

# **MICROSTRUCTURAL APPROACH TO FROST RESISTANCE OF HIGHLY POROUS MATERIALS**

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## **Abstract**

Highly porous materials like aerated concrete with entrained air content more than 45 % is nevertheless damaged during freezing. This should be attributed to its pore structure and degree of saturation rather than its low strength. This paper develops the concept of the critical saturation to which a microstructural explanation will be given, and a mechanism of frost damage to highly porous materials is discussed through the results of the following three experiments. DSC measurement has shown that an adsorbed water film remains unfrozen in between solid surface and ice. The critical saturation has been determined and the pore space occupied by the moisture has been identified, while the observation of frozen samples having critical moisture content by cryo-SEM has confirmed the compatibility with these results. A formula linking critical saturation with pore structure has been derived.

Keywords: Pore structure, frost resistance, critical degree of saturation

## **1 Introduction**

The degree of critical saturation method assessing frost resistance of concrete proposed by Fagerlund[1] comprises two separate experiments of measuring a critical moisture level above which concrete shows expansion during freezing, and of measuring actual moisture level during its service life. Frost resistance is evaluated by comparing these two moisture levels. The critical saturation is determined by measuring change in length or in dynamic E-modulus of samples with different moisture content under single freeze/thaw cycle.

In the research on aerated concrete, Nerenst and Berger[2] emphasized the importance of moisture content specially in evaluating highly porous materials. Larsson and Purins[3] and Roulet [4] applied the critical saturation method to aerated concrete, while Funke and Eliasson[5] extended the method over a lower density range from 193 to 472 kg/m<sup>3</sup>. However, any explanation why the wet materials behave so differently across the critical moisture content has not been given so far.

## 2 Measurement of unfrozen water

### 2.1 Testing procedure

Specimens were made in the mold with dimensions of 4x4x16 cm, and introduced immediately after autoclaving to a vacuum desiccator for drying without effects of carbonation. Then the specimens were cut out in a dimension of 7x7x15 mm and conditioned for 15 days under constant relative humidities of 66, 75, 85, 90, 93 and 95 % in desiccators with different salt solutions at 20°C. For a specimen to have the highest moisture content was first vacuum-saturated and dried moderately to have a specified moisture content under 60 % of relative humidity and temperature of 20°C, and sealed in a polyethylene bag for 15 days. These specimens were then put into aluminum cans with special care of their contact and set in the differential scanning calorimetry together with AgI powder applied on the surface of the specimens. The DSC was operated with a cooling rate of 2 deg/min from 20°C to -50°C.

### 2.2 Result of DSC measurement

A result of DSC measurement of aerated concrete with bulk density of 503 kg/m<sup>3</sup> is shown in **Fig.1**. Each curves correspond to each specimens equilibrated with different relative humidities as denoted in the figure. A specimen with much higher moisture content was included for comparison, for which moisture condition is given in degree of saturation S.

The exotherms detected by the DSC are due to phase change of water contained in the specimen and obviously show two peaks implying two different types of water. The first type of water whose phase change may take place at a temperature between -7.2°C to -17.7°C forms the strong first peak, while the second exothermal peaks due to the phase change of the

