was estimated by the results of desorption isotherm of water at 20℃. For the estimation of frozen water, capillary water was considered to be condensed from a minimum size and to freeze from the pore of larger size. Applying the results of frozen water measurement to the pore volume under radius 32 Å together with the results obtained from mercury porosimeter, for the volume of frozen water in hardened cement paste can be estimated respective sizes of radius. Table 1 is one example of this estimation in hardened cement paste age 28 days.

In thermodynamics it is known that the melting point of water in porous materials is lowered by the restriction of capillary walls and water in the smaller capillaries freeze under the temperature below the normal melting point. Fig.6 shows the relations between freezing temperature and radius of pore estimated by the above mentioned procedures comparing the values of melting points, which are based on the water condensation theory, introduced in other papers[10),11),12)]. The correlation is a somewhat rough, but it seems to show a similar tendency to the relation between pore size and melting point, and that the temperature at which water freezes in pores is much lower than obtained from the values for the melting

process.

4. Freezing Point Depression and Frost Damage of Concrete

Two different types of deterioration appeared when freezing and thawing was carried out by using slender specimens of hardened cement paste. Specimens of the group that showed large longitudinal cracks, seemed to be relatively sound as a whole. Other specimens were different in their resistance to freezing and thawing, however, the structure of the whole specimens appeared to be loosened by expansion. Both types of deterioration are shown in Photo 1.

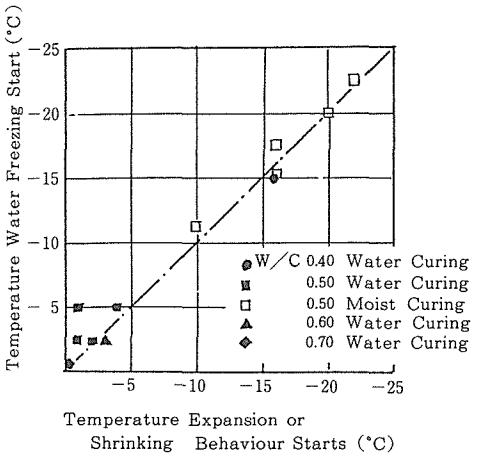


Fig. 5 Correlation between the Starting Temperature of Water Freezing and of Length Change Behaviour

Differences of the types of deterioration were dependent on the existence of pores of some 1000 Å order (Fig. 7). All the specimens that showed longitudinal cracks had a large amount of pores of this order, and such specimens corresponded to the hardened cement paste of early age or very high water−cement ratio.

As mentioned above, it is known that melting point of water in small capillaries goes down. However, it will be difficult to explain the relation between the type of deterioration and pore structures from this theoretical aspect. To take the values from Helmuth in Fig. 6, for example, the melting point of water is higher than −2℃ in pores of larger than radius of 100 Å, and it is about −0.1℃ in pores radius near 1000 Å whose the size seem to have a relation with difference of the type of the deterioration. These shows that the melting point of water in both pores are very close to 0℃.

Results of Fig. 6 estimated from the test in the freezing process shows that the freezing point of water is lower than melting point calculated from the water condensation theory, and it seems to be reasonable that the water in the pore radius of some 1000 Å order freezes at the temperature very close to 0 ℃, and that the water in the pore with a radius from some 100 Å to 1000 Å size freezes in a different temperature, according to the radius of pore.

In light of the water freezing in pores as described above, the mechanisms of the frost damage of concrete becomes somewhat different from that had been considered. In the case when water in pores freeze under the particular freezing temperature (namely 0 ℃), it freezes from the surface to the inner part of concrete, and the water pressure shows a direction from out to in. As an ordinary concrete specimen is frozen from the outer part, the pressure to destroy it would be the greatest when the water at the center of the concrete freezes. And even if the surface of it suffers no damaging force, the pressure may destroy the concrete by the expansion of the center. The damage form longitudinal crack shown in

Table 1 Estimation of Water Content in the Pore of Each Radius

			Cumulated Value from Small Size Pore				Cumulated Value from Water Content to Small Size Pore			
			W/C 0.40	0.50	0.60	0.70	W/C 0.40	0.50	0.60	0.70
Cumulated Pore Volume (o/vol)	Water Content		—	—	—	—	38.9	44.6	49.6	53.6
	Desorption Isotherm	0~32 Å	25.5	26.0	20.0	22.0				
	Mercury Porosimeter	32~56	30.0	30.9	25.2	27.3	13.4	18.6	29.6	31.6
		56~100	34.0	36.3	31.8	34.0	8.9	13.7	24.4	26.3
		100~178	38.2	41.3	36.6	38.5	4.9	8.3	17.8	19.6
		178~320	42.3	47.0	41.5	43.6	0.7	3.3	13.0	15.1
		320~560	42.6	48.2	46.6	46.1			8.1	10.0
		560~1000	42.7	48.8	48.6	49.4			3.0	7.5
		1000~1780	42.9	49.0	49.7	52.9			1.0	4.2
		1780~3200	43.0	49.1	50.3	55.1				0.7
		3200~5600	43.1	49.3	50.6	56.7				
		5600~10000	43.2	49.7	50.9	57.2				
		10000~17800	43.2	49.8	51.0	57.5				
Total Pore Volume (o/vol)			44.0	51.8	52.7	59.1				

