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FROST RESISTANCE OF HIGH PERFORMANCE CONCRETE- SOME THEORETICAL CONSIDERATIONS

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Content

1. Introduction

According to some experimental studies, concretes with very low water/cement ratios -so-called high performance concretes- seem to be frost resistant even when they lack air-entrainment. Some examples are shown in Fig 1 which is based on a work performed at our department by Lindmark (1991). Twelve different concretes were tested in 3% NaCl solution according to the Swedish standard method of testing the salt scaling resistance. In this method, the specimen is pre-dried at room climate and is then re-saturated by sucking pure water for 1 week before the freeze/thaw test starts. The specimen is heat insulated on all sides during the test except on the top surface which is covered by a thin layer of the salt solution. This is protected from evaporation by a plastic foil. Each freeze/thaw cycle consists of 16 hours of freezing to about -18°C and 8 hours of thawing to room temperature. The material which is scaled off is weighed at 7 days interval. The salt solution is renewed in connection with this.

The characteristics of the 12 concretes were as follows:

Water/binder ratio	silica fume (% of cement)	air entrainment	air content (%)
0,22	0	no	1,8
		yes	4,1
	10	no	1,5
		yes	5,0
0,31	0	no	0,8
		yes	4,1
	10	no	0,6
		yes	2,4
0,40	0	no	0,8
		yes	4,3
	10	no	1,4
		yes	4,2

The accumulated scaling after 56 cycles is plotted in Fig 1. A concrete with good scaling resistance ought to have a scaling after 56 cycles that is lower than 0,5 kg/m^2. It is quite clear from Fig 1 that a concrete with a water/binder ratio of 0,40 needs air in order to be frost resistant. All concretes with the water/binder ratios 0,31 and 0,22 were frost resistant even without air-entrainment. Air did not improve their frost resistance. A parallell set of specimens was exposed to an artificial ageing consisting of repeated dryings and re-saturations. This treatment was not found to change the frost resistance in any significant manner

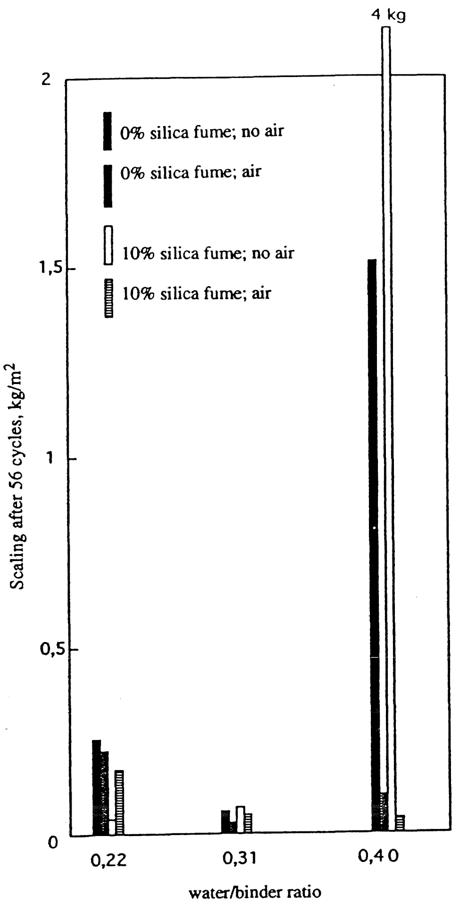

Fig 1: Results of salt scaling tests of concretes with different water/binder ratio, different air content and different amount of silica fume; Lindmark (1991).

Similar results have been obtained by other researchers for example by Saucier (1984) who studied the ordinary frost resistance of air entrained and non-air-entrained concrete with the water/cement ratio 0,24. All concretes had a high degree of frost resistance. He found a slight tendency of a larger damage of the air-entrained concretes which is remarkable but which can be explained theoretically as shown below in paragraph 4.

On the other hand, other experiments indicate that concrete is not always frost resistant even when the water/cement ratio is very low. Some examples can be found in Malhotra et al (1987). Air-entrained and non-air-entrained concretes with the water/binder ratios 0,25 and 0,35 and with the addition of 0, 10 or 20% silica fume were freeze-tested in pure water according to ASTM C666. All concretes without extra air were more or less completely destroyed afer a few freeze/thaw cycles. Only 2 concretes with air-entrainment had good frost resistance. There are also other researchers that have found frost damage on low-porosity, non-air-entrained concrete; e.g Hammer and Sellevold (1990).

It is therefore evident that one cannot safely state that a concrete with a low water/cement ratio is automatically frost resistant even when it has no air-entrainment. It seems as if many factors such as the concrete age, the type of binder, the pre-treatment before the test , the minimum temperature during the test, etc will have a profound influence on the frost resistance. In this report some possible influences on the frost resistance of concrete with low water/cement ratio are treated theoretically. It is shown that much of the divergent experimental findings might have natural explanations.

2. Damage mechanisms

2.1 Closed container

2.1.1 Maximum tolerable freezable water in a saturated material

In the simpliest case every small ”unit cell” of the cement paste can be looked upon as a closed container. No water transfer is possible from the place where ice is formed. The reason might be that the concrete does not contain any air-filled space or that the permeability of the pore walls is so low that water is practically immobilized. The 9% volume increase when water is transformed to ice must therefore be taken care of in the neighbourhood of the freezing site; i.e. in the ”local container”. Very high pressures might develop if the container is completely water-filled. The phase diagram of ice-water shows that a pressure of 10 MPa is needed in order to lower the freezing point by 1°C. Therefore, at -20°C a pressure of about 200 MPa is needed if ice formation shall be prevented.

Two simple models can be used for estimating the maximum pressures in the saturated concrete; see Fig 2. In both models, the cement paste phase is supposed to be a water-filled and incompressible hole-sphere of unit volume.

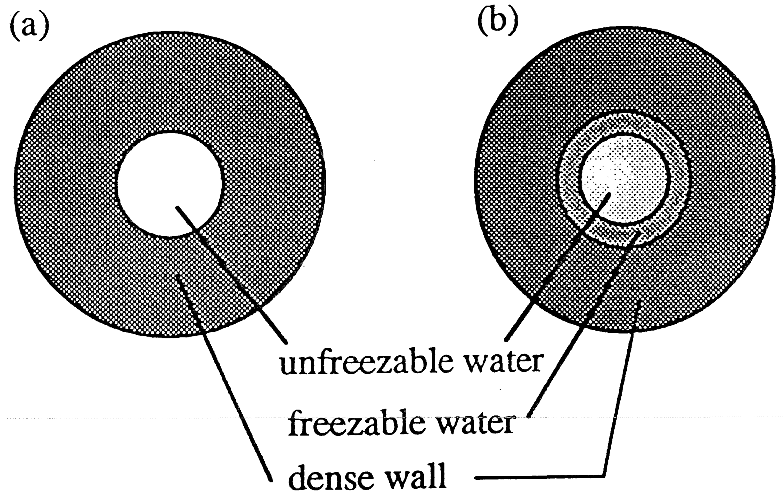

Fig 2: Illustration to the model ”closed container”. (a) only freezable water in the hole. (b) All evaporable water in the hole.

Model 1: All potentially freezable water is located in the hole while all non-freezable water is located to the wall; Fig 2a. The container wall is supposed to be impermeable and no pressure in the water inside the hole is supposed to be transferred by hydraulic action to the unfrozen water in the wall. The material is supposed to be linear-elastic to fracture.Then, the maximum tangential stress in the wall due to an inner pressure acting along the periphery of the hole is; Timoshenko and Goodier (1951):

$$\sigma t = \frac{0{,}5 + Wf}{1 - Wf} \cdot p \qquad (1)$$

Where,

σt the maximum tangential stress in the container wall (MPa)
Wf the total freezable water (m^3/m^3)
p the inner pressure in the water in the hole (MPa)

The pressure p is only a function of the temperature since no volume expansion is supposed to take place. As said above, $p \approx 10 \cdot \Delta\theta$ where $\Delta\theta$ is the freezing point depression due to the internal pressure in the water. Therefore,

$$\sigma t = \frac{0{,}5 + Wf}{1 - Wf} \cdot 10 \cdot \Delta\theta \qquad (2)$$

The direct tensile strength of cement paste is hardly above 8 MPa. This means that a saturated cement paste cannot resist freezing to a temperature that is lower than about -1,6°C even if the freezable water content is as low as 1% of the cement paste volume or 10 litres per m^3 or even lower.

Eq (2) erroneously predicts that a certain stress appears in the material even when the freezable water content is approaching zero. This depends on the assumption of an ideal-elastic material. Another, and perhaps more reasonable approach, is to assume that the internal pressure is evenly distributed across the container wall. Then, the tangential stress in this is:

$$\sigma t = \frac{Wf^{2/3}}{1 - Wf^{2/3}} \cdot 10 \cdot \Delta\theta \qquad (3)$$

For a completely saturated cement paste with the tensile strength 8 MPa the maximum tolerable amount of freezable water is 5% of the cement paste volume for a freezing temperature of -5°C, 2% for a freezing temperature of -10°C and 0,7% for a freezing temperature of -20°C. The tensile stresses appearing in a saturated cement paste with a freezable water content as low as 1% (10 litres per m^3) is 10 MPa at -20°C and 19 MPa at -20°C. This is more than the tensile strength of the cement paste.

Model 2: All pore water is supposed to be contained in the hole and all solid material in the wall. The maximum stresses are given by eq (2) or (3) with W_f exchanged for the total water-filled cement paste porosity P (m^3/m^3). Eq (3) is changed to:

$$\sigma_t = \frac{P^{2/3}}{1 - P^{2/3}} \cdot 10 \cdot \Delta\theta \qquad (3a)$$

Also a very dense cement paste, with low water/cement ratio, has a total porosity higher than 20%. With this porosity the lowest allowable freezing temperature is only -1,5°C. Thus, model 2 which is physically more reasonable than Model 1, gives even smaller allowable freezing point depressions. A freezing temperature of -20°C can according to eq (3a) only be accepted in a saturated cement paste containing any freezable water if the total porosity is less than 0,8%. Such a cement paste does not exist.