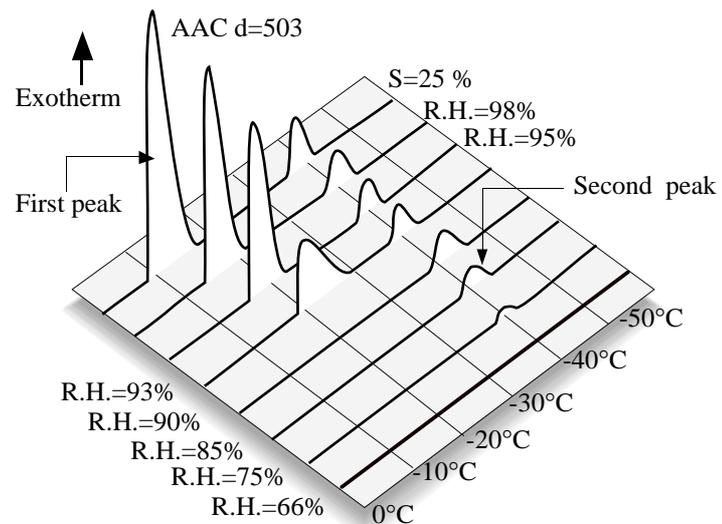


Fig. 1 Phase transition of adsorbed water film

second type of water at about  $-37^{\circ}\text{C}$  show constant height. Any other indication of phase change of water down to  $-60^{\circ}\text{C}$  could not be detected at highest resolution. The second peak could not be found for specimens equilibrated in a relative humidity smaller than 66%. A moisture retained as an equilibrium moisture content under relative humidity of 66 % can be evaporable at  $105^{\circ}\text{C}$  but virtually unfrozen until  $-60^{\circ}\text{C}$ .

### 2.3 Discussion on unfrozen water

The statistical thickness of adsorbed water film  $t$ , as a function of relative humidity can be introduced to discuss the influences of solid surface upon water molecules and can be calculated by the following formula.

$$t = V_w / A \cdot Q, \quad (1)$$

where  $A$  is BET surface area and  $Q$  is the weight of specimen. Using sorption isotherm of aerated concrete, quasi linear relationship between  $\log t$  and double log of relative humidity can be obtained as shown in **Fig.2**. A moisture retained in equilibrium with a relative humidity of 66 % corresponds to the second molecular layer which would be highly bound to solid surface under van der Waals interaction, whereby a moisture forming the second exothermal peak corresponds to the third to sixth molecular layer and can be frozen at  $-37^{\circ}\text{C}$  though it is also bound to a certain extent. These types of moisture exist as unfrozen water in between solid surface and ice under the temperature range used in the standard freeze/thaw testing. Similar calorimetric measurements have been reported for hardened cement pastes[6][7] and briks[8].

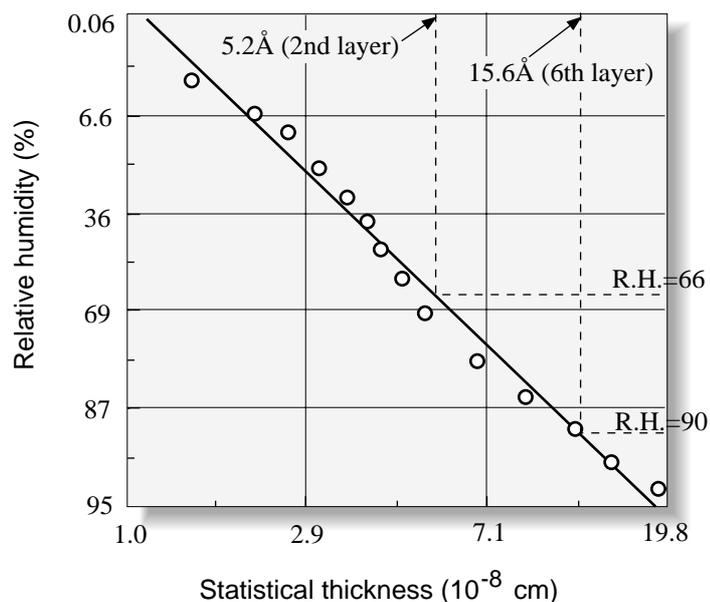


Fig. 2 Relative humidity and statistical thickness of adsorbed water films

## 3 Measurement of dilatation during freezing

### 3.1 Testing procedure

Specimens were prepared in conjunction with those for DSC whereas the keeping after sealing extended over 4 weeks due to larger cross section of the specimens. Degree of saturation of the specimens were conditioned so as to have 5, 20, 30, 35, 40, 42, 45,

50, 52, 55, 60, 65, 70 %, and the specimens sealed with polypropylene bag were set in the specimen cell and subjected to freeze/thaw at a cooling rate of 3 deg/hour, temperature range between +5°C to -20 °C in the methanol bath. Dilatation during a freeze/thaw was measured by a differential transducer with a quartz glass extension rod. The cooling rate was determined based on the preliminary experiment of the specimen with the lowest moisture content, which was most difficult to adjust the temperature at the center to that of the cooling bath.

