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Aspects of freezing process in porous material-water system Part 2. Freezing and properties of frozen porous materials

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Abstract

In Part 1 of this series it has been shown that ice is a strong material and adheres well with hydrophilic materials. In this part of the series the strengths of ice-infiltrated porous, both unconsolidated and consolidated, materials have been reviewed. Ice-infiltrated porous materials are much stronger than the original materials. The contribution of ice to strengths of frozen materials is higher than is expected from strengths of bulk ice itself. The disruptive pressure needed to cause damage during freezing of porous materials has also to be much higher; this fact seems not to have been considered in often-quoted mechanisms of frost attack. Ice infiltrates porous bodies in the form of dendrites and in the process encapsulates still unfrozen water in many places. During further cooling unfrozen water develops high hydrostatic pressure capable of causing damage. Different proposed mechanisms of frost damage have been examined against the above background.

Keywords: Bond strength; Compressive strength; Degradation; Freezing and Thawing; Concrete

In Part 1 of this series it has been shown that ice is a very strong material and its adhesion to hydrophilic materials such as soil or concrete is also very high [1]. It is therefore expected that the infiltration of ice in a moist porous body during freezing will alter its strengths. For any damage to occur in a freezing body, the disrupting pressure must be sufficiently high to overcome the bursting strength of the frozen part of the body. To evaluate the order of magnitude of a damage-causing pressure, it is necessary to know the strengths of the ice-infiltrated porous materials. In this part of the series, properties of both unconsolidated porous materials such as silt and soil, as well as consolidated materials (e.g., concrete), will be reviewed. Freezing processes in wet concrete will also be examined.

1. Strengths of frozen unconsolidated porous materials

Table 1 shows strengths of some selected soils in their frozen state along with their moisture contents; strengths of bulk ice are also shown [2]. Table 1 shows that the presence of a hydrophilic material not only increases the strengths of frozen bodies above those of ice in short-term loading, it also imparts long-term strengths, whereas pure ice has no long-term strengths. Table 1 also shows that strengths of ice-soil composites increase with the decreasing temperature. Since soils with 20–40% moisture content generally are of very low strengths, the higher strengths of ice-soil composites over those of pure ice must be due to a lowering of stress in ice during freezing and adhesion of ice to soils [1].

2. Properties of frozen consolidated materials

2.1. Normal processes of freezing of outdoor structures

In colder countries, winter is normally preceded by a rainy autumn. During autumn outdoor structures gradually get cooler and at the same time can absorb water. Under proper conditions, porous structures such as road pavements, especially the top layers, may become saturated with water. A vertical structure seldom gets saturated unless it is in a splash zone.

The cooling rate of a large concrete structure is generally low, for example, about 1.7–5°C/h in Sweden [3]. Ice and snow, which often accompany subzero temperatures, hinder high supercooling of water by acting as seeds [4]. As a result an outdoor concrete structure is seldom supercooled below about −2°C. High supercooling, recorded in many laboratory experiments with small and thin samples and high rate of cooling, seldom occurs in normal outdoor structures. Temperature of concrete structures seldom falls below

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Table 1
Short- and long-term strengths of frozen soils

Soil type	% water	Temperature (°C)	Uniaxial strength, MPa			
			Short term		Long term	
			Compressive	Tensile	Compressive	Tensile
Silty sand	20–25	−0.3	1.1	0.6	0.3	0.1
		−5	3.4	2.2	0.8	0.4
		−10	6.4	4.4	3.4	1.1
		−20	12.7	5.4	5.9	2.1
Clayey silt	20–25	−5	2.3	2.0	2.0	1.0
		−20	6.5	3.9	3.9	1.8
	30–35	−3	3.1	1.4	0.4	0.3
	35–40	−0.5	0.9	0.5	0.2	0.1
Clay	25–35	−1	1.5	0.5	–	0.1
		−5	3.4	1.3	–	0.5
Ice	100	−3	1.8	1.1	0	0
		−10	3.5	1.8	0	0

about −25°C. Freezing of a concrete structure usually starts at the outer surfaces and then proceeds inward.

In this paper the main emphasis will be on the properties of plain (non-air-entrained) concrete. Low temperature testing of plain concrete has been carried out in the context of development of concrete containers for the storage of liquefied natural gas at a temperature of −165°C. Unfortunately in all these studies the cooling rates were much higher than those encountered in most outdoor concrete, for example, 2°C/min in one study [5]. The literature on frozen concrete up to 1981 has been reviewed by Browne and Bamforth [6]. The present review revealed that although the general trends (e.g., strengths-temperature relation, etc.) are well confirmed by different workers, the quantitative agreement among the results is not high. In view of varied experimental conditions used by different workers the observed quantitative differences are not unexpected.