2.1.2 The minimum air content

The calculations performed above for the models 1 and 2 clearly show that a completely water saturated concrete containing even low amounts of freezable water cannot resist freezing without being damaged. Therefore, the concrete must contain a certain amount of air-filled space. One can make an estimate of the maximum allowable effective degree of saturation of the closed container by neglecting the compressibility of ice and water and assuming that fracture occurrs when the 9% volume expansion of water corresponds exactly to the relative volume ductility of the container. These assumptions lead to the following relation:

$$S_{eff,CR} = 0{,}917 + 3 \cdot \varepsilon_b(1-2\nu)/[1{,}09 \cdot P(1-k_\theta)] \qquad (4)$$

Where,

S_{eff}	the effective degree of saturation defined by eq(5)
$S_{eff,CR}$	the critical effective degree of saturation
ε_b	the linear relative ductility (m/m)
ν	Poissons ratio
P	the total porosity (m^3/m^3)
k_θ	the non freezable water as fraction of the total porosity (m^3/m^3)

k_θ is a function of the freezing temperature; the lower the temperature the lower the value of k_θ. In the following, the lowest value of k_θ occurring in the practical case is used; i.e. when the temperature is about -30°C for the Scandinavian climate.

The second term on the right hand side in eq (4) expresses the ductility of the container. For a completely stiff material $\varepsilon_b=0$ and therefore $S_{eff,CR}$ is always 0,917.

The effective degree of saturation is defined:

$$S_{eff} = W_f/(W_f+a) = 1 - a/[P(1-k\theta)] \qquad (5)$$

Where,

a the air-filled volume as a fraction of the entire container volume (m^3/m^3)

Often, it is more suitable to use the concept (total) degree of saturation (S) which is defined:

$$S = W_e/P = S_{eff}(1-k\theta) + k\theta \qquad (6)$$

Where,

W_e the total water volume in the container (m^3/m^3)

The following values can be used for a high performance concrete: $\nu = 0{,}20$; $\varepsilon_b = 0{,}2‰$. Then, eq (4) can be written:

$$S_{eff,CR} = 0{,}917 + 3{,}3 \cdot 10^{-4}/[P(1-k\theta)] \qquad (7)$$

This equation can be used for a calculation of the absolute maximum amount of freezable water in a completely water saturated material as well as the absolute minimum of air-filled space. This will be shown by three examples.

Example 1; maximum allowable freezable water in a saturated paste: Even in a dense cement paste with the water/cement ratio 0,25 the total porosity P is about 25%. Then, by eq (7) it is found that the maximum allowable value of the freezable water, which is expressed by the parameter $P(1-k\theta)$, is 0,004 m^3/m^3 or 4 litres per m^3 of cement paste when the cement paste is saturated. Thus, very little freezable water is sufficient to damage the cement paste when this is fully saturated.

As will be shown below in paragraph 3, one cannot exclude that a cement paste with the water/cement ratio 0,25 contains much more freezable water than that needed for damaging the paste. According to Table 3 the freezable water content of a pre-dried and re-saturated cement paste with the water/cement ratio of 0,25 can be as high as 30% of the total evaporable water or 7,5% of the paste volume.

Example 2: required air space in normal concrete: A cement paste in an outdoor concrete with the water/cement ratio 0,6 and the porosity 50% is regarded. According to Table 3 below the freezable water content at -20°C can be as high as 60% of the total pore volume or 30% of the total cement paste volume; i.e.

the parameter $P(1\text{-}k\theta)$ expressing the freezable water is 0,30. Then, according to eq (7) the value of $S_{eff,CR}$ is 0,918. Thus, according to eq (5) the minimum air content in the cement paste is 0,025 m^3/m^3 or 2,5%. The cement paste fraction in a concrete with the actual water/cement ratio is about 30%. Then, the required air content in the concrete is about $0,3\cdot 2,5=0,8\%$.

This example shows that a very small air content is sufficient to protect the concrete assuming this air volume is located directly at the freezing site. As will be seen below in paragraph 2.2, in the practical case, water has to move a rather long distance before it can be taken care of in an air-filled pore. This flow creates stresses. The consequence is that the real air content needed is higher then the theoretical calculated above; see eq (28).

Example 3; required air space in a high performance concrete: In a dense cement paste with the water/cement ratio 0,25, the freezable water at -20°C can be at maximum 30% of the total pore volume. This is about 25% of the cement paste volume.; i.e the parameter $P(1\text{-}k\theta)=0,3\cdot 0.25=0,075$. Therefore, $S_{eff,CR}=0,921$. The air content needed in the cement paste is only 0,6% and in the concrete only 0,2%.

This example shows that a very low air content is needed in order to protect a low-porosity concrete from frost damage. This low air content can for example be created by a slight drying such as that caused by self-desiccation. This important effect of a slight drying can be one explanation why there is no indisputable opinion about the frost resistance of high performance concrete; in one freeze/thaw experiment the concrete does perhaps not become fully saturated. Then , it is judged to be frost resistant in the test. In another test performed in a slightly different manner, the concrete becomes completely saturated and therefore it is judged to be non-resistant to frost.

2.2 Hydraulic pressure

As shown above, even a very dense concrete will suffer frost damage if it contains only a very small amount of freezable water and freezes in a completely saturated condition. It is also shown that a very small amount of air-filled pores is needed for such a concrete to be frost resistant provided these air pores are located so close to the site of freezing that no water flow is actually necessary; i.e. the closed container condition is valid. This condition prevails if the air-filled pores are created by a certain drying of the capillary pore water. Then, the emptied capillary pores are probably located so close to each other that the expelled water created by the 9% volume increase of water that is transferred into ice has to move a negligible distance before it is taken care of in the air-filled space. The minimum and very small air contents calculated by examples 2 and 3 above are then high enough to protect the concrete.

In a situation where there is no drying, so that all gel and capillary pores are saturated, a certain amount of entrained air is required. The absolute minimum value of the air content is the same as that calculated in paragraph 2.1.3 above. In reality, however, expelled water has to move quite a long distance before it reaches an air-filled air-pore. Thereby a hydraulic pressure develops; Powers (1949). This is a function of the distance and the geometry of the flow path. The following general equation is valid; Fagerlund (1993a).

$$p_{max} = 0{,}09\cdot [dW_f/d\theta]\cdot [d\theta/dt] \cdot \frac{1}{K} \cdot f(X) \qquad (8)$$

Where,

p_{max} the maximum hydraulic pressure (Pa)
$dW_f/d\theta$ the slope of the freezable water-temperature curve $[m^3/(m^3\cdot°C)]$
dq/dt the rate of temperature lowering of the concrete (°C/s)
K the permeability defined by eq (9) $[m^2/(Pa\cdot s)]$
$f(X)$ a measure of the geometry and maximum distance of flow (m^2)

The permeability K is defined by:

$$q = K\cdot dP/dx \qquad (9)$$

Where,

q the volume flux ($m^3/m^2\cdot s$)
dP/dx the pressure gradient (Pa/m)

The parameter $[dW_f/d\theta]\cdot [d\theta/dt]=dW_f/dt$ is the rate of ice formation. This is evidently, for given outer conditions, proportional to the amount of freezable water at each temperature; the lower the ratio $dW_f/d\theta$ the lower the rate of ice formation and the lower the pressure. The parameter f(X) depends on the geometry of the saturated materials volume within which the water flow is generated and transferred. Many possibilities exist; e.g.:

* The one-directional flow through a porous plate of thickness D. The flow is zero at the centre of the plate and goes towards the free sides:

$$f(X) = D^2/8 \qquad (10)$$

* The flow through a porous spherical shell of thickness L surrounding a spherical air-filled inclusion with the specific area α $[m^{-1}]$. The flow starts at the periphery of the shell and goes towards the inclusion:

$$f(X) = [L\cdot\alpha/9+1/2]\cdot L^2 \qquad (11)$$

Fracture occurs when the hydraulic pressure equals the tensile strength of the porous material. This means that a critical size of the material exist. A general expression for this is:

$$f(X)_{CR} = \frac{ft\cdot K}{0{,}09[dWf/d\theta]\cdot[d\theta/dt]} \qquad (12)$$

Where,

$f(X)_{CR}$ the critical (maximum allowable) value of f(X) (m^2)

ft the tensile strength (Pa)

Inserting the expressions (10) and (11) in (12) gives:

$$D_{CR} = \left\{\frac{8\cdot ft\cdot K}{0{,}09\cdot[dWf/d\theta)\cdot[d\theta/dt]}\right\}^{1/2} \qquad (13)$$

$$L_{CR}^2[L_{CR}\cdot\alpha/9+1/2] = \frac{ft\cdot K}{0{,}09\cdot[dWf/d\theta]\cdot[d\theta/dt]} \qquad (14)$$

Where DCR is the so-called critical thickness and LCR the so-called Powers spacing factor. The relation between DCR and LCR is:

$$D_{CR} = 2\cdot L_{CR}[2\cdot\alpha\cdot L_{CR}/9+1]^{1/2} \qquad (15)$$

Thus, the maximum allowable spacing between a place where ice formation takes place and the nearest air-filled space increases with increasing tensile strength (ft), increasing permeability (K), decreasing amount of freezable water (dWf/dθ) and decreasing rate of temperature lowering (dθ/dt). In a high performance concrete with low water/cement ratio the strength is higher than normal and the amount of freezable water is lower than normal. These are positive factors. On the other hand, the permeability might be lower which is a negative factor. The net effect is difficult to estimate. Some approximative calculations will however now be made.