### 3.2 Result of length change measurement

Relationships between temperature at the center of specimen and the dilatation during freezing for aerated concrete with bulk density of 503 kg/m<sup>3</sup> is shown in **Fig.3**, though measurement was executed for 39 specimens of three different bulk density with each 13 different moisture level. The length change behavior falls into two groups, those who dilate or shrink according to their moisture content, whereas only typical examples are presented.

It is observed that for specimens of any bulk density, the preceding shrinkage should turn to dilatation when the degree of saturation increases up to a certain level, which was estimated as 45 % for aerated concrete with bulk density of 503 kg/m<sup>3</sup>. In order to show more clearly the length change behavior, the difference of length at -17 °C from the simple thermal dilatation was measured as  $\Delta L$ , and plotted against degree of saturation as shown in **Fig.4**. The critical degree of saturation defined

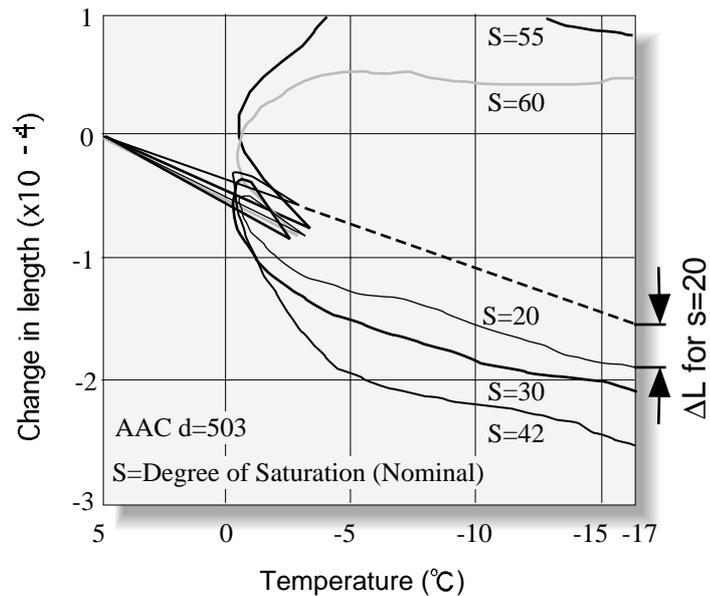


Fig. 3 Change in length during freezing

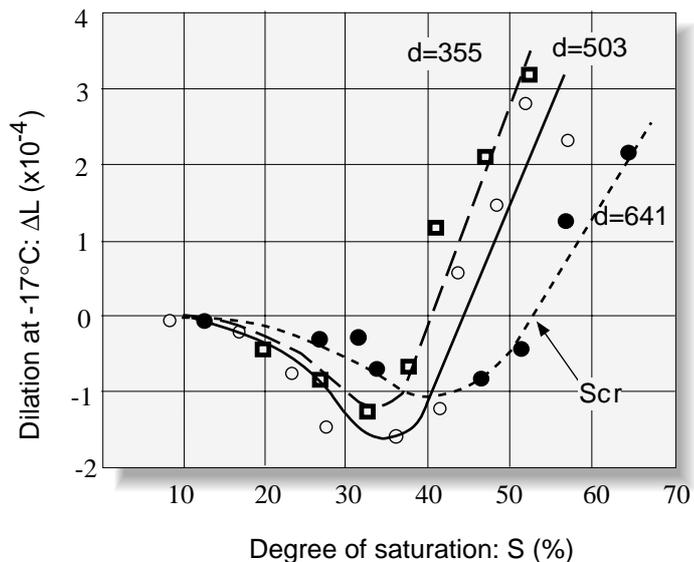


Fig. 4 Dependency of change in length during freezing upon degree of saturation

in the RILEM recommendation can be so determined as the turning point from shrinkage to dilatation as shown in the Figure. The critical degree of saturation for aerated concrete with bulk density of 355, 503 and 641 kg/m<sup>3</sup> is 40, 44 and 52 % respectively.

