Internal frost attack - state of the art : suggestions for future research

Fagerlund, Göran

1997

Citation for published version (APA):
Fagerlund, G. (1997). *Internal frost attack - state of the art : suggestions for future research*. (Report TVBM (Intern 7000-rapport); Vol. 7110). Division of Building Materials, LTH, Lund University.

Total number of authors:
1

LUND INSTITUTE OF TECHNOLOGY
Division of Building Materials

INTERNAL FROST ATTACK - STATE OF THE ART

Suggestions for future research

Göran Fagerlund

Contribution to
International Workshop on Resistance of Concrete to Freezing and Thawing

Essen September 22-23, 1997

Rapport TVBM-7110
Lund May 1997

INTERNAL FROST ATTACK - STATE OF THE ART

Suggestions for future research

G. FAGERLUND
Div. of Building Materials, Lund Institute of Technology, Lund, Sweden

Abstract

Different internal frost damage mechanisms are described briefly. For each mechanism, some of the most relevant applications and consequences are described, together with a discussion of research required for acquiring a deeper knowledge of the mechanism, and its relevance for concrete destruction. The importance of understanding moisture uptake and moisture redistribution processes for clarifying the frost resistance problem is emphasized.

Keywords: Concrete, frost resistance, moisture, durability, service life

1 Introduction. Internal frost attack versus surface scaling

There are two main types of frost attack; (i) internal frost attack caused by freezing of moisture inside the material; (ii) surface scaling, normally caused by freezing of weak salt solutions at the surface. Probably, the two types of attack depend on the same basic mechanism, namely that too much moisture is present in the material, either in its interior, or at the surface. The salt-frost attack is, however, normally treated as a separate problem, because it only occurs during unsealed freezing where the concrete stays in contact with a salt solution. Therefore, it is to a very high degree coupled to the manner by which freeze/thaw is performed. Internal frost attack, on the other hand, can take place also when there is no moisture exchange, or moisture contact, between the material and its surroundings. In this paper, only internal frost attack is considered.

2 Destruction mechanisms

2.1 Introduction

In the following, an isolated representative unit cell of the concrete -or cement paste- is considered. By "representative unit cell" is meant a material volume that is big enough to be representative of the material in bulk, but not much bigger than that; i.e. it shall be big enough to contain the same porosity and the same pore-size distribution as the material in bulk. For cement paste, this means a volume that might be 500 mm^3 (sphere with radius about 5 mm). For a coarse aggregate particle with its surrounding mortar, "belonging" to the particle, it might be 50 000 mm^3 (sphere with radius about 25 mm). This means that moisture movements to, or from, an adjacent unit cell is not considered. Besides, the cell is so small that the effect of moisture gradients can be neglected.

The three mechanisms, that are briefly described below, might very well be active simultaneously within the same concrete. So for example, porous saturated coarse aggregate particles, or porous interface zones, might freeze as "closed containers", while the cement paste within the same concrete might, when it freezes, cause both hydraulic pressure and ice-lens growth. Thus, the effect of freezing on the behaviour of the concrete is the sum of of more than one destruction type.

2.2 The closed container

2.2.1 Theory

The simplest material model is the "closed container" according to which the concrete (or rather, the cement paste) is supposed to be built up by "unit cells" consisting of hole-spheres with impermeable walls and with the external radius R, and the internal radius r. All evaporable water (freezable and non-freezable) is supposed to be located to the centrical hole. When water freezes, a pressure p [Pa] is built up in the ice/water phase. The magnitude of the pressure depends on the freezing temperature, θ_f [°C]:

$$p \approx -10^6 \cdot \theta_f \tag{1}$$

This pressure is transferred to the wall where tensile stresses appear. The magnitude of these depends on the degree of saturation of the container.

(a) Completely saturated container:

If no consideration is taken to the compressibility and ductility of the three phases solid wall, ice, non-freezable water, the following average tensile stress σ [Pa] is built up in the solid wall, provided the wall is completely plasticized:

$$\sigma \approx -10^6 \cdot \theta_f \cdot \pi \cdot r^2 / \pi(R^2 - r^2) = -10^6 \cdot \theta_f \cdot P^{2/3} / (1 - P^{2/3}) \tag{2}$$

where θ_f is the temperature of the unit cell, and P is the porosity [m^3/m^3]. Let us assume that the temperature θ_f is -10°C and the tensile strength of the wall is 8 MPa, which is a high value for cement paste. Then, the maximum allowable porosity is only 2% if the container shall not burst. *This calculation shows, that it is not possible for a concrete to survive freezing when it is completely saturated.*

(b) Unsaturated container:

The volume expansion of water is about 9% when it is transformed into ice. Consequently, no tensile stresses will occur when the *effective* degreee of saturation S_f is below a critical value, that is:

$$S_{f,cr} = w_f / (w_f + 0.09 \cdot w_f) = 0.917 \tag{3}$$

where w_f is the amount of freezable water [m^3/m^3]. The *total* degree of saturation S is defined:

$$S = w_e/P \tag{4}$$

where w_e is the total evaporable water [m^3/m^3]. Let us assume that the fraction of non-freezable water, w_{nf}, at the temperature θ is k_θ ($k_\theta=w_{nf}/w_e=(w_e-w_f)/w_e=1-w_f/w_e$). Then, the critical total degree of saturation is:

$$S_{cr} = S_{f,cr}/\{1-k_\theta(1-S_{f,cr})\}=0.917/\{1-k_\theta \cdot 0.083\} \tag{5}$$

If 50% If the evaporable water is unfreezable, the maximum allowable degree of saturation is 0.957, etc.

Equations (3) and (5) can be used for a calculation of the minimum amount of air-filled space required for frost resistance. Let us assume that the total evaporable water in a cement paste is 300 l/m^3 and the non-freezable water is 100 l/m^3. Then, the minimum allowable amount of air-filled pore volume is 18 l/m^3 or about 2%.

Note: The closed container model is a special case of the hydraulic pressure model described below. The only difference is that water in the closed container model has to freeze in-situ, because the pore walls are supposed to be impermeable.