Calculation 1. The assumptions are:

1: The tensile strength is supposed to be inversely proportional to the water/cement ratio:

$$ft = \frac{const}{w/c} \qquad (16)$$

2: The permeability is supposed to be proportional to the square of the capillary porosity. This relation is for example valid for diffusion of gases through cement paste but not for water flow under pressure. The capillary porosity, Pc, is calculated by:

$$Pc = \frac{w/c-0{,}39\cdot\alpha}{w/c+0{,}32} \qquad (17)$$

Where,

w	the water content of the fresh mix (litres or kg)
c	the cement weight in the mix (kg)
0,32	the specific volume of cement (litres/kg)
α	the degree of hydration

Then the permeability is:

$$K = \text{const}\cdot \frac{(w/c\ -0{,}39\cdot\alpha)^2}{(w/c+0{,}32)^2} \qquad (18)$$

Where, α is the degree of hydration which is supposed to be a certain fraction β of the maximum possible degree of hydration. Thus, since full hydration can only be obtained for water/cement ratios above 0,39:

$$\alpha = \beta\cdot\frac{w/c}{0{,}39} \qquad \text{for } w/c<0{,}39 \qquad (19a)$$

$$\alpha = \beta \qquad \text{for } w/c>0{,}39 \qquad (19b)$$

Inserted in eq(18):

$$K = \text{const}\cdot \frac{(w/c)^2\cdot[1-\beta]^2}{(w/c+0{,}32)^2} \qquad \text{for } w/c<0{,}39 \qquad (20a)$$

$$K = \text{const}\cdot \frac{(w/c-0{,}39\cdot\beta)^2}{(w/c+0{,}32)^2} \qquad \text{for } w/c>0{,}39 \qquad (20b)$$

3: The freezable water is supposed to be a certain constant fraction γ of the capillary porosity; see paragraph 3.1 below:

$$dWf/d\theta = \text{const}\cdot\gamma\cdot\frac{[w/c-0{,}39\cdot\alpha]}{w/c+0{,}32} = \text{const}\cdot\gamma\cdot\frac{(w/c)\cdot[1-\beta]}{w/c+0{,}32} \qquad \text{for } w/c<0{,}39 \qquad (21a)$$

$$dWf/d\theta = \text{const}\cdot\gamma\cdot\frac{w/c-0{,}39\cdot\beta}{w/c+0{,}32} \qquad \text{for } w/c>0{,}39 \qquad (21b)$$

Eq (16), (20) and (21) inserted in eq(13) gives the following relation for the critical thickness:

$$D_{CR} = \text{const}\cdot\left\{\frac{(1-\beta)}{\gamma\cdot(w/c+0{,}32)}\right\}^{1/2} \qquad \text{for } w/c<0{,}39 \qquad (22a)$$

$$D_{CR} = \text{const}\cdot\left\{\frac{w/c-0{,}39\cdot\beta}{\gamma\cdot(w/c)\cdot(w/c+0{,}32)}\right\}^{1/2} \qquad \text{for } w/c>0{,}39 \qquad (22b)$$

The following relative values of DCR are valid for β=0,75. D_{CR} is supposed to be 1 for w/c=0,40. The values are independent of the amount of freezable water which is expressed in terms of the factor γ:

w/c	DCR
0,70	1,24
0,60	1,22
0,50	1,17
0,40	1
0,35	1,00
0,30	1,04
0,25	1,09
0,20	1,14

The assumptions behind calculation 1 leads to a critical thickness and also a critical spacing factor that is somewhat dependent of the water/cement ratio. It leads to a small increase in the critical spacing factor when the water/cement ratio becomes very low. This is a positive factor with regard to frost resistance.

Calculation 2: The assumptions 1 and 3 above are kept but the assumption 2 for permeability is changed so that consideration is also taken to the effect of ice formation in the pore system.

The permeability of the cement paste is reduced when ice is formed. This was neglected in calculation 1. The residual permeability is supposed to be directly proportional to the non-freezable water. Pores containing ice are not supposed to take part in the transport process. Then it is valid:

$$K = \text{const}\cdot\frac{w_{nf}/c}{w/c+0{,}32} = \text{const}\cdot\frac{w_e/c - w_f/c}{w/c+0{,}32} \qquad (23)$$

Where,

wnf	the non-freezable water (kg)
we	the total evaporable water (kg)
wf	the freezable water (kg)
c	the cement content (kg)

The total evaporable water is supposed to correspond to the total pore volume and the freezable water is a fraction γ of the capillary water. Thus:

$$we/c = w/c - 0{,}19 \cdot \alpha \qquad (24)$$

$$wf/c = \gamma(w/c - 0{,}39 \cdot \alpha) \qquad (25)$$

The permeability of the frozen cement paste therefore is:

$$K = \text{const} \cdot \frac{w/c - 0{,}19 \cdot \alpha - \gamma(w/c - 0{,}39 \cdot \alpha)}{w/c + 0{,}32} \qquad (26)$$

Finally, after inserting equations (16), (19), (21) and (26) in (13) the following relation for the critical thickness is obtained:

$$D_{CR} = \text{const} \cdot \left\{ \frac{(1-\gamma) + \beta \cdot \gamma - \beta \cdot 0{,}19/0{,}39}{\gamma \cdot (w/c) \cdot (1-\beta)} \right\}^{1/2} \qquad \text{for } w/c < 0{,}39 \qquad (27a)$$

$$D_{CR} = \text{const} \cdot \left\{ \frac{w/c \cdot (1-\gamma) + \beta(0{,}39 \cdot \gamma - 0{,}19)}{\gamma \cdot w/c \cdot (w/c - 0{,}39 \cdot \beta)} \right\}^{1/2} \qquad \text{for } w/c > 0{,}39 \qquad (27b)$$

The following relative values are valid for $\beta = 0{,}75$. DCR is supposed to be 1 for w/c=0,40:

$\gamma=0{,}75$		$\gamma=1{,}00$	
w/c	DCR	w/c	DCR
0,70	0,46	0,70	0,39
0,60	0,55	0,60	0,48
0,50	0,69	0,50	0,64
0,40	1	0,40	1
0,35	1,11	0,35	1,12
0,30	1,20	0,30	1,21
0,25	1,32	0,25	1,33
0,20	1,47	0,20	1,48

Thus,according to the theoretical calculation the critical thickness increases continuously with decreasing water/cement ratio. The same is valid for the critical spacing factor which can be calculated by eq (15) when DCR is known. The real relation between the water/cement ratio and the critical spacing factor can only be obtained when the specific area is known. Let us assume that the specific area is 30 mm^{-1} corresponding to a pore diameter of 200 μm and that the critical thickness D_{CR} is 1 mm at w/c=0,40. Then, calculation 2 gives the following theoretical critical spacing factors for γ=0,75:

w/c	L_{CR} (mm)	$L_{CR}/(L_{CR})_{w/c=0,40}$
0,70	0,16	0,53
0,60	0,19	0,63
0,50	0,22	0,73
0,40	0,30	1
0,35	0,32	1,07
0,30	0,33	1,10
0,25	0,36	1,20
0,20	0,39	1,30

Thus, theoretically, the critical spacing factor is a bit less influenced by the water/cement ratio than is the critical thickness.

Both calculations 1 and 2 indicate that the critical spacing factor increases with decreasing water/cement ratio when this is lower than 0,40. This is a very favourable situation leading to a reduction of the required air content.

Example 4: The critical spacing factor of a certain cement paste is supposed to be 0,20 mm when the water/cement ratio is 0,40. The specific area of the air pore system is supposed to be 30 mm^{-1}. The required air content of the cement paste is calculated by the Powers´ equation:

$$a = \frac{1}{0{,}364(L_{CR}\cdot\alpha/3+1)^3-1} = \frac{1}{0{,}364(L_{CR}\cdot 10+1)^3-1} \qquad (28)$$

Then, the following air contents are required in the cement paste:

w/c	L_{CR} (mm)	a (%)
0,40	0,20	11,3
0,35	0,21	10,2
0,30	0,22	9,2
0,25	0,24	7,5
0,20	0,26	6,3

Obviously, according to the calculation 2 the air content required in a dense concrete with low water/cement ratio is rather low under condition that the air pores are small and assuming that no air pores become water-filled.

2.3 Microscopic ice lens growth

Every concrete will, due to its fine pore structure, at the same time contain ice bodies in the coarser capillaries and in certain air pores and unfrozen water in the finest capillaries and in gel pores. As shown below, some capillary water is supercooled. The lower the w/c-ratio the larger the fraction of unfrozen water; see paragraph 3 below. At any temperature below 0°C the free energy of water is higher than that of stress-free ice. The small ice-bodies will therefore attract water and one will obtain a water transfer towards the ice-bodies where the water freezes. The ice bodies will grow and expose the pore walls to pressure. The free energy of the ice will therefore increase at the same time as the free energy of the remaining unfrozen pore water will reduce due to the drying effect brought about by the water transfer. The ice growth will however not cease until there is a balance in free energy between the two phases, ice and liquid water.

The mechanism described predicts the existence of a critical spacing btween air-filled pores as does the hydraulic pressure mechanism. Ice located in air pores vill attract water and will therefore grow. This growth does, however, occur without causing any stresses. It will therefore be favoured in comparison with ice growth in capillaries. The shorter the air pore spacing the larger the water flow to ice in air pores and the smaller the pressures caused by ice growth; Powers and Helmuth (1953).

The pressures are very difficult to quantify since they depend on geometrical factors and on the types of meniscus systems that appear inside the pore system. It is quite clear however that the destruction mechanism is promoted by a large fraction of unfrozen water because then, a larger moisture flow towards the ice bodies can take place without reducing the free energy of the remaining water too much. Thus, a lowered water/cement ratio should be a negative factor. On the other hand, the pressure is also dependent of the amount of freezable water. If the water/cement ratio is very low the ice formed is probably so small that the pressure excerted by the growing ice is too small to cause damage. Therefore, it might very well be that the maximum pressure appears at a certain pessimal water/cement ratio. If this is the case both a high and a very low water/cement ratio give less pressure due to ice crystal growth than does an ”average” water/cement ratio.

The total pressure in the cement paste is the sum of the hydraulic pressure and the pressure from growing ice bodies. As described above, it is reasonable to assume that both pressures decrease when the water/cement ratio becomes very low. This is favourable with regard to frost resistance.

3. Freezable water

3.1 Potentially freezable water in the cement paste phase

The freezing point of water in a pore is lower the smaller the pore diameter. The exact relation between the pore size and the freezing point is not fully clarified. It depends on which types and arrangements of different meniscus systems ice-water, ice-vapour and water-vapour that appear in the complex pore system; Defay et al (1966). One reasonable assumption is that the ice phase remains under ordinary atmospheric pressure while the unfrozen water is exposed to an under-pressure that is described by the Kelvin law of capillary condensation. Besides, water that is adsorbed on the pore walls is supposed to be unfreezable. Then, the following relation is valid.

$$r = -\frac{2 \cdot \sigma_{lg} \cdot M}{\rho_l \cdot \Delta H} \cdot \frac{1}{\ln\{(T_o - \Delta T)/T_o\}} + t_a \qquad (29)$$

Where,

r	the pore radius (m)
σ_{lg}	the surface tension water-vapour (N/m)
M	the molecular wight of water (kg/mole)
ρ_l	the density of water (kg/m^3)
T_o	the freezing point of pure water (°K)
ΔT	the freezing point depression (°K)
ΔH	The molar heat of fusion of water (J/mole)
t_a	the thickness of the adsorbed layer (m)

The value ta is small compared with the first term on the right hand side in eq (1); about 5% at -6°C and 10% at -20°C.