2.2. Compressive strength

The compressive strength of frozen concrete increases with the water content and with decreasing temperature. For a saturated concrete the increase in the compressive strength, $\Delta\sigma$, is nearly independent of its room temperature strength and increases between 0°C and about −100°C. Browne and Bamforth has suggested the correlation [shown in Eq. (1)] between $\Delta\sigma$ in MPa, moisture content, m%, and temperature, Φ in °C. Eq. (1) applies within the range of 0° and −120°C. For a saturated concrete with a moisture content of 10%, the strength increase at −40°C would be 33 MPa; the reported increase ranged between 40 and 25 MPa. This means that a saturated concrete with a room temperature strength of 30 MPa will have a strength of about 60 MPa at −40°C. Even at −10°C the strength increase would be about 8 MPa; this has to be compared with the strength of 4 MPa of bulk ice at this temperature [1] (see also Table 1). The reasons for this difference are the same as those in clay and soils.

$$\Delta\sigma = -\frac{[\Phi \cdot m]}{12} \quad (1)$$

A saturated concrete shows a loss of strength when measured at room temperature, compared to its virgin strength, at every freeze-thaw cycle [5], whereas a concrete dried at 85% relative humidity shows no such loss in strength [7]. Thus only saturated or nearly saturated concrete suffers internal damage during freezing even though strength measured on frozen concrete does not reveal it.

2.3. Tensile strength

Tensile strength of a frozen concrete also increases with increasing moisture content and lowering temperature between 0 and about −60°C. At −10°C the reported mean increase in the tensile strength of a saturated concrete over that at virgin state is about 1.4 MPa; at −20°C the mean strength increase is about 3.5 MPa. This means that a concrete with a virgin tensile strength of 3 MPa will have a tensile strength of about 6.5 MPa at −20°C. A saturated concrete also loses its tensile strength during every freeze-thaw cycle.

2.4. Infiltration of a concrete structure by ice

Freezing of water in a porous body is different from that of bulk water. Ice infiltrates a porous body as dendrites and the pore dimensions determine the size of ice crystals at each point. Ice infiltration can only continue if the local size of the pore is larger than the equilibrium size of ice crystal under the experimental temperature and pressure conditions. There are at least two different processes that determine this ice infiltration.

2.4.1. Ice infiltration due to supercooling of water

This process has been discussed by Helmuth [4]. Under atmospheric pressure only a macroscopic ice crystal is in thermodynamic equilibrium with a saturated porous body at 273°K. However, a microscopic ice crystal requires supercooled water to penetrate a porous body. The size of a microscopic ice crystal is related to the temperature of supercooled water by the Thomson's Eq. (2) where T_S is 273°K, T_r is the temperature of supercooled water in °K, r_c is the radius of ice crystal in equilibrium with the supercooled water, γ_{iw} is the ice-water interfacial energy, Q is the molar heat of fusion of ice, d is the density of water, and M is the molar weight of water. From Eq. (2) it is possible to calculate r_c at different degree of supercooling.

$$T_r = T_S \exp\left(\frac{-2\gamma_{iw}M}{r_c Q d}\right) \quad (2)$$

Under the atmospheric pressure the first u molecular layers of adsorbed water could not be frozen even below −20°C [8]. The numerical value of u is about 4 and varies slightly with temperature. The diameter of a capillary, D, that allows an ice crystal of size r_c to propagate through it, is therefore $(2ut + 2r_c)$, where t is the thickness of a mono-

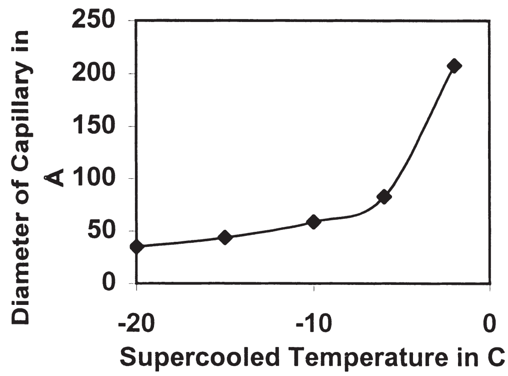

Fig. 1. Capillary size needed for ice penetration in a supercooled porous body.

layer of adsorbed water. Assuming t to be 3.1 Å and γ_{iw} to be 10.1 mJ/m^2 along with standard values of other parameters, Helmuth calculated D at different degree of supercooling. These are shown in Fig. 1. At any given degree of supercooling ice will infiltrate only interconnected pores that are equal to or larger than the critical D. Adjacent capillaries of larger sizes will not be infiltrated if connected by capillaries of smaller sizes.