### 3.3 Discussion on critical saturation and pore structure

The relationship of pore size and the amount of moisture that can occupy the pore volume for aerated concrete has been determined as a relationship between volumetric moisture content and the hydraulic radius[9]. The relationship measured for specimen with bulk density of 503 kg/m<sup>3</sup> is shown in Fig.5, where degree of saturation is used instead of volumetric moisture content. It is

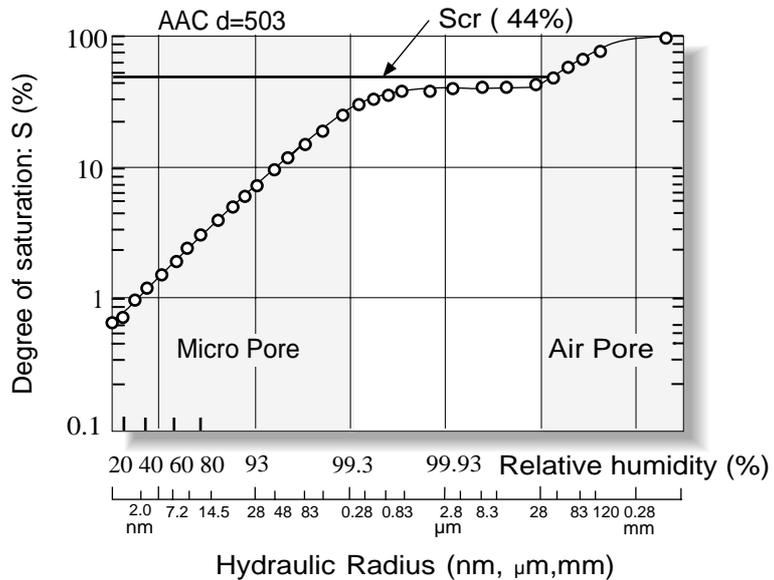


Fig. 5 Pore size and degree of saturation

shown that the amount of 44 % of moisture measured as the critical degree of saturation corresponds to a pore region including certain portion of air pore in addition to all micropore.

Nearly all specimen with moisture content less than critical saturation showed further contraction than single thermal contraction during freezing. In this moisture condition, there are sufficient space available for free ice formation whereby unfrozen water could find their way to turn into ice without altering total pressure condition. The unfrozen water would migrate in between solid surface and ice, and eventually freeze when it reaches an adsorbed water film at ice - air interface. The contraction behavior could be thus attributed to a drying shrinkage occurring in a decrease of the thickness of adsorbed water film.

## 4 SEM observation of frozen specimens at critical degree of saturation

### 4.1 Testing procedure

Specimens with bulk density of 503 kg/m<sup>3</sup> were cut out to have 5 mm in diameter and 7 mm in length and conditioned so as to have degree of saturation of 47.5 and 78 %. After being cured in a sealed plastic bag for 7 days, specimens were introduced in an cooling box at -15 °C for 3 days and then moved to the specimen chamber of

field-emission scanning electron microscopy with cryo system. Specimens were cooled down to liquid nitrogen temperature followed by evacuation up to 0.8 torr when they were cut to have fresh cross section for observation. Observation was made without gold deposition at an accelerating voltage of 5 kV.