In Table 1 some examples of this relation are shown. The corresponding relative humidity (RH) according to the Kelvin equation for capillary condensation in the pore is also listed in the table.

Table 1: Relation between the pore diameter, the corresponding relative humidity when capillary condensation takes place in the pore and the freezing point according to eq (29).

Diameter (Å)	RH (%)	Freezing point (°C)
450	95	-6
280	92	-10
200	88	-15
160	85	-20
115	80	-30
95	76	-40

This relation between freezing temperature and pore size implies that all the pore space in a cement paste must be located in pores smaller than 115 Å if the paste shall not contain any freezable water at -30°C. This means, however, that even a very dense cement paste ought to contain a large amount of potentially freezable water; viz. measurements of the pore size distribution indicate that such pastes have a large fraction of pores larger than 115Å. Some examples are shown in Fig 3; Zhang and Gjørv (1991)

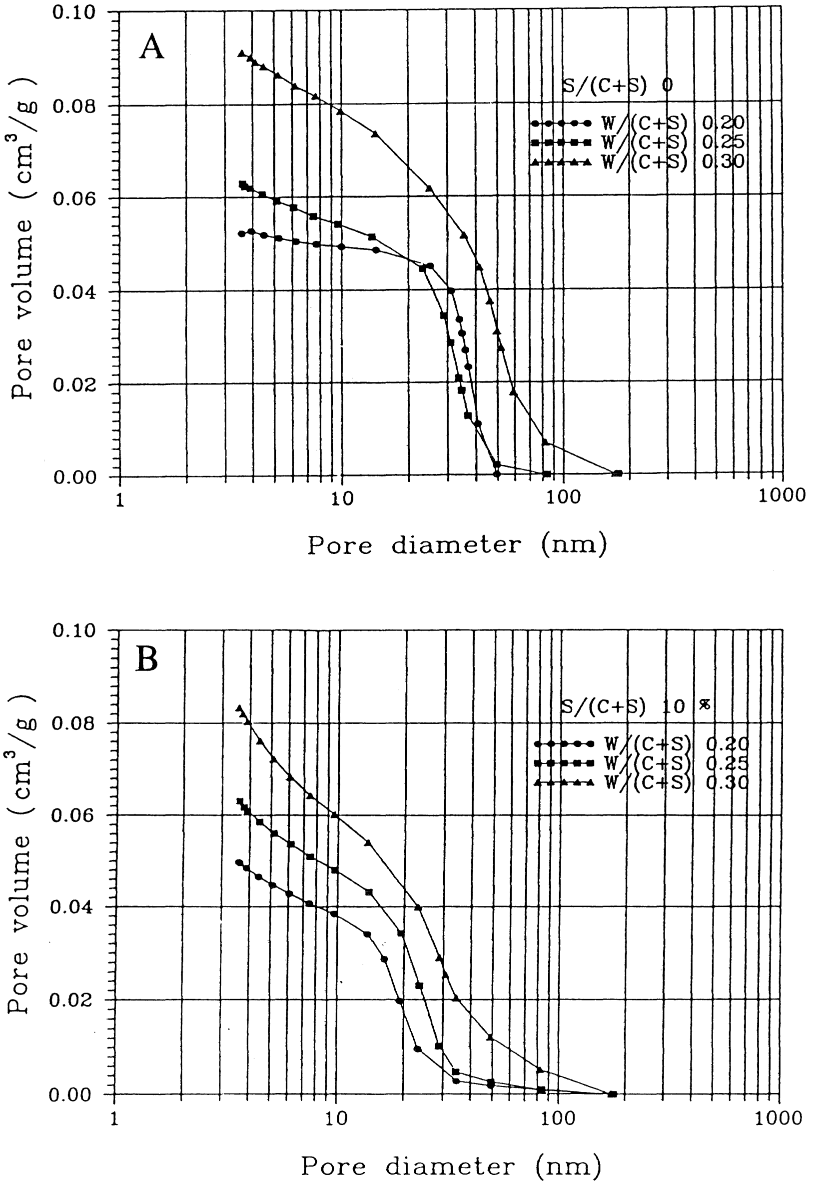

Fig 3: Pore size distribution of cement paste with low water cement ratios and different amount of silica fume; Zhang and Gjørv (1991). A: 0% Silica fume. B: 10% silica fume.

The good relation between the freezable water calculated from the adsorption water vapour isotherm using eq (29) and direct measurements of the freezable water by thawing experiments on specimens pre-frozen to -78°C was demonstrated by Powers and Brownyard (1948). Theoretically, melting of ice corresponds to adsorption and freezing of water to desorption.

Some examples of their measurments and calculations of the non-freezable water contents are listed in Table 2. The non-freezable water (Wnf m^3/m^3) is expressed in terms of the amount of adsorbed water in one monolayer, Vm.

Table 2: Non-freezable water calculated from the adsorption isotherm of cement paste specimens and non-freezable water measured by thawing cement paste specimens that have been pre-frozen to -78°C; Powers and Brownyard (1948). The constant κθ expressing the non-freezable water in terms of the amount of non-evaporable water is also shown.

Temperature (°C)	Wnf/Vm (number of water layers)			κθ=wnf/wn
	observed	calculated	ratio	
-12 °C	4,00	3,72	1,08	1,04
-20 °C	3,70	3,25	1,13	0,96
-30 °C	3,20	2,93	1,09	0,83

Powers and Brownyard (1948) found the following relation between freezable water in cement paste and the total evaporable water:

$$wf/c = we/c - wnf/c = we/c - \kappa\theta \cdot wn/c \qquad (30)$$

Where,

wf the freezable water (kg)
we the total evaporable water (kg)
wnf the non-freezable water (kg)
wn the chemically bound, non-evaporablewater (kg)
c the cement content (kg)
κθ a temperature dependent constant given in Table 2 and expressing the amount of non-freezable water in terms of the amount of non-evaporable water.

The maximum amount of evaporable water is obtained when the specimen is stored in water for a very long time. Therefore, it corresponds to the water-filling of all pores. For a non-air-entrained portland cement paste this is:

$$(we/c)_{max} = wo/c - 0{,}75 \cdot wn/c \qquad (31)$$

Where,

wo/c the water/cement ratio
0,75 the specific volume of non-evaporable water (litres/kg)

The maximum amount of freezable water therefore is, according to Powers and Brownyard (1948).

$$(wf/c)_{max} = wo/c - (0{,}75+\kappa\theta)\cdot wn/c \qquad (32)$$

Expressed in terms of degree of hydration α, assuming that full hydration of all cement corresponds to $wn/c=0{,}25$:

$$(wf/c)_{max} = wo/c - (0{,}19+0{,}25\cdot\kappa\theta)\cdot\alpha \qquad (33)$$

This equation can be used for calculating the maximum amount of freezable water in a cement paste. Some examples are shown in Table 3.

Table 3: Maximum amount of freezable water in saturated cement pastes at a degree of hydration that corresponds to 75% of maximum possible hydration ($\alpha_{max} = 1$ for $wo/c>0{,}39$. $\alpha_{max} = (wo/c)/0{,}39$ for $wo/c<0{,}39$). The calculations are based on the Powers and Brownyard data.

wo/c	we/c	-12°C		-20°C		-30°C	
		wf/c	wf/we	wf/c	wf/we	wf/c	wf/we
0,20	0,129	0,031	0,24	0,039	0,30	0,050	0,39
0,30	0,193	0,047	0,24	0,058	0,30	0,075	0,39
0,40	0,258	0,063	0,24	0,078	0,30	0,100	0,39
0,50	0,358	0,163	0,46	0,178	0,50	0,200	0,56
0,60	0,458	0,263	0,57	0,278	0,61	0,300	0,66

According to these data even a very dense concrete with low water cement ratio could theoretically contain large amounts of potentially freezable water. The freezable water in a concrete with the water/cement ratio of 0,30 and a cement content of 500 kg/m^3 could be as high as 29 kg/m^3 at -20°C which is, according to the calculations shown above in paragraph 2.1, much more than needed in order to destroy the concrete. To this freezable water should be added the freezable water in air pores, in aggregate pores, in cracks and in interfaces between aggregate and cement paste. This will be treated below in paragraphs 4-7.

It can be interesting to compare the freezable water according to eq(33) with the so-called capillary pore volume wc which can be calculated by:

$$wc/c = wo/c - 0{,}39\cdot\alpha \qquad (34)$$

Where,

wc the capillary water at full saturation (kg)

Examples of the relation between the freezable water and the capillary pore volume is shown in table 4.

Table 4: Relation between the maximum amount of freezable water and the capillary water (water in capillary pores when these are fully saturated).

wo/c	wc/c	wf/wc -12°C	 -20°C	 -30°C
0,20	0,054	0,574	0,722	0,926
0,30	0,081	0,580	0,716	0,926
0,40	0,108	0,583	0,722	0,926
0,50	0,208	0,784	0,856	0,962
0,60	0,308	0,854	0,903	0,974

The Powers and Brownyard data therefore imply that almost all capillary water is freezable at about -30°C and that about 70% of the capillary water is freezable at -20°C in a dense concrete with water/cement ratio below 0,40. All these data are based on the assumption that the degree of hydration is 75% of the maximum possible.