2.4.2. Ice infiltration under pressure

Consider the case of an ice crystal-saturated porous matrix system maintained at a subzero temperature, say −2°C. Everett has shown that in this case the curvature of the ice-water interface is governed by Eq. (3) where Δp_i is the restraining pressure acting on the ice crystal, Δp_w is the suction pressure in water, γ_{iw} is the ice-water interfacial tension, and r_i is the radius of the interface [9].

$$\Delta p_i + \Delta p_w = \frac{2\gamma_{iw}}{r_i} \quad (3)$$

In the absence of both a restraining pressure on the ice crystal and suction in water, water migrates to the ice-water interface and then freezes, lifting the original ice crystal and the ice-water interface remains plane. If the ice crystal is restrained from lifting up the ice-water interface infiltrates the porous matrix following Eq. (3). In this case also the diameter D of the ice infiltrated pore is ($2ut + 2r_i$). Helmuth quotes a value of 14 Å for ut at −2°C. Fig. 2 shows calculated D at different pressure at −2°C. At any given pressure ice will infiltrate only interconnected pores that are equal to or larger than the critical diameter. High ice-concrete bond between external ice or snow may act as the initial restraining pressure; high tensile strength of ice infiltrated concrete, due to any of the above two reasons, will ensure continuing restraining pressure.

2.5. Effect of ice infiltration

Ice infiltration by the above two processes, either singly or jointly, has two side effects.

1. At a number of places in a concrete, yet-unfrozen water gets entrapped by infiltrated ice. Subsequent cooling ensures in situ freezing of entrapped water and pressure generation [1].
2. In an air-entrained concrete, infiltrating ice will reach surfaces of many air bubbles. As the curvatures of the air bubbles are infinitely larger than those of pores in cement paste, ice layers will preferentially form on the bubble surfaces drawing water from the surrounding volumes and thereby sealing the bubbles against ingress of water and in the process a certain amount of pressure will be released. The smaller pore size infiltrated by ice, the higher will be the fraction of air bubbles covered with ice layers.

3. Magnitude of required pressure for and mechanisms of frost damage

To cause damage to a freezing concrete by an internally generated pressure, its magnitude needs to be about two times the tensile strength of the frozen part of the concrete [10]. The tensile strength of a reasonable quality saturated concrete is about 2.5 MPa at room temperature. This means the tensile strength of the same concrete will be about 4 MPa at −10°C and 6 MPa at −20°C. It is, however, seldom known exactly at what temperature of the freezing cycle of a concrete damage occurs. The damage-producing pressure can therefore be between 8 and 12 MPa or approximately 10 MPa. The popular mechanisms of frost damage must be examined against this background.

3.1. Powers hydraulic pressure mechanism

It appears that Powers never considered the strength of frozen concrete. It is difficult to visualize a realistic situation under which the required pressure of 10 MPa may be generated by this mechanism. Furthermore, Powers' suggested equation for the calculation of the hydraulic pressure predicts a pressure only above about 91.7% saturation [11]. Concrete samples show damage even below this degree of saturation.

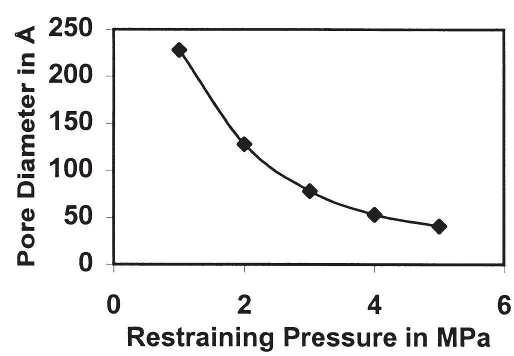

Fig. 2. Pore size needed for ice penetration at different restraining pressure.

3.2. Litvan's mechanism

Litvan seems to have not considered the strength of frozen concrete. Moreover, Litvan has not proposed any method for the calculation of pressure generation from his mechanism [12].

3.3. The mechanism of micro ice-lens formation

Movement of water through concrete is very restricted and as such it behaves like a closed system during freezing. In a closed system the pressure generation due to formation of ice may be calculated using the Clapeyron equation. The calculated pressure is about 1.25 MPa/°C [13]. This mechanism needs about 8°C supercooling to cause any damage.

3.4. Freezing of entrapped water

It is of interest to note that a pressure of about 7.6 MPa has been measured in freezing water drops of 7–10 mm sizes with very little supercooling and higher pressure development is expected in a larger volume of water [1]. A similar pressure generation may occur in entrapped water in freezing concrete [14]. This mechanism has certain affinity with the Litvan's mechanism.

It would thus appear that the last two mechanisms are capable of producing the required disruptive pressure. Further research will be needed to evaluate the relative importance of these two mechanisms.

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