2.2.2 Applications and consequences

The closed container model might be used for the following cases:

1. *Porous coarse aggregate grains.* The freezable water must be contained inside the grain. Therefore, this must have an effective degree of saturation below 0.917. If the grains are small, or if the porosity of the grains is very low, they can be allowed to be completely saturated. In such cases, the tensile stresses in the cement paste, imposed by the aggregate grains that freeze, are too small to cause damage. The criterions for maximum aggregate size and porosity are theoretically treated in [1].
2. *Freezing of water in porous interfaces between aggregate and cement paste.* The total volume of such porous interfaces might be rather high. A calculation performed in [2], based on direct observations of the size of the interface zone, indicates that the total volume might be as high as 4 litres/m^3 if only the coarse aggregate is considered, but as much as 45 litres/m^3 if all aggregate is considered. This means that considerable pressure can be exerted on the cement paste. Probably the pressure will be sufficiently high to severely harm the concrete in cases where the air content is low. The best way to avoid damage is to dry the concrete once. Then, water will leave the interface zones irreversibly, so that in the future, the degree of saturation of the interfaces will always be below 0.917.
3. *High performance concrete with extremely low water/cement ratio.* Such concrete might be so dense that water cannot flow from sites where it freezes to air-filled spaces. Thus, the water expansion at freezing must be taken care of locally. This means, that the effective degree of saturation of the cement paste, air pores excluded, must be below 0.917.
4. *Freezing of the green concrete.* In this case, the tensile strength of the cement paste is so low, that water expansion due to freezing must be taken care of locally; air-entrained pores have no function at this stage. Therefore, a self-desiccation by hydration, corresponding to at least 9 % of the freezable water volume, must take place before the concrete can be allowed to freeze. The positive effect of self desiccation was shown for the first time by Powers [3], and has been further inve-

stigated in [4]. In [4], it was shown theoretically, that the required self-desiccation corresponds to a degree of hydration α_{req} of:

$$\alpha_{req} \approx 0.5 \cdot w/c \tag{6}$$

This value corresponds well with experiments, [5].

5. *Freezing of water in deep cracks.* The expansion can normally be taken care of by air-pores in the cement paste. If the cracks are too wide, and the air content is too low, freezing will occur as in a closed container. Thus, it will be difficult to avoid damage since the cracks will probably be saturated during moist conditions.
6. *Freezing of water absorbed in air-pores.* Under certain circumstances, air-pores can become water-filled before, or during, freeze/thaw. The absorption mechanism can be a dissolution-of-air and replacement-by-water process of the type described in [6]. This process will, however, be very slow when the pores are big, and, therefore, complete water-filling of numerous air-pores is unlikely unless the concrete is stored in water for a very long period. Another, and more rapid pore-filling mechanism, is pure capillary suction due to a collapse of the air-pore system before the concrete was set. By "collapse" is meant that the air pore system of the fresh concrete is unstable causing continuous channels linking the individual air-pores to the outside water source. When water in air-pores freezes, there will normally be no place for the expelled water. Therefore, freezing of each individual "air-pore" will take place more or less as in a closed container, that is completely saturated. This is a dangerous situation since air-entrainment of this inferior type will worsen, the situation. High performance concretes ought to be especially vulnerable, due to their low permeability.

2.2.3 Needed research

The closed container model ought to be studied by systematic investigations of the different cases described in 2.2.2. The tests are not simple, because one has to make one variation at a time. The following example indicates the difficulties; if one wants to investigate the application of the model to coarse aggregate, one must be able to vary the degree of saturation of the aggregate without changing the degree of saturation of the cement mortar. Similarly, if one wants to test the model on high performance concrete by determining the critical effective degree of saturation, one has to know the freezable water inside the cement paste and to be able to distinguish freezable water in the cement paste from freezable water in air-pores, cracks, interfaces etc. If one wants to investigate the effect of freezable water in interfaces, one has to know that the water content in the other phases -aggregate and cement paste- is the same in all tests.

2.3 The hydraulic pressure

2.3.1 Theory

The closed container model predicts low required air contents when concrete as a whole is seen as a container. The real air requirement is considerably higher. One plausible reason is that excess water caused by freezing has to flow from saturated areas to air-filled spaces. This water flow creates a hydraulic pressure, [7], which in turn produces tensile stresses in the material. A simple model is shown in Fig 1. A piece of the saturated cement paste is freezing. The pressure is at maximum at point C at the centre of the piece. The hydraulic pressure p [Pa] inside the material sector considered is; [8]:

$$p = (0.09/K)\cdot(dw_f/d\theta)/(d\theta/dt)\int_{o}^{X} [v(x)/a(x)]\cdot dx \qquad (7)$$

where K is the effective permeability [$m^2/(Pa\cdot s)$], $dw_f/d\theta$ is the change in freezable water at a change in temperature [$m^3/(m^3\cdot degree)$], $d\theta/dt$ is the rate of temperature lowering (the freeezing rate) [degree/s], v(x) is the volume of the sector considered between x=x and x=X, where X is the distance from the surface of the piece to point C, a(x) is the cross section of flow at x=x.

The material fractures when the hydraulic pressure p equals the tensile strength of the material, f_t [Pa]. This means that there will be a maximum allowable distance X, or a maximum allowable size 2·X.

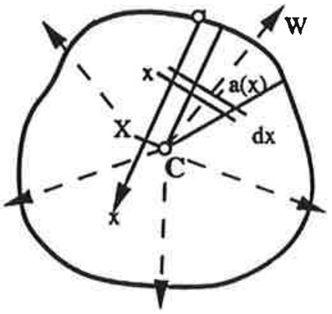

Fig 1: A piece of a saturated material. Moisture flow caused by freezing.

The maximum size depends on the geometry of the piece. Two geometries are considered in more detail, and one geometry in more principally.

(a) The critical thickness: For a slice of thickness D, the critical thickness D_{cr} [m] is [$a(x)=a$; $v(x)= a(D_{cr}/2-x)$]:

$$D_{cr} = \{8\cdot K\cdot f_t \;/\; [0.09\cdot(dw_f/d\theta)/(d\theta/dt)]\}^{1/2} \qquad (8)$$

(b) The critical wall thickness, or the critical spacing factor: For a hole-sphere with a wall thickness L, an impermeable outer periphery and a centrical hole with the specific area α ($\alpha=3/r$ where r is the radius of the hole), the critical shell thickness L_{cr} is obtained by; [$a(x)= =4\cdot\pi\cdot(r+x)$; $v(x)=(4/3)\cdot\pi\cdot\{(r+L)^3-(r+x)^3$]:

$$L_{cr}^{2}\cdot\{(L_{cr}\cdot\alpha)/9+1/2\} = f_t\cdot K/[0.09\cdot(dw_f/d\theta)/(d\theta/dt)] \qquad (9)$$

L_{cr} is the critical spacing factor, derived originally by Powers [7]. L_{cr} is half the maximum distance water has to be transported from a place where it freeezes in the cement paste to the nearest air void; see Fig 2(b).