Eq (33) shows that there will be no freezable water in a cement paste with water/cement ratio below 0,40 under condition that the degree of hydration has reached a certain value $\alpha_{required}$. This is:

$$\alpha_{required} = \frac{wo/c}{0{,}19+0{,}25\cdot\kappa\theta} \tag{35}$$

Or, expressed in terms of the maximum possible degree of hydration, α_{max} [$\alpha_{max}=(wo/c)/0{,}39$].

$$\alpha_{required}/\alpha_{max} = \frac{0{,}39}{0{,}19+0{,}25\cdot\kappa\theta} \tag{36}$$

This last relation is independent of the water/cement ratio. It is 0,87, 0,91 and 0,98 for the temperatures -12°C, -20°C and -30°C respectively. Thus, very high degrees of hydration are needed in concretes with low water/cement ratio if they shall contain no potentially freezable water.

This also means that concretes with low water/cement ratios are much more sensitive to the degree of hydration than are ordinary concretes. When such high performance concretes are young they contain rather large amounts of freezable water; when they are old they might be immune to frost due to the fact that they do not contain any freezable water. This must be considered when a freeze/thaw test is made with such concretes. The test result of a high performance concrete is probably more depending on the concrete age than is ordinary concrete containing large amounts of freezable water at all degrees of hydration.

The Powers and Brownyard experiments were made by thawing cement paste that had been pre-frozen to -78°C. Hence, all super-cooling phenomenons described below were absent which means that the freezable water detected is probably the maximum possible.

3.2 Potentially freezable water in concrete

Freezable water has also been determined for concrete. Some measurements for the temperature -15°C are shown in Fig 4; Vuorinen (1973). Curve A shows the results for concrete that has been stored in water all the time from mixing until the test. Curve B shows the results for companion specimens that have been pre-dried once at +105°C and then re-saturated by means of vacuum treatment. The total evaporable water content is also shown in the figure.

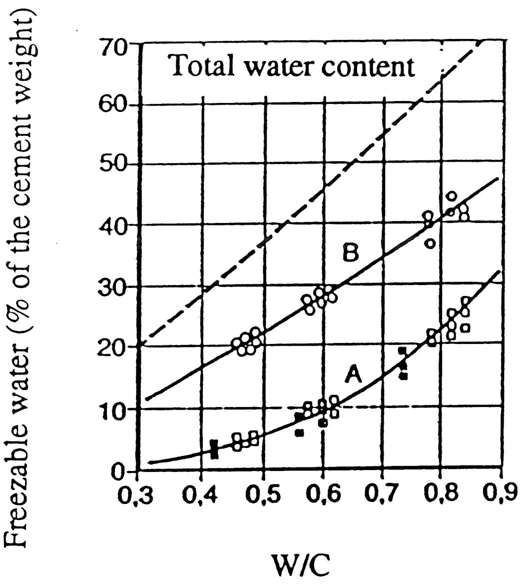

Fig 4: Freezable water of concrete at -15°C; Vuorinen (1973). Curve A: Never dried specimens. Curve B: Pre-dried and re-saturated specimens.

The freezable water content is always lower than the total water content. For a never-dried concrete it seems as if there is almost no freezable water if the water/cement ratio is below 0,3. For a pre-dried and re-saturated concrete, however, the freezable water content is much higher at all water/cement ratios. So for example, for a pre-dried concrete with w/c=0,3 the freezable water is almost exactly as high as for a never-dried concrete with w/c=0,6. Similar effects have also been observed for pure cement paste by Sellevold et al (1982). There are also indications that an increase in the freezable water content occurs even when the concrete has been exposed to much milder dryings at room temperature; Fagerlund and Modéer (1974).

As shown above, the Powers and Brownyard data for pure cement pastes indicate that almost all capillary water is freezable at -30°C; see Table 4. It can be shown that the same is valid for the Vuorinen data in Fig 4 for pre-dried specimens. The total capillary water is given by eq (34). Then, the calculated amount of freezable water is:

$$(wf/c)_{calc} \approx wc/c = wo/c - 0{,}39 \cdot \alpha \tag{34a}$$

The measured and the calculated freezable water contents are listed in Table 5. The degrees of hydration α are not measured but estimated.

Table 5: The freezable water in concrete determined experimentally by Vuorinen (1973) for pre-dried specimens and calculated by eq (34a).

wo/c	α	wf/c measured	calculated	$k\theta$ calculated by eq(37)
0,30	0,50	0,11	0,11	0,49
0,45	0,70	0,19	0,18	0,44
0,55	0,75	0,25	0,26	0,37
0,65	0,80	0,31	0,31	0,32

Thus, the agreement between the calculated and the measured freezable water content is excellent. It indicates, as does the Powers and Brownyard data, that even a concrete with very low water/cement ratio might contain considerable amounts of freezable water.

One can, as done above in paragraph 2, express the non-freezable water in terms of a fraction $k\theta$ of the total evaporable water content at full saturation of the gel and capillary pores, $(we)_{max}$, which is given by eq (31). Then, according to eq(34a) the following relation is valid:

$$k\theta = 1 - \frac{wo/c - 0{,}39 \cdot \alpha}{wo/c - 0{,}19 \cdot \alpha} \tag{37}$$

The value of the parameter $k\theta$ is also listed in Table 5 for Vuorinens experiments. It shows that a considerable fraction of the evaporable water is freezable also in a very dense concrete; at least under the condition that the concrete has undergone a severe drying process as in Fig 4, curve A, or has been exposed to very low freezing temperatures as in the Powers and Brownyard experiments.

2.3 Effect of ageing; Hysteresis freezing-melting

As shown in Fig 4 drying causes considerable increases in the amount of freezable water. The reason behind this feature has never been fully clarified. It ought to depend on some sort of structural change brought about by drying. The most plausible explanation is that a very large fraction of the potentially freezable water in the never-dried concrete is located in isolated small capillary pores. This water remains unfrozen -supercooled- until it freezes by homogeneous nucleation at about -40°C. The supercooling of water increases with decreasing size of the water volume. The average freezing point of 1 mm water drops is about -24°C. For 0,01 mm drops it is about -40°C; Bigg (1953). Below this temperature supercooling does not occur. Therefore water in completely isolated pores will have very low tendency of freezing until about -40°C. By "completely isolated" is meant that the entrance pores to the pore in question is so small that it cannot contain any ice crystal at -40°C; i.e. its diameter must according to Table 1 be below 95Å. Large ice formation at about -40°C is often observed in calorimeter experiments with never-dried dense cement pastes; see Fig 5. This might very well depend on the suggested homogeneous nucleation of supercooled water in numerous isolated capillaries and not on freezing in pores with the diameter 95Å corresponding to the freezing temperature -40°C. All measurements of the pore structure of cement pastes with low water/cement ratios indicate that they contain a large volume of pores with potentially freezable water far above -40°C; some examples are shown in Fig 3.

When the cement paste is dried it is quite possible that a micro-crack system develops in the cement gel surrounding the previous isolated capillaries. Thereby, ice-formation can be initiated by ice penetrating the cracks. Therefore, ice formation in the pre-dried and re-saturated specimen occurrs closer to the correct temperature determined by the actual pore size. The correctness of this explanation based on local supercooling is strengthened by the fact that ice-melting in never-dried specimens occurrs at considerably higher temperatures than ice-formation. Some examples are shown in Fig 5; Bager and Sellevold (1982). Such a hysteresis between ice melting and ice formation should appear if supercooling phenomenons of the type discussed appears. The hysteresis between ice formation and ice melting is also considerably smaller for pre-dried specimens as it should was the theory presented above correct.

Thus, the effect of drying on the freezable water that has been observed by many researchers must not necessarily depend on a profound structural change such as a coarsening of the pore structure as it has often been claimed. It might just as well depend on a natural microcracking brought about by even a rather mild drying; a microcracking that does also bring about a considerable increase the permeability of the cement paste; c.f Powers et al (1954/55).

The practical implication of this is that one cannot exclude that a concrete with low water/cement ratio will get a gradually increasing freezable water content due to natural ageing processes. A concrete that is immune to frost at early ages might therefore in some cases become frost sensitive at later ages due to microcracking opening the previously isolated capillaries to ice nucleation. This means that one must consider natural ageing processes in testing the frost resistance of high performance concretes.

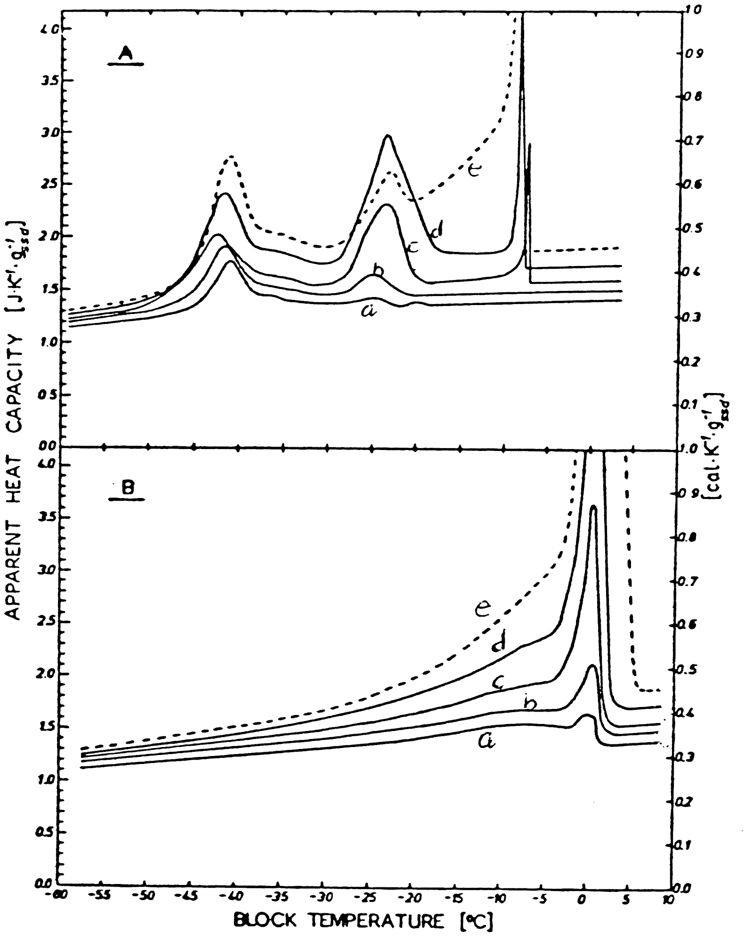

Fig 5: Calorimeter measurements of never dried cement pastes with different water/cement ratio; Bager and Sellevold (1982).A: Cooling phase. B: Thawing phase. (a. w/c=0,35; b. w/c=0,40; c. w/c=0,45; d. w/c=0,50; e. w/c=0,60).