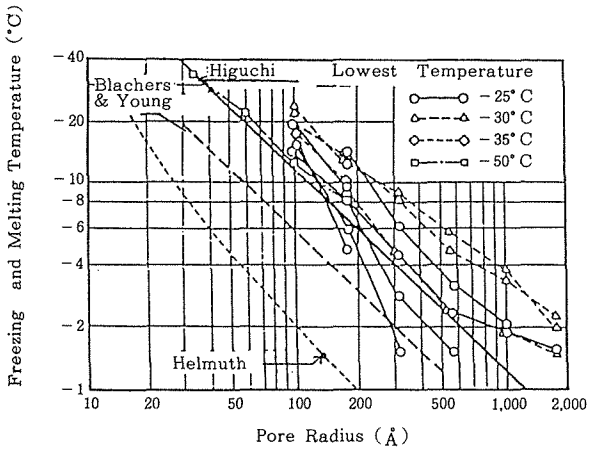


Fig. 6 Comparison between Freezing Temperature Estimated by Test Results and Melting Temperature by Water Condensation Theory

Photo 1 describes this.

The crack damage on the surface can also be observed in concrete specimens of early ages when the test is aimed at early freezing. The original hydraulic pressure theory[1] which makes no mention of the different freezing temperature in pores may correspond to such conditions.

Concrete sufficiently hardened has many pores of some 100 Å to some 1000 Å in radius

which has a close relation to freezing point depression. Also in this case, the temperature difference between the surface and the inner part will cause the direction of water movement, however, the largest pressure arises when freezing in fine pores occurs under the condition when water has already frozen in large pores. In this case, damaging pressure will be dispersed to the whole structure of the concrete. In usual freezing and thawing tests for hardened concrete the appearance of the damage which indicate the looseness of the structure such as in the case shown in Photo 1. As the ordinary frost damage of hardened concrete seems to be basically under those conditions, it is important to consider the freezing temperature depression depending on the the size effect (melting point depression) and supercooling of capillary water.

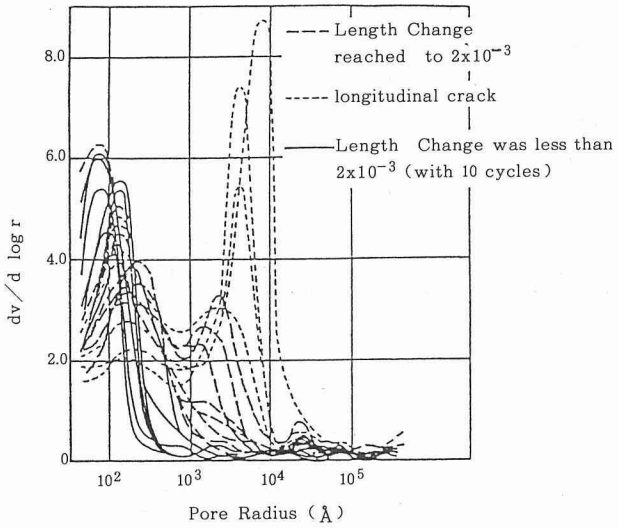
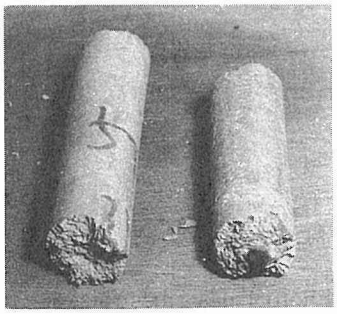


Fig. 7 Relations between Type of Deterioration and Pore Size Distribution

(1) Longitudinal Cracking (W/c 0.60 Age 2days)



(2) Looseness of the Structure (W/C 0.50 Age 28 days)

Photo 1 Appearances of Frost Damage of Hardened Cement Paste

5. Conclusion

The hardened concrete has numerous pores of some 100 Å to some 1000 Å in radius, which has a close relation to the freezing point depression depending on the size effect and supercooling. In this case, the frost damage would appeared as the looseness of the structure.

The original hydraulic pressure theory seems not to explain the frost damage of hardened concrete but to explain that of early age concrete which has numerous large pores in the structure.

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