(c) The critical flow distance

A real material is neither composed of slices, as in (a), nor of hole-spheres, as in (b). It consists of a water saturated matrix enclosing a complicated array of more or less spherical air-filled pores. For each material, there will be numerous flow paths for expelled water; Fig 2(a). Each flow path will give rise to a hydraulic pressure. Theoretically, there will be a certain distance L′ causing the biggest pressure, thus determining if the material shall be frost resistant or not. This distance is a measure of the biggest distance water can flow from a point where freezing occurs to the periphery of the nearsest air-filled pore. When L' transgresses a critical value L'_{cr} fracture occurs. This value L'_{cr} cannot be calculated theoretically due to the big geometrical complexity of the matrix and air-pore system. It must be determined experimentally from the critical degree of saturation; see below. For the simple geometry in Fig 2(b), L'_{cr} is equal to the critical wall thickness L_{cr} defined by eq (9). Then all air-filled pores are supposed to be of equal size (specific area α) and placed in a cubic array. L_{cr} is, as mentioned above, the critical Powers spacing factor.

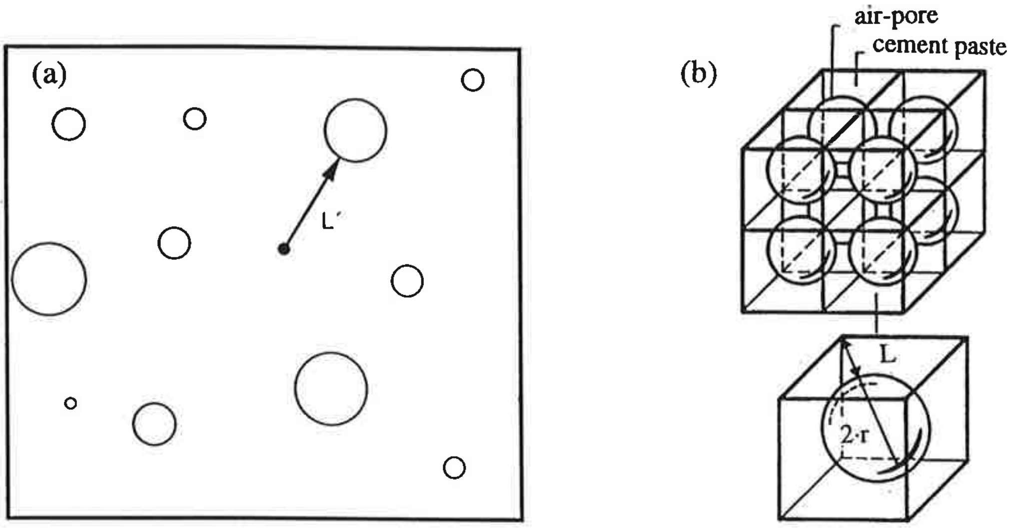

Fig 2: (a) The real material; the "flow distance", L´. (b) The Powers model, [7].

2.3.2 Applications and consequences

As mentioned above, the hydraulic pressure model is a special case of the closed container model. The difference is that the container walls are supposed to be permeable in the hydraulic pressure model. This model is probably applicable to most concretes, and especially to concretes with high water/cement ratio, where the amount of nonfreezable water is low. According to the model, the concrete shall stop to expand when the temperature lowering, $d\theta/dt$, is zero, because then no more excess water is then generated. Such a behaviour has also been observed; see Fig 3(a), [9]. When the temperature is kept constant at about -8°C, the cement paste stops to expand. When cooling is resumed, expansion starts again. According to the theory, the specimen should even contract a bit when temperature lowering is stopped, since the hydraulic pressure ceases. It is reasonable to assume, however, that so much ice has been formed before cooling is stopped, that contraction is physically hindered, since the ice keeps the specimen in an expanded condition.

The hydraulic pressure model leads to the existence of a critical degree of saturation of the cement paste, or a critical content of air-filled pores. The critical degree of saturation is reached when half the distance between pores that are still air-filled equals the critical flow distance. Thus, in order to calculate the critical degree of saturation one must know how water is distributed in the air-pore system.

For the general model in Fig 2(a) the following relation between the air content of the cement paste, a [m^3/m^3], the specific area of the air-pores, α, [$m^2/m^3=m^{-1}$], and the flow distance L´ [m], can be used; [10]. (*Note:* only the cement paste is considered. Therefore, the values a, α and L´ in the equation are valid for the cement paste phase):

$$a\{1+L'\cdot\alpha+2\cdot L'^2\cdot\alpha\cdot[u]_1/[u]_2+1.33\cdot L'^3\cdot\alpha\cdot[u]_0/[u]_2\} = C \qquad (10)$$

where $[u]_i$ is the i:th statistical moment of the size distribution of air-filled pores. C is a constant determining the volume fraction of the matrix within which all points have a distance shorter than L´ to the nearest air-pore. Thus, C describes the "protected volume fraction" of the paste. C=1 for the probability 63% (it can be proven, [10], that L´corresponds to the so called Philleo spacing factor, [11], when C=1). C= 2.3 for the probability 90%. Thus, the value of C increases rapidly with increasing protected volume fraction.

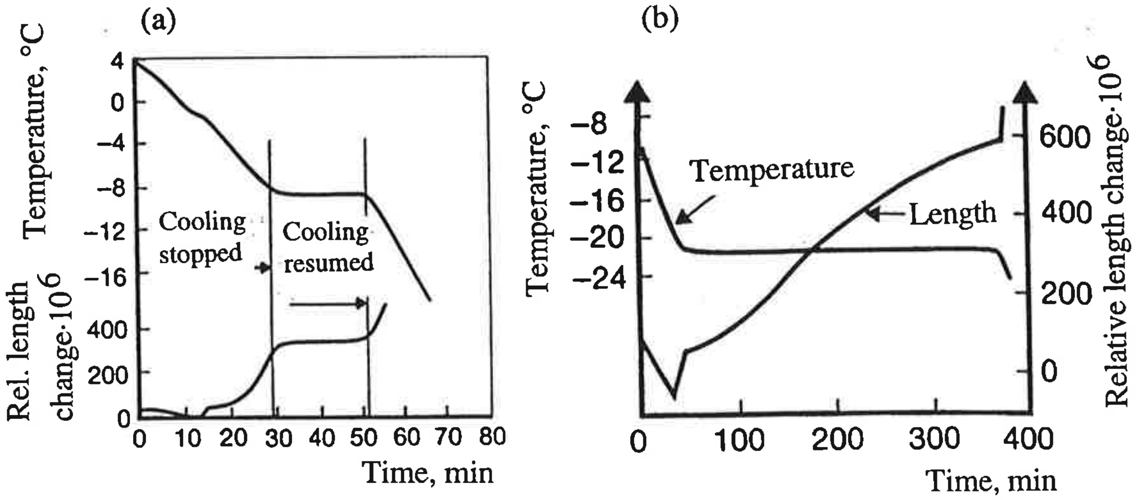

Fig 3: Length-temperature-time curves at freezing of cement paste; [9].
(a) w/c-ratio 0,60. (b) w/c-ratio 0.45.