#### 4.2 Result of cryo-SEM

The degree of saturation of the specimen was 47.5 %, which is nearly equal to the measured critical degree of saturation that is a moisture condition when a certain portion of small air pores and all micropore, 38 % of the total pore volume, are filled with moisture. The observed cross section of air pore subjected to freezing at this moisture condition is shown in Fig. 6 and 7. For comparison, specimens with degree

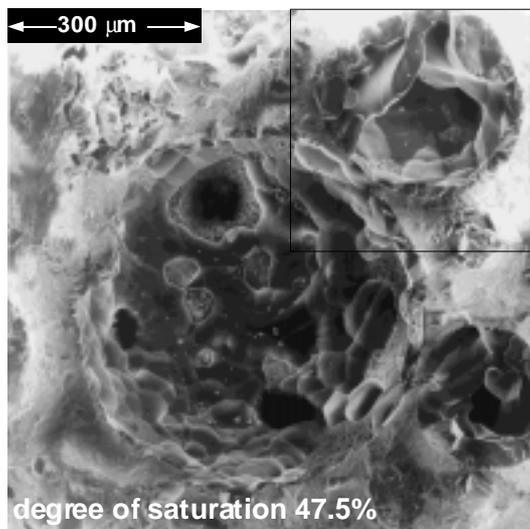


Fig. 6 Ice segregation on the surface of air pore of frozen aerated concrete

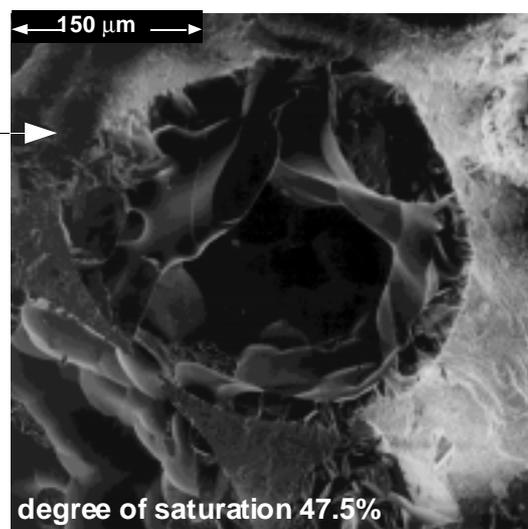


Fig. 7 Magnified view of a small air pore

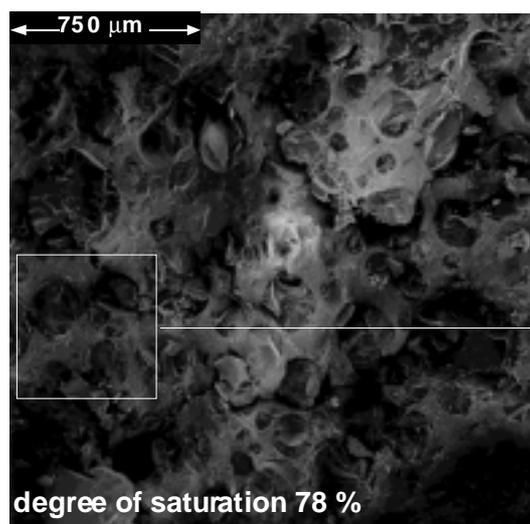


Fig. 8 Ice segregation on the surface of air pore of frozen aerated concrete

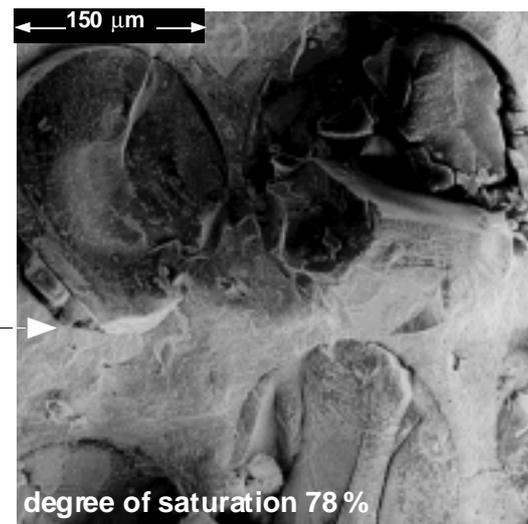


Fig. 9 Magnified view of a small air pore

of saturation as high as 78 % , at which nearly all air pores are filled with moisture are also shown in **Fig. 8** and **9**.

