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Communication

Aspects of the freezing process in a porous material–water system Part 1. Freezing and the properties of water and ice

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Abstract

In spite of a large volume of work carried out on the frost damage of consolidated porous materials such as concrete, the mechanism of damage remains unresolved. As the damage is associated with the freezing of water, so the physical properties of water and ice near the freezing point are reviewed in this, Part I of the series. The macroscopic process of the freezing of water has also been analyzed. These analyses show that ice is a very strong material and its adhesion to hydrophilic substances like cement and concrete is high. In the normal freezing of water, the initially formed ice forms a jacket around still, unfrozen water. During subsequent freezing, pressure develops within still unfrozen water, and at some point the ice jacket breaks. The nature of this breakage and the thickness of the ice jacket at the breaking point depend on the initial volume of water. The larger the initial volume of water, the thicker is the ice jacket and the more explosive is the breakage. The relevance of these properties to concrete breakdown are discussed.

Keywords: Bond strength; Degradation; Freezing and thawing; Compressive strength; Tensile properties

The deterioration of consolidated porous materials, such as concrete due to freezing, has been observed in a number of structures that are simultaneously exposed to water and subfreezing temperatures. This deterioration is of great importance in areas with a wet autumn and a cold winter. The wet autumn tends to saturate, at least at the outer regions, the structures in these areas. This deterioration has been shown to involve cement paste, aggregates, and the mineral and organic additives that comprise the structures. As a result, the total number of published reports regarding the observed deterioration is enormous. In spite of this large volume of work, the mechanism of frost damage still remains unresolved [1]. In the course of a review of these circumstances it was observed that some aspects of water near freezing point, ice, and ice-filled porous materials have not been considered by any of the proposed mechanisms. These aspects are examined herein so that a better mechanism may be formulated.

1. Behaviour of wet and dry concrete in a freeze–thaw environment

Table 1 shows the strength of concrete cylinders after a number of freeze–thaw cycles [2]. This table also demonstrates that the deterioration of concrete is associated with the freezing of water in wet concrete samples, and it takes a number of freezing cycles to show any sign of deterioration. Furthermore, the first few freezing cycles may actually increase the strength of wet concrete. To understand the deterioration, it is necessary to start with the properties of water near its freezing point, the freezing process of water, and the properties of ice.

2. Specific volume of water near freezing temperature and the freezing process of water

2.1. Specific volume of supercooled water

In an outdoor structure, because of the nucleation by snow and ice, water is seldom supercooled below approximately −10°C. It is therefore necessary to consider only the temperature range down to −10°C. Fig. 1 shows the specific volume of water in this temperature range [3]. Fig. 1 further shows that the volume of supercooled water increases with decreasing temperature. This volume increase of water, at a temperature below 4°C, means that a porous structure, saturated with water at 4°C, is supersaturated with water at the freezing temperature and below. As a result of this supersaturation, water is pressed out of the porous body either to the outside or to any unfilled void in the body.

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Table 1
Effect of freezin and thawing on dry and wet concrete

	Compressive strength as percent of strength after 7-day wet curing	
No. cycles	Frozen wet	Frozen dry
0	100	100
10	141	165
30	119	201
50	63	220
60	0	228

2.2. Freezing of bulk water

The process of the freezing of water has been studied in the context of frost damage to concrete [4,5]. Distilled water, in the absence of a nucleating agent, could be supercooled to approximately $-15°C$ and maintained at that temperature for several hours. When supercooled water freezes, it quickly forms a mass of semiparallel fibrous ice crystals accompanied by a rise in temperature to approximately 0°C and an increase in the total volume. At this stage, these fibrous crystals are separated from each other by water layers. On subsequent cooling, the whole mass solidifies without any damage to the container. The solidified mass is easy to split, that is, it has a low strength. Some organic chemicals favour fibrous ice formation.

If, however, water at 0° C is seeded with an ice particle, as often happens with the outdoor freezing of concrete, then it freezes slowly, forming blocky ice crystals both on the inside surface of the container and on the free surface of water. With continued cooling, the thickness of blocky ice layers—both on the sides of the container and on the surface of water—increases, thereby enclosing a mass of liquid water within. All this happens with very little increase in volume. With continued cooling, the process may take one of two courses. If the starting volume of water is below approximately 4 mL, then apparently the whole mass freezes without any visible cracks. However, if the starting volume is more than approximately 10 mL, then the last stage of freezing is accompanied by visible fracturing of the ice block. This breakage can be explosive when the starting volume is above approximately 20 mL. The explosive nature of the breakdown indicates that the ice layer was under a considerable tensile stress before the breakdown. If the freezing ice block is not removed from its container, then both the ice block and the container may break if the starting volume of water is sufficiently large [4]. The above results indicate that ice is an intrinsically high-strength material and that pressure development that occurs in unfrozen water, enclosed within a freezing block of ice, can be high. The actual pressure in water depends on the initial volume of water enclosed by an ice block and on the temperature of the ice block.