For the model in Fig 2(b) the following relation between a, α and L is valid; [7]. (Like eq (10,) only the cement paste phase is considered in the equation):

$$L=(3/\alpha)\{1.4(1/a)^{1/3}-1\} \qquad (11a)$$

or:

$$a=1/\{0.364\cdot(L\cdot\alpha/3+1)^3\} \qquad (11b)$$

Increase of the water content of the cement paste leads to a decrease of the air content. Besides, the specific area of the air-pore system is changed. It is reasonable to assume that the smallest air-pores are water-filled at first; [6]. Therefore, a gradual water absorption leads to a reduction of α. Consequently, according to eq (10) or (11), the flow distance, or the Powers spacing factor, increases. At a certain water-filling, corresponding to the critical degree of saturation, or the critical air content, the critical flow distance L'_{cr}, or the critical Powers spacing factor L_{cr} is reached. Theoretically, the critical degree of saturation can be calculated if the size distribution of coarse pores, or, in other words, air-pores, (radius >1 μm) is known. A hypothetical example is shown in Fig 4. The smallest pore-class is 40 μm and the biggest 480 μm. The total volume of all coarse pores is 7%. The total porosity is 35% (including coarse pores). The critical Powers spacing factor L_{cr} is 0.6 mm. The water absorption is supposed to

start with the smallest pores. The result of the calculation is shown in Fig 4(b). The critical distance is reached when all pores smaller than 140 μm are water-filled. This corresponds to a residual air content of 5%, which is the critical air content, and a residual specific area of 14 000 m^{-1}. The critical degree of saturation is;
$S_{cr} = (0.35-0.05)/0.35 = 0.86$.

In the normal case, the critical degree of saturation of a cement paste is considerably lower than 0.917 which was valid for the closed container model. The reason for this is that expelled water is not taken care of locally, where freezing occurs, but on a certain distance from the freezing site. The degree of saturation will, therefore, be a function not only of the critical distance, but also of the size and shape of the recipient pores (the air-pores).

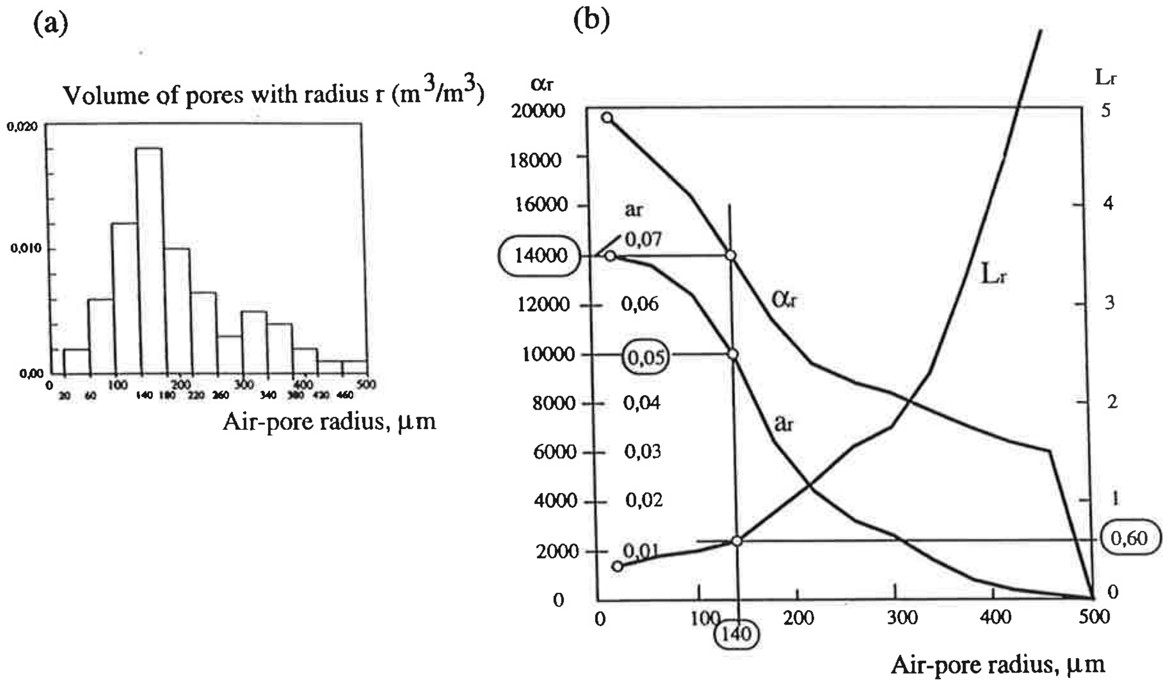

Fig 4: Example of a calculation of the critical air content and the critical degree of saturation. (a) Assumed air-pore size distribution. (b) Effect of a gradual water absorption on the air content, the specific area of air-filled pores, and the Powers spacing factor.

2.3.3 Needed research

The hydraulic pressure model ought to be studied by tests where the ice formation, the specimen dilation and the permeability are studied at the same time, using many different temperature curves for freezing and thawing. A combination of dilatometry and calorimetry was suggested by Verbeck and Klieger [12]. It was applied by the author in [13]. An example is shown in Fig 5. The material is a cement paste with a high degree of saturation.

From the ice formation curve, the parameter $(dw_f/d\theta)/(d\theta/dt)=dw_f/dt$, which is the freezing rate, can be evaluated. The expansion curve is a measure of the internal pressure caused by ice formation. A comparison between the measured expansion curve and a calculated expansion curve based on the hydraulic pressure model will, therefore, tell whether this is a reasonable destruction mechanism or not. The tests should be made on sealed specimens, pre-conditioned to different moisture contents. In an unsealed experiment, the spacing factor will gradually decrease during the test due to water absorption, and therefore, the experiment will be difficult to interprete.

It is remarkable, that the biggest expansions in Fig 5 occur when the rate of ice formation is at its lowest. One possible explanation is that ice already formed at higher temperatures block the pores so that the parameter K in eq (8) or (9) is reduced. The net effect might be that the biggest pressure occurs at the lowest temperature despite the fact that the rate of ice formation then is the lowest . In order to verify the hydraulic pressure model it is, therefore, necessary to estimate the effect of temperature on permeability. This can be done theoretically or experimentally.