A bigger air pore with diameter about 0.5 mm at the center of Fig.6 shows rather small amount of ice on its surface whereas three small air pores located at the right of the big air pore are nearly filled with ice, which is shown with twice magnification in Fig.7. Optical microscopic observation of larger air pore of a specimen with the equal degree of saturation was made before freezing and no moisture could be seen, whereby the ice segregated on the surface of air pores could be attributed to the moisture coming from inside of the matrix part.

### 4.3 Discussion on unfrozen water migration

No apparent damage can be seen in the micrograph as a matter of course, since the critical degree of saturation has been estimated from the utmost sign of internal damage such as changes in length or dynamic modulus. At a smaller air pore with diameter less than 100  $\mu\text{m}$  as shown at the bottom of Fig.7 however, considerable volume is being occupied with ice to form a hollow ice sphere with thick shell. In air pores of this type, unfrozen water migration from the matrix part to the ice - air interface becomes no longer possible at the critical degree of saturation, and the pressure of this system could increase. This condition may coincide with the fact that change in length turns from contraction to dilatation when the amount of moisture reaches the critical degree of saturation, as schematically shown in **Fig.10**.

## 5 Pore structure and the critical degree of saturation

Bulk density of aerated concrete can be varied by controlling the amount of air , while its true density  $d_s$  and the bulk density of matrix part  $d_m$  can be assumed to be constant. To represent the critical degree of saturation  $S_{cr}$  of aerated concrete as a function of bulk density  $d$ , a ratio of pore volume of the matrix part  $V_{pm}$  to the total pore volume  $V_p$  and a ratio of air pore volume  $V_{pa}$  to the total pore volume  $V_p$  are introduced.  $S_{cr}$  can be given as follows,

$$S_{cr} = \frac{V_{pm}}{V_p} + \frac{V_{pa}}{V_p} a , \quad (2)$$

where  $a$  assumes between 0 and 1 as a constant to be determined by experiment. Taking bulk density  $d$  as a variable and introducing true density  $d_s$  and the bulk density of matrix part  $d_m$  , the expression can be rearranged as follows,

$$S_{cr} = \frac{d(d_s - d_m)}{d_m(d_s - d)} + \frac{d_s(d_m - d)}{d_m(d_s - d)} a . \quad (3)$$

Substituting 2620 and 950 into  $d_s$  and  $d_m$  respectively, and using 0.44 and 503 as obtained in this experiment for  $S_{cr}$  and  $d$  respectively,  $a$  can be calculated as 0.06.