The above observations may be analyzed as follows. Consider a spherical volume of water, V_w (Fig. 2), being slowly frozen and a layer of ice having formed on the outer surface. Then

$$V_w = \frac{4}{3}\pi R^3, \tag{1}$$

$$V_{ice} = 4\pi R^2 dr, \tag{2}$$

$$dV_w = 0.09 V_{ice} = 0.36\pi R^2 dr. \tag{3}$$

In Eqs. (1–3) above, V_{ice} is the volume of ice formed, dr is the thickness of the ice layer, and dV_w is the excess volume production resulting from ice formation.

The volume increase, resulting from the formation of ice, has to be contained by compressing as yet unfrozen water. The necessary pressure, P, may be calculated from Eq. (4), where κ is the isothermal compressibility of water:

$$P = \frac{0.27 dr}{\kappa R}. \tag{4}$$

When the pressure, P, exceeds twice the tensile strength, f_t, of ice, the shell breaks [6]. From Eq. (4) it can be seen that when the initial water volume is small, that is, when R has a

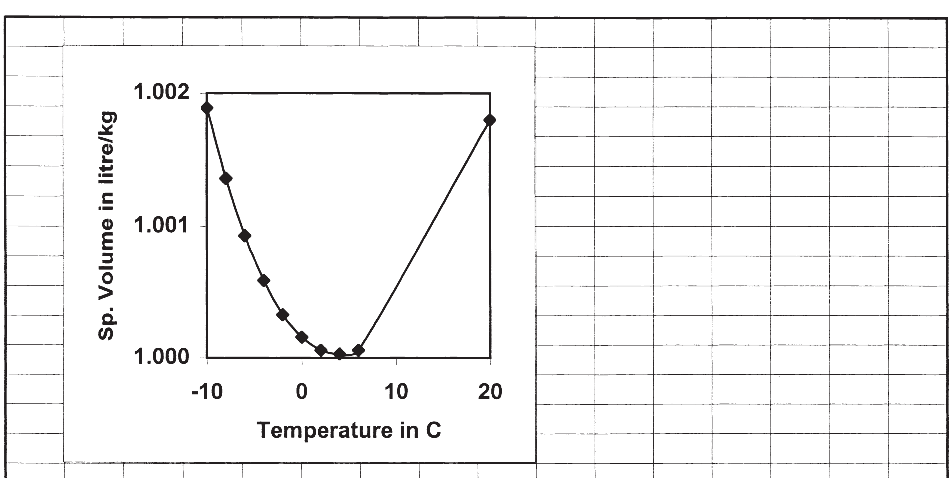

Fig. 1. Specific volume of water at different temperatures.

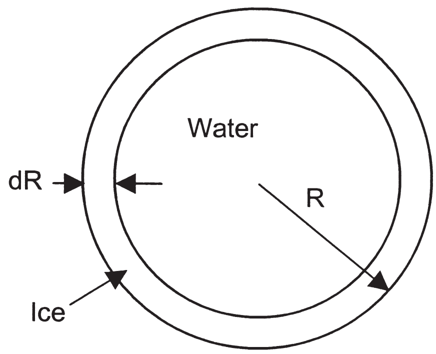

Fig. 2. Geometry of freezing.

small value, *dr* is also small and the ice layer breaks at the early stages of freezing. Unfrozen water freezes again, forming a new ice shell, and the process repeats until all water is frozen. The pressure repeatedly rises and then falls as the ice shell forms, cracks, and reforms. This rise and fall of pressure has been measured within a 7- to 10-mm diameter freezing water drops, and a pressure rise up to 7.6 MPa has been measured [7]. Because of the thinness of the ice shells and their repeated cracking, the fracture planes are indistinct, as has been observed by Chatterji et al. [4]. With a large volume of water, that is, a large value for *R, dr* is also large, and cracking of the ice shell occurs at longer intervals. In this case, the fracture planes are easily visible. The cracking pressure increases with the thickness of the ice shell and the rate of freezing. The effect of the rate of freezing is mainly the result of the increase in ice strength at lowered temperatures (see below).

Eq. (4) also warns against extrapolating properties of small-sized samples, that is, those containing a small volume of water, to large samples containing a large volume of water.

3. Selected properties of ice

3.1. Strength of ice

The crushing strength of commercial (bulk) ice, under short time loading, increases with the decreasing temperature [8]. Fig. 3 shows a set of such strength data. Both higher and lower strengths of bulk ice than those shown in Fig. 3 have been reported [9,10]. At approximately $-10°$ C, a commercial block of bulk ice can have a crushing strength of approximately 4 MPa. A probable reason for this variation in the crushing strength of commercial (bulk) ice may also be the stress that develops during the freezing of bulk water. Table 2 shows the effects of both short- and long-term loading on the strengths of ice [11]. This table demonstrates that under short-term loading, ice has both a compressive and a tensile strength; however, under long-term loading it has none, that is, ice is viscoelastic. It will be shown in the second part of this series that the strength of ice in a porous medium is much higher than Fig. 3 suggests and that the viscoelastic property of ice also changes. The strength of ice is also affected by the presence of dissolved materials; some of the solutes increase the strength and others decrease it [12].