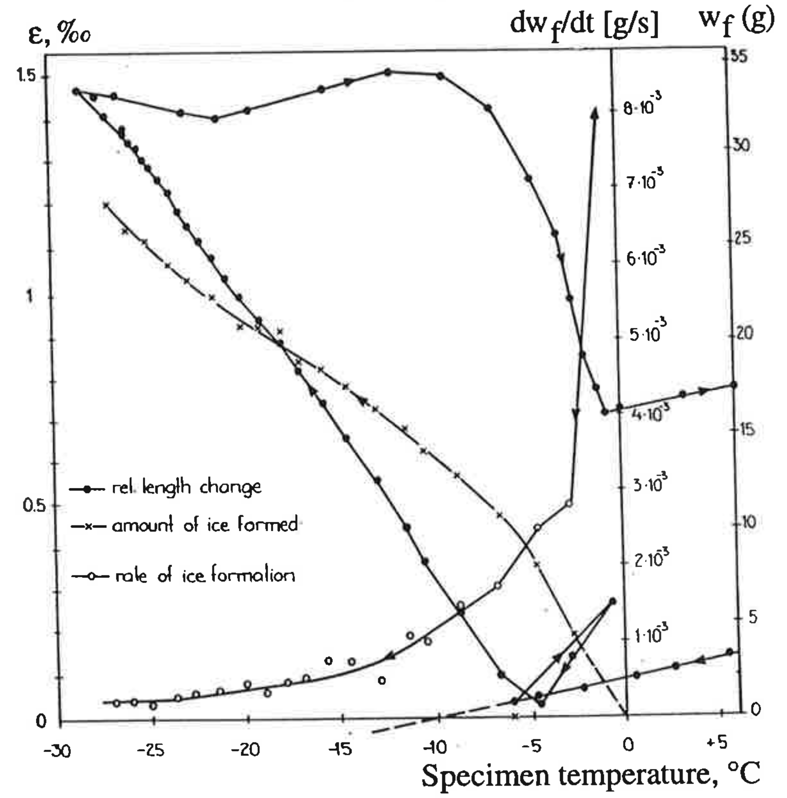

Fig 5: Measurements of the dilation, the freezable water and the rate of freezing of a cement paste with w/c-ratio 0,83; [13]. S=0,90, $S_{cr}\approx 0{,}86$.

A simple theoretical calculation of the effect of ice formation on the hydraulic pressure can be made by assuming that all pores are straight parallell cylinders assembled in a bunch with pore radii varying from r_{min} to $r_{max,\theta}$ where r_{min} is the smallest radius of pores containing unfrozen water, that is "movable". $r_{max,\theta}$ is the biggest pore containing unfrozen water. Before freezing, r_{max} is the biggest of all pores in the material.

The hydraulic prsssure p [Pa] is:

$$p=k\cdot L\cdot(dw/dt)\,/\Sigma\, r_i^4\cdot n_i \qquad (12)$$

where k is a constant including the viscosity of the flowing substance (the ice-water mixture), L is the distance of flow, dw/dt is the total rate of flow [m^3/s], r_i is the radius of the pore, and n_i is the number of pores with radius r_i. $n_i=f(r)\cdot dr$ [number/m^3] where f(r) is the frequency function of pore radii. The water flow can be replaced by the rate of formation of excess water, $dw/dt = 0.09\cdot dw_f/dt = 0.09\cdot(dw_f/d\theta)/(d\theta/dt)$. Thus eq (12) can be written:

$$p=k'\cdot L\cdot(dw_f/d\theta)/(d\theta/dt) \Big/ \int_{r_{min}}^{r_{max,\theta}} r^4\cdot f(r)\cdot dr \tag{13}$$

$r_{max,\theta}$ is a function of the freezing temperature; the lower the temperature, the smaller the value of $r_{max,\theta}$. A purely theoretical equation for $r_{max,q}$, assuming equilibrium conditions (no local supercooling) is:

$$r_{max,\theta} = -\sigma\cdot v_s/[\Delta H\cdot \ln(T/T_0)]+t \tag{14}$$

Where σ is the surface tension between air and water [N/m], v_s is the molar volume of water [m^3/mole], ΔH is the molar heat of fusion (a function of temperature) [Nm/mole], T is the freezing temperature [K] and T_0 the normal freezing temperature [273 K]. t is the thickness of the adsorbed layer [m].

$r_{max,\theta}$ can also be obtained directly from the measurement of the amount of frozen water, combined with a determination of the total pore size distribution.

Another important research task is to determine the critical distance experimentally. This can be done by experimental determinations of the critical degree of saturation, in combination with a determination of the size distribution of coarse pores (bigger than about 1 µm). The method is the inverse of calculating the critical degree of saturation; see Fig 4. Some determinations have been made on basis of freeze experiments and pore size analyses, using image analysis of polished surfaces; [14]. Examples are shown in Fig 6.

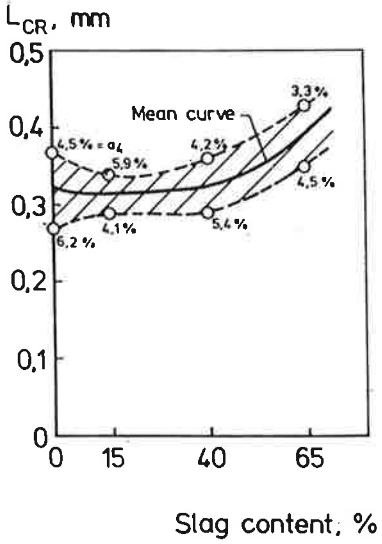

Fig 6: Experimentally/theoretically determined critical Powers spacing factors for concrete made with different types of cement and with different air contents; [14].

The materials tested were concretes made with cements of different type. The water/cement ratio is 0.45, and different air contents were used. It is interesting to note that the calculated Powers spacing factor is considerably higher than values normally given in the literature. The reason is, that such values are based on measurements of the spacing factor of the entire air-pore system; also pores that were water-filled during the freeze test on basis of which the determination of the critical spacing factor was made. There are many indications that the true critical Powers spacing factor for concrete is closer to 0.35 mm than to 0.25 mm, a value often maintained in the literature.

2.4 The microscopic ice lens growth mechanism

2.4.1 Theory

A cement paste will always contain both unfrozen water and ice; the lower the water/cement ratio, the higher the fraction of unfrozen water. Differences in free energy between water and ice will draw water to ice that was formed in the coarser capillaries and to ice formed in air-pores by freezing of water, that was expelled during the initial freezing phase. Consequently, the ice-bodies in filled capillaries will grow and exert a pressure on the pore walls. Thereby, the free energy of the ice increases. Ice in air-pores, that are only partly filled, can grow without obstruction from the pore walls; i.e. they grow in a stress-less condition. Water is primarily drawn from very small capillaries and from gel pores. This will cause a drying which will decrease the residual free energy of unfrozen water. Consequently, the energy differences between ice in filled pores and unfrozen water will finally disappear, whereby ice growth stops. Before that happens, considerable damage might occur. So far, it has not been possible to derive an expression for the stress in the material. Some estimates are made in [15] showing that the pressure can be very high in a concrete with free access to moisture from outside.