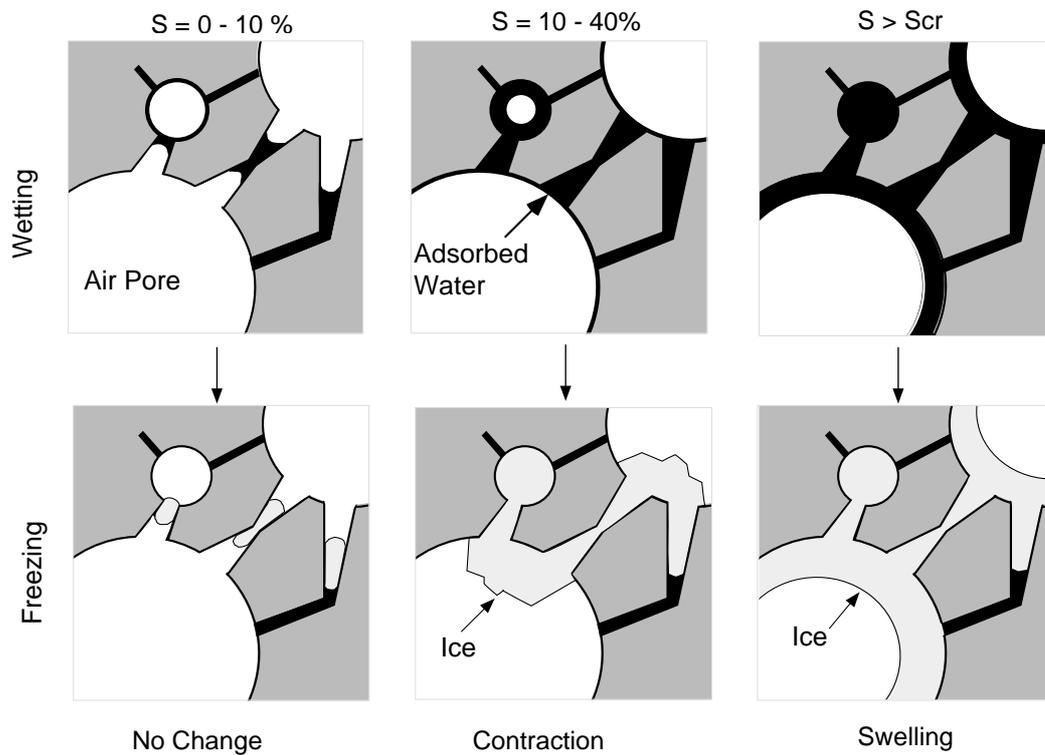


Fig. 10 Pore structure and the critical degree of saturation

This does imply that the critical degree of saturation  $S_{cr}$  is a moisture condition when water occupies all micropore volume existing in the matrix part and extends over 6 % of air pore volume. The value of  $a$  may be varied depending on the air pore size distribution below 100  $\mu\text{m}$  in diameter.

Compared with experimental  $S_{cr}$  values given in literatures, calculated  $S_{cr}$  shows good agreement as shown in Fig.11. An increase of  $S_{cr}$  with the increase of bulk density should be attributed not to an increase of strength but to an increase of micropore volume.

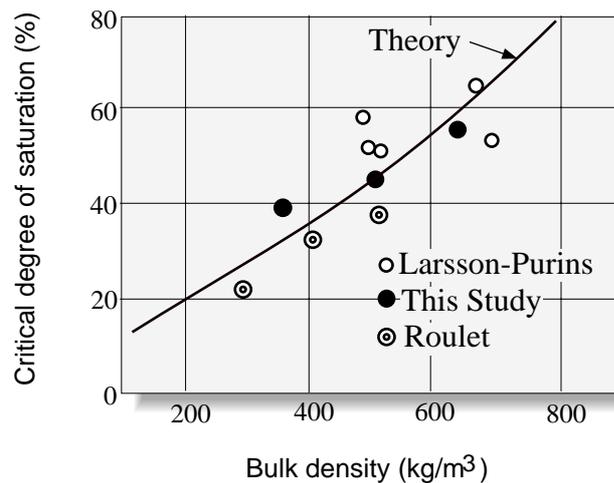


Fig. 11 Bulk density of aerated concrete and the critical degree of saturation

## 6 Conclusions

### 6.1 Existence of unfrozen water

Low temperature DSC measurement down to  $-60\text{ }^{\circ}\text{C}$  for aerated concrete conditioned to have adsorbed water films of 0 to 20 molecular layer implied that the adsorbed water film of the first two molecular layer was virtually unfrozen water, and the third to sixth layer froze at  $-36^{\circ}\text{C}$ , whereby the adsorbed water film of sixth molecular layer remains unfrozen at the temperature range specified in existing freeze/thaw test methods. The freezing point depression can be attributed to the surface forces of the solid, and the resulting unfrozen water may be present between solid surface and ice.