4. Water in air pores and its effects

Entrained air pores can take up water if the concrete is stored for a very long time in water. The mechanism is described in Fagerlund (1993b). During a capillary absorption process air is more or less temporarily enclosed in coarser pores surrounded by finer. The enclosed air is however exposed to an over-pressure given by the Laplace law:

$$\Delta P = \frac{2 \cdot \sigma}{r} \tag{38}$$

Where,

σ surface tension water-air (N/m)
r radius of the enclosed air bubble (m)

This means that the air bubble will be compressed. Using Boyle´s law it is easy to show that the following relation is valid for the volume of the compressed bubble and the volume of the initial pore in which the bubble became enclosed; Fagerlund (1993b):

$$(V_1/V_o)^{1/3} \cdot (V_o/V_1 - 1) = \frac{2 \cdot \sigma}{10^5 \cdot R} \tag{39}$$

Where,

V_o the pore volume (m^3)
V_1 the volume of the compressed air bubble (m^3)
R the radius of the pore containing the air bubble (m)
10^5 the atmospheric pressure (Pa)

Some relations are:

R (μm)	V_1/V_o
0,05	0,006
0,10	0,018
1	0,32
10	0,87

This means that bubbles in pores with diameter smaller than about 0,1 μm will vanish completely already during the capillary absorption process. Such pores are therefore almost always saturated during moist conditions. All capillary pores in a cement paste are smaller than 0,1 μm. Therefore, all pores except the air pores can always be expected to be saturated during natural moist conditions. Even pores as big as 2 μm in diameter become readily water-filled to more than 30% during the very capillary absorption process. The mechanism just described also explains why so few air pores with diameter smaller than 10 μm are found in concrete; such pores simply collapse during the fresh state of the concrete due to the internal over-pressure.

The high air-pressure in the enclosed small air bubbles make them take up water gradually. Due to the enhanced air-pressure the solubility of air in pore-water is higher than normal whereby the air gradually dissolves and becomes replaced by water. In Fagerlund (1993b) it is calculated that all air can be solved quite easily in the "local" pore water surrounding the bubble under condition that the bubble size is below a certain limiting value. The following relation is valid:

$$Vw = \frac{4\cdot\pi}{3}\cdot 42(1+10^5/\Delta P)\cdot r^3 = \frac{4\cdot\pi}{3}\, 42(1+10^5\cdot r/2\cdot\sigma)\cdot r^3 \tag{40}$$

Where,

Vw the local water volume needed in order to solve the bubble (m^3)

r the bubble radius (m)

The volume Vw can be expressed in terms ot the thickness t of the cement paste shell surrounding the bubble.

$$Vw = \frac{4\cdot\pi}{3}\cdot (t+r)^3\cdot \frac{1}{P} \tag{41}$$

Where,

P the total porosity exclusive of air pores (m^3/m^3)

Therefore, the required thickness of this shell is:

$$t > \left\{\left(1+\frac{42(1+10^5\cdot r/2\cdot\sigma)}{P}\right)^{1/3} - 1\right\} r \tag{42}$$

Where P is:

$$P = \frac{w/c - 0{,}19\cdot\alpha}{w/c + 0{,}32} \tag{43}$$

Where,

α the degree of hydration

0,32 the specific volume of cement (litres/kg)

Thus, the following relations are valid for the shell thickness t and the bubble radius r (the degree of hydration is 75% of the maximum possible):

w/c=0,40 (P=0,36)		w/c=0,20 (P=0,25)	
r (µm)	t (µm)	r (µm)	t (µm)
5	32	5	40
10	82	10	99
15	149	15	170
20	219	20	249

This means that all air pores with a diameter of 10 µm will dissolve readily if the air pore spacing is larger than 2·32=64 µm for w/c=0,40 and larger than 2·40=80 µm for w/c=0,20. With a typical air pore spacing of 250 µm all pores with diameter smaller than about 40 µm are probably water-filled after a few days of water storage, especially when the water/cement ratio is high. For low water/cement ratios the water-filling process is probably slower.

When the concrete is stored in water during a very long time also the coarser pores become water-filled due to a diffusion of dissolved air to air-filled pores nearby. The mechanism is described and quantfied in Fagerlund (1993b). The smaller the air-bubble the more rapid the water-filling.

The fact that air-pores can become water-filled implies that air-entrainment might be a negative factor for a concrete with very low water/cement ratio. In such a concrete there will in many cases be no or almost no freezable water as long as the concrete is air-free. If the concrete is air-entrained, however, some of the air pores will as shown above, contain freezable water. As shown in paragraph 2.1, very little freezable water is required in order to damage the concrete. Therefore, if the air content is so low that the spacing between really air-filled pores is bigger than the critical spacing, frost damage will occur in the air-entrained concrete. No damage should have occurred, due to the lack of freezable water, if the concrete had been non-air-entrained.

The fact that air-entrainment sometimes might increase frost damage in concrete with low w/c-ratios (<0,25) has been observed experimentally; Saucier (1984), Gagne et al (1992).

5. Water in aggregate and its effects

Only natural, normal-density aggregate is considered in this paragraph. The importance of light-weight aggregate in concretes with low water/cement ratios is not considered. Normally, they cause no problem since they cannot become water-filled to any higher degree when embedded in cement paste; see Fagerlund (1978). Besides, the reasoning below is only valid for a concrete that has undergone a pre-drying before being exposed to water once again. A concrete containing porous aggregate that was saturated already at mixing and which have had no chance of drying will always have a low degree of frost resistance irrespectively of the water/cement ratio and air content of the concrete. This is therefore a "trivial case" which is not treated below.

As shown above in paragraph 4, all gel and capillary pores are water-filled during moist conditions because they are smaller than 0,1 μm. Also aggregate pores with diameter smaller than about 0,1 μm are readily saturated when the concrete is stored in water. Bigger pores in the cement paste and in the aggregate can also become saturated due to the air-dissolution process described above. It is however not possible for a coarse pore in the embedded aggregate to become water-filled until all pores of equal size or smaller in the cement paste is water-filled. Therefore, embedded aggregate with the total porosity located in the size range below 0,1 μm in pore diameter can always be assumed to be saturated. Embedded aggregate with a certain fraction of the pores above 0,1 µm but with all pores smaller than about 1 to 5 µm will become saturated during very moist conditions. Embedded aggregate with a certain fraction of its pores above 5 µm will become completely saturated only after a very long time of water storage of the concrete. Embedded aggregate with very big pores will never become saturated. Natural aggregate having all its pores in the size range below about 1 µm can be assumed to become saturated also in a case where the concrete has undergone a pre-drying before it is once again exposed to water.

When an embedded and more than critically saturated aggregate grain freezes it exposes the surrounding cement paste or mortar to stresses. In Fagerlund (1978), the following expression is derived for the stress in the cement paste caused by freezing of an embedded spherical aggregate particle under the condition that no flow from the aggregate to the cement paste is possible; e.g. the cement paste is saturated and contains no air pores.

$$\sigma_t = \frac{W_{f,a}[0{,}09-(1-S_{eff,a})/S_{eff,a}]\cdot E_m}{3[(1-\nu_m)-\nu_m\cdot 2(1-g_a)/(2\cdot g_a+1)]} \tag{44}$$

Where,

σ_t	the maximum tangential stress in the cement mortar (Pa)
$W_{f,a}$	the freezable water in the aggregate (m^3/m^3)
$S_{eff,a}$	the effective degree of saturation of the aggregate (m^3/m^3)
E_m	the E-modulus of the cement mortar (Pa)
ν_m	Poisson´s ratio of the cement mortar
g_a	the volume fraction of the actual aggregate (m^3/m^3)

The maximum stress is obtained when the aggregate is completely saturated ($S_{eff,a}=1$).

Fracture occurrs when the stress according to eq (44) exceeds the tensile strength, f_t. Then the maximum allowable freezable water in the aggregate is reached.

The E-modulus of the cement paste, E_p, is a function of its total porosity, P. The following expression can be used:

$$E_p = 75\cdot 10^9(1-P)^3 \tag{45}$$

The porosity can be calculated by eq (43).

The E-modulus of the mortar E_m can be calculated by Hashin´s formula which can be written (for ν=0,2):

$$E_m = E_p \cdot \frac{(1-g)E_p+(1+g)E_a}{(1+g)E_p+(1-g)E_a} \tag{46}$$

Where,

E_a	the E-modulus of the sand grains (Pa)
g	the volume fraction of sand in the mortar (m^3/m^3)

A comparison between the maximum allowable freezable water in the coarse aggregate is made below for two types of concrete.

Ordinary concrete; w/c=0,40	Dense concrete;w/c=0,25
* $E_a=75$ GPa	* $E_a=75$ GPa
* $\nu_m=0{,}2$	* $\nu_m=0{,}2$
* $g=0{,}50$	* $g=0{,}50$
* $g_a=0{,}33$	* $g_a=0{,}30$
* $P_p=0{,}36$	* $P_p=0{,}28$
* $S_{eff,a}=1$ (full saturation of the aggregate)	* $S_{eff,a}=1$
This gives:	This gives:
* $E_p=20$ GPa	* $E_p=28$ GPa
* $E_m=36$ GPa	* $E_m=45$ GPa
$\sigma_m = \frac{W_{f,a}\cdot 0{,}09\cdot 36000}{3[0{,}8-0{,}2\cdot 2(1-0{,}33)/(2\cdot 0{,}33+1)]}$	$\sigma_m = \frac{W_{f,a}\cdot 0{,}09\cdot 45000}{3[0{,}8-0{,}2\cdot 2(1-0{,}3)/(2\cdot 0{,}3+1)]}$
$\sigma_m=1690\cdot W_{f,a}$ [MPa]	$\sigma_m=2160\cdot W_{f,a}$ [MPa]
$\sigma_m=f_t\approx 4$ MPa gives:	$\sigma_m=f_t\approx 8$ MPa gives:
$(W_{f,a})_{max}\approx 0{,}003\ m^3/m^3$ (0,3 %)	**$(W_{f,a})_{max}\approx 0{,}004\ m^3/m^3$ (0,4 %)**

This calculation shows that very little freezable water can be tolerated in the aggregate when this is freezing in a saturated condition and the cement paste is also saturated and contains no air pores. Therefore a concrete might very well be undurable despite the fact that the cement paste contains no freezable water and is durable in itself. The porosity required for frost damage to occur is of an order of size that is normal also for very dense aggregate such as dense limestones etc.