Ice in partly filled air voids can grow without hinder from the pore walls. Therefore, water transport to air-pore ice reduces the possibility of water transport to capillary ice. If the air pores are numerous, capillary ice growth will not take place at all since the free energy of air-pore ice is much lower promoting their growth. This means, that also the microscopic ice lens growth mechanism predicts the existence of critical distances between air-filled spaces; [9]. In contrast to the hydraulic pressure model, it is not possible at present to derive a theoretical expression for the critical distance. It has to be determined experimentally through a determination of the critical degree of saturation combined with a determination of the size distribution of the coarse pore structure (the "air-pores").

Examples of measurements of length changes of cement paste during freezing is shown in Fig 7; [9]. The Powers spacing factor was different in different specimens. It is interesting to note the big contractions when the spacing factor is low. This indicates that shrinkage due to the drying effect caused by withdrawal of water from the finer pores dominates over the expansion due to the pressure caused by ice lens growth. The most plausible explanation is that ice growth takes place primarily (or only) in air-pores, that are only partly filled. When the spacing factor is high, the specimen expands considerably, indicating that ice lens growth takes place in completely filled capillaries.

2.4.2 Applications and consequences

Like the hydraulic pressure model, the ice lens growth model is probably applicable to most concretes, and especially to concrete with low water/cement ratio, in which the amount of non-freezable water is high. According to the model, the concrete shall not stop to expand when temperature lowering is zero, because stresses are not promoted by a high rate of temperature lowering, but by a long duration of low temperature. It has also been observed, for cement paste with low w/c-ratio, that damage continues to increase despite the temperature is kept constant; see Fig 3(b). When the temperature is kept constant at about -22°C, the cement paste continues to expand. This behaviour is contradictory to the behaviour shown in Fig 3(a) for the cement paste with the higher water/cement ratio.

The ice lens growth model also leads to the existence of a critical degree of saturation of the cement paste, or a critical content of air-filled pores. This is a consequence of the fact that critical distances pobably exist.

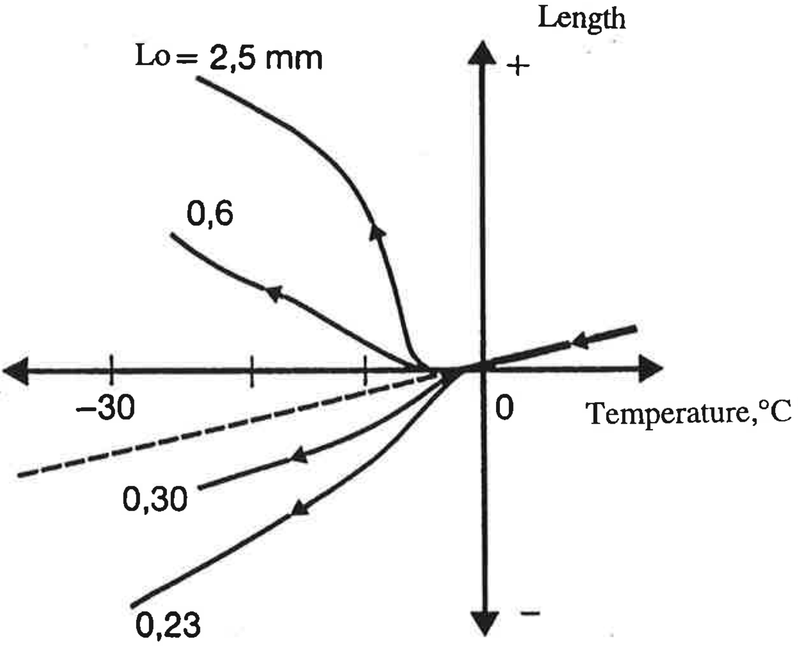

Fig 7: Length-temperature curves for air-entrained cement pastes with different spacing factor; [9].

2.4.3 Needed research

The ice lens segregation model could be studied by the same type of tests as was suggested for the hydraulic pressure model; i.e. tests where ice formation, specimen dilation and permeability are studied simultaneously, using many different temperature curves for freezing and thawing. A combined dilatometer and calorimeter is the most suitable instrument. By keeping the temperature constant for longer or shorter times and noting the ice formation and the expansion (or contraction), the significance of the destruction mechanism can be estimated. By knowledge of the elastic constants of the material, the pressures exerted by the growing ice can be estimated.

The tests should be made on specimens conditioned to different moisture contents and frozen in sealed condition. Ice lens growth can also occur when the specimen is placed in contact with unfrozen water. This is, however, a much more complex (and much more dangerous) situation, and it is not so well suited for mechanism studies. By a gradual water uptake, the spacing factor will gradually decrease during the experiment which makes the interpretation very difficult.

3 Effect of external parameters on the critical moisture content

3.1 Effect of repeated freeze/thaw cycles

Repeated freeze/thaw cycles will have a marginal effect on the value of the critical degree of saturation. This has been shown experimentally in [16], [17], and [18]. On the other hand, for water contents above the critical, there seems to be a fatigue effect. The following relation seems to be valid; [19]:

$$S<S_{cr}: \quad D=0 \text{ for all } N \qquad (15a)$$

$$S>S_{cr}: \quad D=K_N(S-S_{cr})=K_N \cdot \Delta S \qquad (15b)$$

Where D is damage expressed as loss in dynamic E-modulus, K_N is a "coefficient of fatigue". Experiments indicate that there exists a fatigue limit that is reached after a rather small number of freezings; [19]:

$$K_N \approx A \cdot N/(B+N) \qquad (16)$$

Where the "fatigue limit" A is of the order 1 to 10, and B is about 4. This means that very small additional damage occurs after about 20 freeze/thaw cycles. For a typical concrete with A=8 and ΔS=0,05 the loss in E-modulus is 29% after 10 cycles, 33% after 20 cycles, 39% after 100 cycles and 40% after 1000 cycles.

The damage equation (15) can possibly be used for an estimation of the future deterioration of frost damaged concrete; see [20].

3.2 Effect of the freezing rate

The freezing rate has small influence on the critical degree of saturation; [21]. This can be explained by the hydraulic pressure model. A doubling of the freezing rate will according to eq (9) decrease the critical Powers spacing factor by a factor of about 0.2. This will not influence the critical degree of saturation so much. For the hypothetical example in Fig 4, the critical spacing factor will be reduced from 0.60 mm to 0.48 mm. This will increase the critical air content from 5% to 6.1% and decrease the critical degree of saturation from 0.86 to 0.83. The effect on the service life might, however, be significant because it takes longer time to fill a concrete by water to a degree of saturation 0.86 than to 0.83.