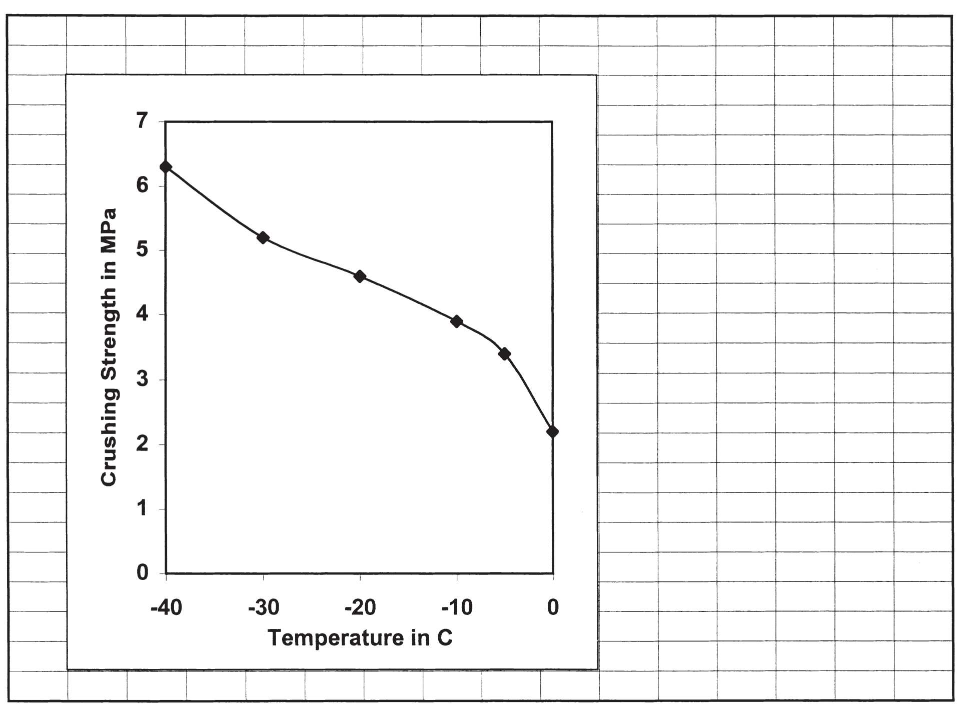

Fig. 3. Strength of ice at different temperatures.

Table 2
Short- and long-term strengths of ice

	Uniaxial strenght (MPa)			
	Short-term loading		Long-term loading	
Temperature (°C)	Compressive	Tensile	Compressive	Tensile
−3.0	1.6–2.0	1.0–1.2	0	0
−10.0	3.2–4.0	1.7–2.0	0	0

3.2. The specific volume of ice

The specific volume of ice decreases as the temperature decreases. This is in contrast with supercooled water [13]. This decrease is perfectly described by Eq. (5):

$$V_{ice} = C_0 + C_1 \times t, \tag{5}$$

where C_0 is 1.09078 dm^3/kg, C_1 is 1.677×10^{-4} dm^3/kg, and t is the temperature in ° C. Because of this volume contraction of ice, a partially frozen body is under compression. To cause any damage the internal pressure must overcome the above compression, that is, a higher pressure is needed than would be otherwise.

3.3. Adhesion of ice to other substances

The ice–substrate adhesion has been studied by a number of investigators [14–17]. It has been observed that the adhesional strength, under shear, of an ice–hydrophilic substrate bond increases with decreasing temperature up to the shear strength of ice itself, or approximately 1.6 MPa between −3° to −13° C. On hydrophobic surfaces the adhesional strength is lower. Most silicates are hydrophilic, and the adhesional strength is as high as the shear strength of ice. One of the interesting features of an ice–substrate bond is that the adhesive strength under tension is much greater than that under shear [17]. This high adhesive strength of ice affects its penetration into porous silicate bodies.

It is important to note that none of the proposed mechanisms of frost damage takes into account the high strength of ice and its adhesion to the matrix. Of the investigators in this field, only Helmuth [18] seems to have considered the effect of supercooling of water and subsequent ice formation.

4. Note added in proof

The AMANDA project provided a dramatic support for Eqs. (1–4). Just before complete refreezing of water in 0.5 × 1400-meter-deep holes in Antarctic ice, water pressure, at 1000-meter depth, spiked to above 500 atmosphere (50 MPa) [19].

Acknowledgments

To my old friends Lars Romben and Eva Bergman. In early summer together we planted some seeds that are germinating in late autumn. Will they survive winter frosts?

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