Experimental examples of the effect of aggregate porosity on the frost resistance of concrete is shown in Fig 6; Larson and Cady (1969). According to this figure a porosity of the order of size 1% by weigh can cause frost damage. This corresponds to about 2,5% volume porosity. The experimental value is a bit bigger compared with the theoretical calculated above. This might depend on one or more of the following three factors:

1: A concrete always contains some air which makes it possible for water that is expelled from the aggregate to be taken care of in the cement paste. This relieves some of the stresses between the aggregate and the cement paste. The stresses occurring during the flow process are treated in Fagerlund (1978).

2: All water in the aggregate was not freezable.

3: The aggregate was not completely saturated when embedded in the concrete. The effect of a partially saturated aggregate can be estimated by means of eq(44).

No stresses will occur when the degree of saturation of the aggregate is below 0,917.

When the degree of saturation of the aggregate is 93% the following amount of freezable water in the aggregate can be tolerated; see eq (44):

Ordinary concrete; w/c=0,40	Dense concrete; w/c=0,25
$(Wf,a)_{max} \approx 0{,}014\ m^3/m^3$ (1,4 %)	**$(Wf,a)_{max} \approx 0{,}023\ m^3/m^3$ (2,3 %)**

These values are close to the experimental values obtained by Larson and Cady.

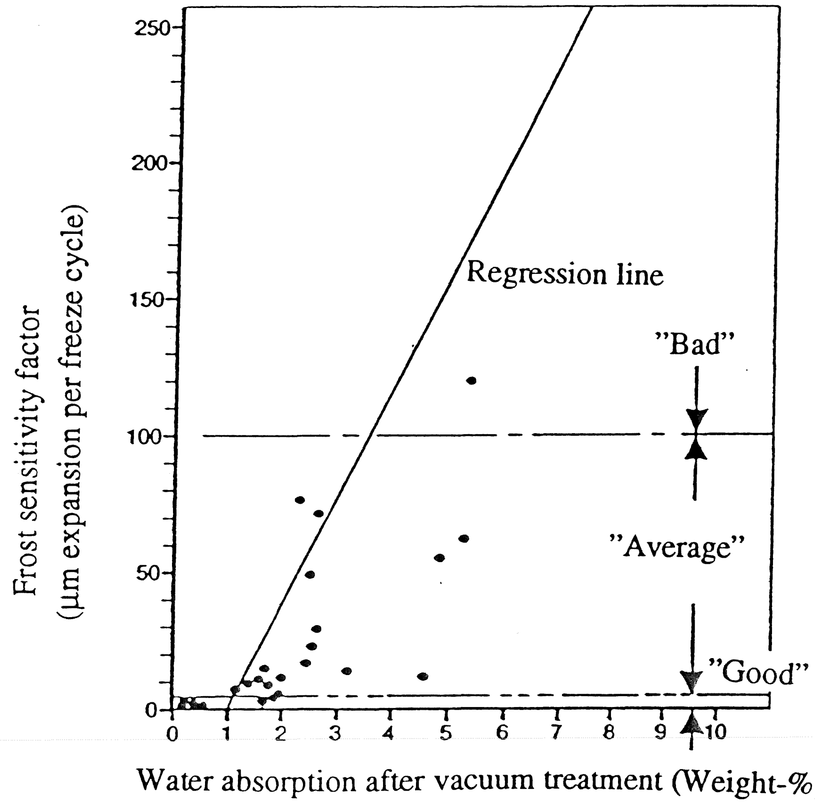

Fig 6: Expansion at freezing of concrete as function of the porosity of the aggregate. Larson and Cady (1969).

6. Water in interfaces and its effects

The interface zone between coarse aggregate and cement paste is sometimes more porous than ordinary cement paste. Therefore, it might contain some freezable water that was not present in the pure cement paste. In a normal concrete some of these interfaces consist of thin cavities caused by bleeding. These cavities are water-filled until the concrete is exposed to a first drying. Even a rather mild drying empties the cavities. They cannot be re-saturated due to the mechanism desribed in paragraph 4; during the water uptake process air bubbles are enclosed in the cavities. Since the cavities are fairly coarse these air bubbles block the water absorption effectively. Water can only enter the cavities when air in them has been dissolved. This takes a very long time due to the low air-pressure in the cavities.

In a dense concrete bleeding is unlikely. However, even in such a concrete the interface zone is often more porous than the bulk cement paste and will probably contain some freezable water.

The total volume of coarse interface zones is difficult to assess. One simple estimate can be made by assuming that the coarse aggregate particles are completely surrounded by a porous zone with thickness ti (m). The total envelope area of coarse aggregate is:

$$Aa = \frac{3 \cdot ga}{ra} \tag{47}$$

Where,

Aa the total envelope area of coarse aggregate (m^2/m^3 of concrete)
ga the volume fraction of coarse aggregate (m^3/m^3 of concrete)
ra the average radius of the coarse aggregate (m)

Then the total volume of the interface zone (Vi m^3/m^3 of concrete) is:

$$Vi = Aa \cdot ti = \frac{3 \cdot ga \cdot ti}{ra} \tag{48}$$

Let us assume that the thickness of the interface zone is 20 μm and that the fraction of coarse aggregate is 35% of the concrete volume. The mean aggregate diameter is 25 mm. Then, the interface volume is:

$Vi = 3 \cdot 0{,}35 \cdot 20 \cdot 10^{-6} / 12{,}5 \cdot 10^{-3} = 0{,}0017\ m^3/m^3$ or 0,2%.

This volume is smaller than that needed in order to destroy a completely saturated concrete. The example therefore shows that the effect of interface zones is small unless the thickness of the zone is rather large. It is therefore not probable that freezable water in the interface should have any larger effect on the frost resistance of dense concretes.

7. Water in cracks and its effects

Cracks that are open to the surface of the concrete will probably become water-filled during very moist conditions. The stresses occurring as a consequence of freezing depend on the crack geometry, on the crack frequency and on the possibilities of the water to be squeezed out from the crack during freezing. The worst case occurrs when the crack is so deep that water cannot be squeezed out at the same time as water transfer into the cement paste is impossible because the cement paste is saturated. Then, high pressures can probably appear. A more stringent calculation is difficult. Probably, a non-linear fracture mechanics approach must be used; viz. the freeze-stresses inside the crack causes stress concentrations in the crack tip and the crack might therefore propagate.
There is no reason to believe that the stresses caused by the freezing of "crack-water" in a saturated concrete will be larger in a high strrength concrete than in an ordinary concrete. The high strength concrete will even resist the stresses better due to the higher tensile strength. On the other hand, it is sometimes claimed that one does not need any air entrainment in a high strength concrete which might be true when it is crack-free. When it is cracked some air is probably needed in order to take care of water that is displaced from the crack. This air content can be calculated by assuming that the expelled water shall be taken care of within the distance DCR/2 from the crack surface (DCR is the critical thickness; see paragraph 2.2). Water that is displaced from the cement paste itself within the distance DCR shall also be taken care of within this distance. This gives the following criterion for the maximum allowable crack width; see Fagerlund (1993a):

$$\mathrm{tmax} = \mathrm{DCR}(a-0{,}09\cdot \mathrm{Wf})/0{,}09 \qquad (49)$$

Where,

tmax	the maximum allowable crack width (m)
Wf	the freezable water in the cement paste (m^3/m^3)
DCR	the critical thickness (m)
a	the air content in tje cement paste (m^3/m^3)

A comparison between an ordinary concrete and a dense concrete is made. Wf is estimated by eq (34) and DCR by the calculation 2 made in paragraph (2.2).

Ordinary concrete; w/c=0,50	Dense concrete; w/c=0,25
* Wf = 0,253	* Wf = 0,110
* DCR = 0,69 mm	* DCR = 1,32 mm
Air content; a=6% (2% in concrete)	
* tmax=0,29 mm	* tmax = 0,73 mm
Air content; a=12% (4% in concrete)	
* tmax=0,75 mm	* tmax=1,61 mm

This very simplified and uncertain calculation indicates that a lower air content is needed in a high performance concrete in order to take care of water from cracks. The exact amount of air required cannot be calculated. Experiments aiming at finding relations between cracking and frost resistance ought to be made.

8. Self-desiccation and its effects

A characteristic of high performance concretes with water/cement ratios well below 0,4 is that in practise they might undergo a self-desiccation due to hydration. The self-dessication might in very dense concretes be so high that it lowers the relative humidity inside the concrete to 80% or 85% even in cases where the concrete is stored in water; see Fig 7, Persson (1992). This means that the amount of evaporable water is lower than that given by eq (31) corresponding to complete saturation of all capillary pores. According to Table 1 a self-desiccation to 85% RH means that the concrete does not contain any freezable water even at -20°C. Therefore, it is immune to frost at this temperature. It was also shown in paragraph 2.1 that a very low desiccation is needed in order to make a dense concrete safe to frost. Self-desiccation does namely create numerous air-filled pores in the vicinity of all capillaries that are still water-filled. Therefore, water flow from the site of freezing is not required in a self-desiccated concrete.

It is very probable that much of the divergent opinions of the frost resistance of high performance concrete emanate from the fact that specimens have been more or less self-desiccated before the test started and during the test. It takes a very long time to saturate a well-cured self-desiccated concrete with low water/cement ratio. The time needed might be longer than that furnished by the freeze/thaw test.

In the real case, during very moist conditions, one cannot expect that the concrete will stay self-desiccated for ever. Sooner or later cement hydration ceases almost completely and therefore no new air space is formed. Then, the previously dried pores will gradually, although slowly, take up water. This means that a certain concrete might be frost resistant when tested during the first years but that it is non-resistant after many years of continuous wet storage.