3.3 Conclusions. Needed research

The critical degree of saturation can be looked upon as a material constant that is not so much influenced by external climatic conditions. This is important because it opens the possibility of using the critical moisture content for service life predictions; [22].

There is however more experiments to be done in order to verify the results so far obtained, and described above. One cannot exclude that prolonged freezing temperatures increase the ice lens growth, which in turn might reduce the critical distance more than what was calculated in paragraph 3.2 on basis of the hydraulic pressure mechanism. Consequently, the critical degree of saturation will be reduced more than calculated above.

4 Freezing involving moisture transfer over longer distances

4.1 Introduction.

In sections 2 and 3, unit cells without moisture exchange with other unit cells were considered. There are freezing conditions, however, where water is taken up by, or transferred to, other unit cells, increasing their degree of saturation before they freeze, or when they freeze. These cases must be treated separately. Probably, it is the same basic mechanisms that determine the inner stresses in these cases as the mechanisms described in section 2.

4.2 Moving ice front. Theory and needed research

Let us assume, that the interior of the material is not critically saturated when freezing starts. Ice is at first formed in the surface layer (or surface unit cells) because freezing temperature is reached there at first. Therefore, if the surface is supposed to be impermeable due to formation of ice, excess water will be forced into the unfrozen layer that is closest to the frozen layer. As the ice front moves, more and more water is forced inwards. At a certain instant, the critical degree of saturation is reached in the unfrozen layer close to the ice front. Then, damage will occur, and possibly the frozen layer will scale off.

One can calculate a "critical depth of unsaturation", $D_{cr,us}$, which is the distance from the ice front to the depth where there must be air space enough to take care of the expelled water. It is a complicated task to calculate this value. It will also depend on the amount of expelled water. Therefore, $D_{cr,us}$ will depend on the depth x from the surface to the ice front. Application of Darcys law to the flow inwards give; cf. eq (8):

$$p \approx 0.09 \cdot [(dw_f/d\theta)/(d\theta/dt)] \cdot dx \cdot (x_{us}-x)/K \tag{17}$$

Where dx is the layer within which freezing occurs, x is the distance from the surface to the ice front, and x_{us} is the depth from the surface to the place where expelled water can be accomodated. It has been assumed that the amount of freezable water is constant for all layers dx, which cannot be the real case since expelled water is taken up in each layer from previous freezings of outer layers. Thus, the freezable water increases with increasing depth x. It has also been assumed, that the pressure gradient is linear from the ice front to the depth of unsaturation. This is a simplification since the water content varies in this zone. Fracture occurs when $p=f_t$ which is the tensile strength. Introducing eq (8) gives:

$$(x_{us}-x)_{cr} = D_{cr,us} = (Dcr^2/8) \cdot (1/dx) \tag{18}$$

This equation is not easy to apply. Warris [23] suggested, on basis of an analysis of the heat balance equation for the surface, that the parameter 1/dx could be replaced by the surface/volume ratio, S/V [m^{-1}] for the specimen.

$$D_{cr,us} \approx (D_{cr}{}^2/8) \cdot (S/V) \tag{19}$$

This equation can only be applied when the moisture profile is known. This will change during the freezing process. Scaling will be avoided when the criterion (18) is fulfilled over the entire frozen part of the specimen.

It is doubtful whether the moving ice front mechanism, as described above, is valid for concrete. There is always unfreezable water, that makes it possible for expelled water to flow outwards. It seems clear, however, by experiments on brick, [24], that the mechanism can be valid for dense materials with low amount of freezable water.

It should be interesting to study the suggested mechanism by letting long specimens conditioned to different initial moisture contents freeze unidirectionally, and measure the damage occurring at different distance from the cold surface.

4.3 Frost heave. Theory and needed research

When unfrozen parts of a concrete has almost unlimited access to free water, a destruction mechanism of the the same type as frost heave in roads might occur. The prerequisites are; [4]:

1: A zero-degree isotherm, separating a frozen surface part from an unfrozen interior part, lies still for a long time. This means that there must be a lasting heat balance between heat leaving the ice front and heat arriving at this. Heat arriving is caused by flow of water to the ice front from the interior of the concrete, or from an outer water source. Heat is brought both by convection and by freezing. The driving mechanism for water transport is the differences in free energy between ice and water that are described in paragraph 2.4.1.
2: The permeability must be so high, that the moisture flow, required for an immobile ice front, can be fulfilled.
3: The tensile strength of the concrete must be so low, that a macroscopic ice lens is able grow at the ice front
4: The concrete must have access to large amounts of unfrozen water

One cannot exclude, that this destruction mechanism is valid for some types of concrete with low quality, such as concrete dams or reservoir walls, foundations founded below the ground water level, etc. It is quite clear, that the mechanism occurs in green concrete that freezes before the concrete is set; [4], [15].

The mechanism ought to be studied by experiments on concrete specimens simulating real cases, such as a dam wall exposed to frost at one face and to free water at the other. Different concrete qualities should be tested.

5 Moisture mechanics and frost damage

5.1 Introduction

Damage of a unit cell will only occur when the water content in the cell exceeds the critical moisture content. Only a few freeze/thaw cycles are needed in order to more or less completely destroy the cell when this is more than critically saturated. Macroscopic frost damage will occur when many unit cells are destroyed simultaneously. *The frost resistance problem is, therefore, to a great extent a moisture mechanics problem, and it can only be solved when the relevant water uptake processes are understood.*

There are many possibilities for water absorption causing frost damage:

1: Moisture is taken up before the concrete is exposed to freezing. This can occur due to isothermal water uptake, or due to water uptake during natural variations of the outer climate.
2: Moisture is taken up from outside during the freeze/thaw process. This might happen in nature, but is more significant during traditional unsealed freeze/thaw tests.
3: Moisture is redistributed internally during the freeze/thaw process. This might occur during natural freezing, but more often during freeze/thaw tests.

All these cases must be considered. So for example, by slight changes in the pre-treatment before freezing, or in the freeze/thaw process in a labtest, the water absorption changes. This might cause very big differences in the test results. The same concrete might be judged both frost resistant and non-frost resistant depending on how the test was performed. The critical moisture content is not changed by variations in the test procedure, only the real moisture content. This is enough to change the test results.