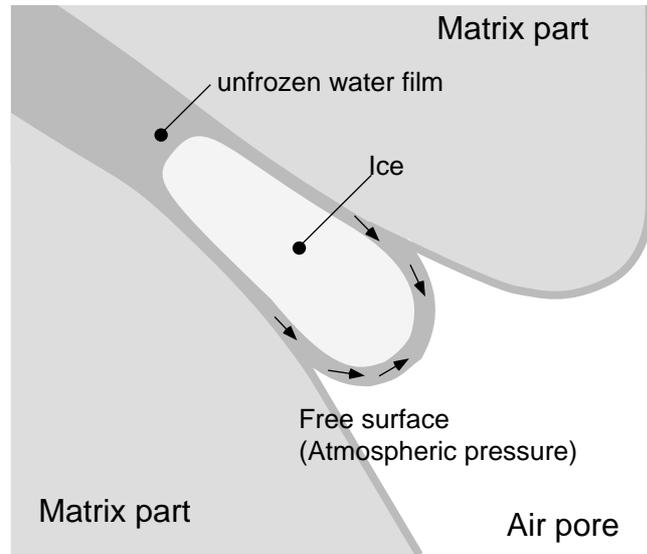


Fig. 12 Free ice formation near the surface of an air pore

### 6.2 Microstructural aspect of the critical degree of saturation

The critical degree of saturations of aerated concrete with bulk density of 355, 503 and 641 were 40, 44 and 52 respectively. The critical degree of saturation corresponds to a moisture condition where all micropores and some portion of small air pores are filled with water. Nearly all specimen with moisture content less than critical saturation showed further contraction than single thermal contraction during freezing. In this moisture condition, there are sufficient space available for free ice formation whereby unfrozen water could find their way to turn into ice without altering the total pressure condition. In this condition, the unfrozen water film applying the disjoining pressure now turns its way to thermodynamically stable ice, resulting thinning of adsorbed water film could cause contraction in a similar fashion to drying shrinkage mechanism as shown in Fig. 12.

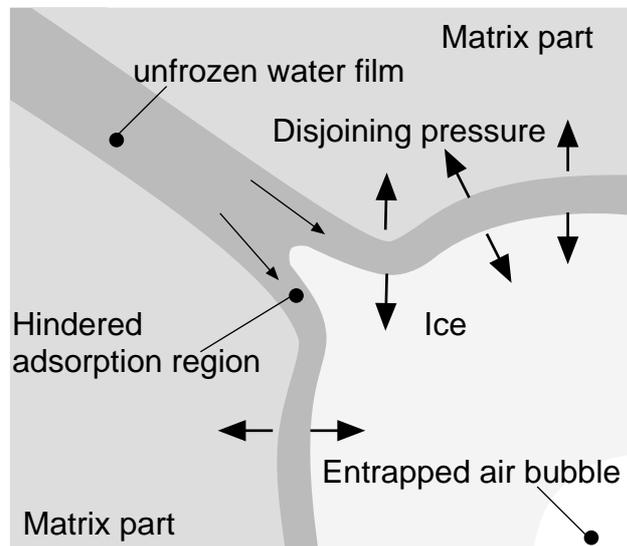


Fig. 13 Disjoining pressure associated with the formation of ice

### 6.3 Mechanism of dilatation during freezing

Direct cryo-SEM observation of frozen aerated concrete conditioned in the critical degree of saturation has shown considerable ice segregation on the surface of air pores. Since the unfrozen water exists as an adsorbed film in between the solid surface and ice, the unfrozen water film could migrate freely and total pressure of the system could not increase as far as the ice segregation may occupy air pore volume partially.

At a smaller air pore with diameter less than 100  $\mu\text{m}$  however, considerable volume is being occupied with ice to form a hollow ice sphere with thick shell. In air pores of this type, unfrozen water migration from the matrix part to the ice - air interface becomes no longer possible, and the pressure of this system could increase as schematically shown in **Fig. 13**.

### 6.4 The critical degree of saturation as a function of porosity

With these experimental results, the critical degree of saturation was taken as a moisture condition where all micropore and some portion of air pore are occupied by water, and a theoretical expression for the critical degree of saturation of aerated concrete was derived as a function of bulk density. Computed results show good agreement with those experimentally determined in the past for different bulk densities.

## 7 References

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