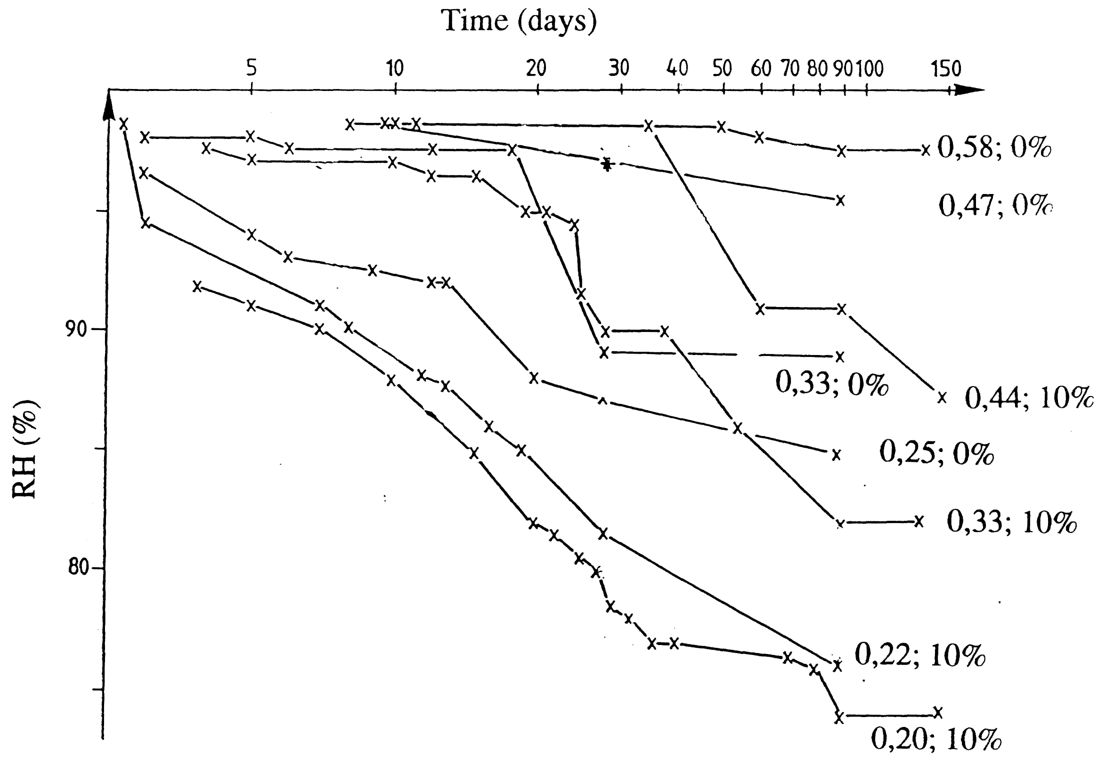

Fig 7: Self-desiccation of concrete with different water/binder ratio and different amount of silica fume; Persson (1992). The water/binder ratio and the amount of silica fume are marked on each curve.

Summary

Only a few experimental studies have been made of the frost resistance and the salt scaling resistance of high performance concrete. Most of these studies indicate that a concrete with a water/cement ratio well below 0,35 can have a high durability despite the lack of air-entrainment. There are other studies, however, indicating that concrete with very low water/cement ratios might have a rather mediocre frost resistance even when it has a certain air-entrainment. Some researhers have found that air-entrainment might be a bit detrimental when the water/cement ratio is very low. In this report some theoretical speculations are made in order to give explanations to these differing observations.

In paragraph 2.1 it is shown that a very low freezable water content is able to harm the cement paste considerably if this is fully saturated; less than 1% (10 litres per m^3 of the cement paste) is sufficient. It is however also shown that a very slight drying will protect the cement paste. Such a drying might be caused by self-desiccation which is a phenomenon taking place in concrete with low water/cement ratios; at least in its interior. It is however also made clear that rather small freezable water contents inside the concrete such as in aggregate particles, in cracks or in air pores might make a concrete undurable despite the fact that the cement paste phase itself is durable due to the lack of freezable water. This can be one explanation to the discrepancy found by some researchers between the frost resistance of cement paste and that of concrete.

In paragraph 2.2 a simplified calculation is made on the effect of the water/cement ratio on the so-called critical thickness and the critical Powers spacing factor. The calculation is based on the hydraulic pressure mechanism and is based on simplified but rather reasonable assumptions concerning the relations between the water/cement ratio and the properties tensile strength, freezable water and permeability. The calculations indicate that the critical spacing factor is increased with decreasing water/cement ratio which is favourable with regard to frost resistance and which makes the air requirement lower the lower the water/cement ratio.

In paragraph 3 the freezable water in concrete and cement paste is treated. On the basis of experimental work performed by Powers and Brownyard (1948) and Vuorinen (1973) it is stated that the maximum amount of freezable water in a concrete at -30°C almost exactly corresponds to the freezing of all water contained in the capillary pore system; Tables 4 and 5. This means that also a concrete with very low water/cement ratio might contain a considerable amount of freezable water. This finding is however based either on specimens that have been either pre-frozen to -78°C and thereafter thawed or on specimens that have been pre-dried to +105°C and then re-saturated. In an "unaged" specimen which has never been exposed to a drying-wetting cycle or which is frozen to a temperature well above -40°C the freezable water is considerably smaller. In a concrete with the water/cement ratio of 0,30 or lower it is almost zero.

This large effect of drying is explained in the report to be a consequence of super-cooling in isolated capillaries. This supercooling takes place more easily when the concrete is unaged. In an aged specimen a micro-crack system might open the capillaries so that ice nucleation can take place more easily. The super-cooling theory is strengthened by the observation that melting takes place at considerably higher temperatures than does freezing. This is the case also for unaged specimens. Freezing to temperatures below -40°C causes homogeneous nucleation of super-cooled water since such water cannot exist below this temperature. This explains the large freezing of water that is often observed at about -40°C and the high freezable water found in the Powers and Brownyard experiment. The large effect of ageing on the freezable water might explain some of the discrepancies found at freeze-testing high performance concrete.

It is also shown that no freezable water will occur even in an aged cement paste with water/cement ratio below 0,39 if the degree of hydration is larger than about 90% of the maximum possible and the temperature is not lower than -20°C; eq (36). The significant effect of the degree of hydration in high performance concrete means that concrete age at testing will have much greater effect on the frost resistance than it has for ordinary concrete.

In paragraph 4 it is theoretically shown that smaller air-pores absorb water quite easily. This means that an air-entrained high performance concete with less air than that needed to create frost resistance might be somewhat more vulnerable to frost than is the same concrete without air. This has also been confirmed in practise.

In paragraph 5 it is shown theoretically that saturated coarse aggregate grains can cause frost damage when embedded in a saturated cement mortar or a mortar with too little air. The maximum tolerable amount of freezable water in the aggregate depends on its degree of saturation. When this is 1 the freezable water must be below 1%, When it is saturated to 93% it must be lower than about 2,5%. A high performance concrete is a bit less sensitive to porous aggregate than is an ordinary concrete.

The large effect of aggregate pores might be one explanation why some researchers have found that a dense concrete with low water/cement ratio is frost resistant even without air while other have found the opposite. The reason might be that different coarse aggregate types have been used.

In paragraph 6 the effect of porous interfaces between aggregate and cement paste is treated. It is found to be marginal unless the interfaces are thick.

In paragraph 7 the effect of cracks is discussed. A very approximative calculation indicates that a certain air content is needed in the concrete in order to take care of expelled water from the crack. This air content might be a bit smaller in a high performance concrete. Experiments aiming at clarifying the effect of cracks are recommended.

In paragraph 8 the self-desiccation of high performance concrete is discussed. Experiments show that this can be very high in concretes with low water/cement ratios and especially when the concrete contains silica fume. The self-desiccation will, as shown in paragraph 2, in many cases save the concrete from frost damage. The self-desiccation effect can be of long duration. Sooner or later, however, a wet-stored self-desiccated concrete ought to take up water and gradually become saturated. This means that a concrete that is tested when young and partially self-desiccated and which is therefore judged to be frost resistant might be non-resistant after some years.

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Addendum

Some practical advice

Concretes with low water cement ratio contain large amounts of water that is potentially freezable at moderate freezing temperatures. This water, or fraction of it, can perhaps, due to natural ageing phenomena occurring in the concrete during its long service life, theoretically become "acitivated" and actually freeze. Rather small amounts of pores in the aggregate can cause frost damage if the dense cement paste does not contain any air pores. Cracks in the concrete can become water-filled and expose a non-air entrained high performance concrete to damaging stresses. Therefore, it seems reasonable to introduce some air-entrainment also to concrete with very low w/c-ratio.

The minimum amount of air needed is difficult to state. Calculations and experiments of the critical spacing factor indicate however that this is increased when the w/c-ratio is decreased. Therefore, the air requirement of a concrete with very low w/c-ratio (below 0,35) is certainly lower than in normal concrete. One shall however avoid to use too small amounts of air since some of the air pores can become water-filled and therefore increase the amount of freezable water, thereby reducing its frost resistance.

It is wise to base the selection of the air requirement on freeze-tests of specimens prepared from concrete which is preferably manufactured in the same manner as in practice. It is suggested that some of the specimens are pre-treated by a natural ageing procedure. This might involve drying-wetting cycles or exposure to the real climate.

The investigation should involve a traditional freezing/thawing test in pure water which reveals the tendency to internal frost damage as well as a salt scaling test revealing the surface durability. The traditional feezing/thawing test can also be used for an investigation of the effect of aggregate, the effect of interfaces between aggregate and cement paste and the effect of cracks.

There are many test metods to select between. They are not discussed here. It has been found in a study at our department[1] that the lowest temperature in the freeze-thaw cycle is of vital importance for the scaling; this is very much increased when the temperature is lowered from -7°C à -14°C to -22°C. Therefore, it is reasonable to adjust the minimum temperature in the test to the actual lowest temperature level in the country in question. This implies that more air in the concrete will probably be needed in a country with very low temperatures than in a country with moderate freezing temperatures.

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[1] S Lindmark: Effect of variations in salt concentration, salt distribution and freeze-thaw cycle at a salt scaling test according to the Swedish Standard SS 137244,. Div. of Building Materials, Lund Institute of Technology, Internal Report M2:01, Lund, 1993. (In Swedish)