It is a difficult task to predict moisture conditions that are high enough to cause frost damage. This depends on the fact that frost damage almost always occur in, what can be called, the "over-capillary range", where we have no calculation or measurement methods, neither for moisture transport, nor for moisture fixation. One can define three "moisture ranges" for a porous material:

1: The hygroscopic range (below about 98% RH). In this range, moisture fixation is described by the sorption isotherms, and moisture transport is described by normal diffusion equations containing transport coefficients, that can be easily determined by many different test methods.
2: The capillary range (from about 98% RH to "capillary saturation"). Moisture fixation is described by "suction curves" describing the relation between capillary pressure and moisture content. Moisture transport is described by the same type of equations as for the hygroscopic range. The transport coefficients can be evaluated from a series of capillary absorption experiments; [25].
3: The over-capillary range (moisture content higher than that corresponding to "capillary saturation"). Moisture transport in this range is governed by quite other mechanisms than the mechanisms acting in the other two ranges. There are no capillary suction gradients or vapour pressure gradients causing water transport. Water is instead forced by differences in external pressure (e.g. "ice pressure" as in the hydraulic pressure mechanism, or "ice suction" as in the ice lens growth mechanism), or by dissolution and diffusion of entrapped air; [6]. The latter mechanism is described in the next paragraph.

5.2 Water uptake before freeze/thaw

Concrete placed for a long time in water will absorb more water than that corresponding to capillary saturation, S_{cap} (S_{cap} is indicated as a nick-point on a water absorption square-root of time curve for a thin specimen). The most plausible mechanism is a dissolution of air due to the over-pressure in enclosed air-bubbles contained in air-pores. The smaller the bubble, the bigger the over-pressure, and the more rapid the dissolution. Consequently, there will be a concentration gradient in dissolved air between small bubbles and coarse. The smallest bubbles will therefore "disappear" at first, and air from them migrates to coarser bubbles. From there, air migrates to bubbles that are even bigger, and finally to the surface. Air, that is dissolved, is replaced by water. It can be shown theoretically, that this inter-pore diffusion process causes an internal "suction" over a large portion of the concrete. Therefore, the water absorption process can be assumed to occur simultaneously across a rather big volume adjacent to the water source. The process is described in detail in [6].

The most simple case is isothermal long-term water absorption, where the specimen absorbs water unidirectionally, or when it is completely immersed. It can be shown, both theoretically and experimentally, that the water absorption process can be described by an equation of the following type:

$$S(t) = S_{cap} + A \cdot t^B \qquad (20)$$

Where $S(t)$ is the total degree of saturation after a period t of water absorption, S_{cap} is the capillary saturation (the nick-point in the absorption curve; see above), A is a coefficient determined mainly by the diffusivity of dissolved air through the saturated matrix, B is a coefficient determined mainly by the size distribution of the air-bubbles; $B < 0{,}50$.

This expression can be used for calculating a sort of potential service life, which is the time the concrete can be allowed to absorb water. The potential service life is:

$$t_{pot} = \{(S_{cr}-S_{cap})/A\}^{1/B} \tag{21}$$

The potential service life is of course not the same as the real service life in the real environment. It only giver en expression for the risk of frost damage in a "standard environment" which is very moist.

5.3 Needed research

Since moisture transport processes are so vital for understanding the frost destruction process, and for estimating the frost resistance, it is important that all kinds of moisture uptake and moisture movements, before and during freeze/thaw, are investigated. This requires many types of experiments, most of which are very difficult to perform, since it is moisture movements on the microscale that determines whether the concrete shall be frost resistant or not.

For composite materials, composed of two or more frost sensitive phases, it is also necessary to investigate the moisture conditions at interfaces, and moisture flow across interfaces. Concrete is such a material, since it always contains both porous interface zones between cement paste and aggregate, and in many cases also porous aggregate. Surface treated concrete or repaired concrete are other composite materials where water at the interface between the phases is to a great extent determining the frost resistance of the composite. The same might be true for carbonated concrete.

In high performance concrete with very low water/cement ratio, self desiccation could make the concrete frost resistant for a certain period; e.g the first years after production. One cannot exclude, however, that this effect is only temporary; c.f. paragraph 2.2.2. Therefore, the effect of self desiccation on the long-term moisture condition and the effect on the frost resistance ought to be studied.

6 References

1. Fagerlund, G. (1973) *Frost Resistance of Concrete with Porous Aggregate*, Swedish Cement and Concrete Research Institute, Research Fo 2:78, Stockholm.
2. Fagerlund, G. (1995) *Freeze-Thaw Resistance of Concrete*, Div. of Building Materials, Lund Insitute of Technology, Report TVBM-3060, Lund
3. Powers, T.C. (1962) Prevention of Concrete to Frost Damage to Green Concrete. *Bulletin RILEM*, No 14.
4. Fagerlund, G. (1980) *Influence of Slag Cement on the Frost Resistance of Concrete- a Theoretical Analysis*, Swedish Cement and Concrete Research Institute, Research Fo 1:80, Stockholm
5. Möller, G. (1962) Early Freezing of Concrete. Swedish Cement and Concrete Research Institute, *Applied Studies* No 5, Stockholm.
6. Fagerlund, G (1996) Predicting the Service Life of Concrete Exposed to Frost Action through a Modelling of the Water Absorption Process in the Air-Pore System, In*The modelling of Microstructure and its Potential for Studying Transport Properties and Durability*, (eds. H. Jennings et al.), Kluwer Academic Publishers.
7. Powers, T.C. (1949) The Air Requirement of of Frost Resistant Concrete, *Highway Res. Board*, Proceedings No 29.
8. Fagerlund, G. (1986) *The critical Size in Connection with Freezing of Porous Materials*, Cementa Report CMT 86039, Danderyd, Sweden.
9. Powers, T.C. and Helmuth, R.A. (1953) Theory of Volume Changes in Hardened Portland Cement Paste, *Highway Res. Board*, Proceedings, No 32.

10. Fagerlund, G. (1977) *Equations for Calculationg the Mean Free Distance between Aggregate Particles or Air-Pores in Concrete*, Swedish Cement and Concrete Research Institute, Research Fo 8:77, Stockholm
11. Philleo, R.E. (1955) *A Method for Analyzing Void Distribution in Air-Entrained Concrete*, Portland Cement Association, Tentative Paper, Chicago.
12. Verbeck, G. and Klieger, P. (1958) Calorimeter-Strain Apparatus for Study of Freezing and Thawing of Concrete, Res. and Devel. Labs. of PCA, Bull. 95.
13. Fagerlund, G. (1973) The Significance of Critical Degrees of Saturation at Freezing of Porous and Brittle Materials, In *Durability of Concrete*, ACI, Special Publication, SP 47.
14. Fagerlund, G. (1982) *The Influence of Slag Cement on the Frost Resistance of the Hardened Concrete*, Swedish Cement and Concrete Research Institute, Research Fo 1:82, Stockholm.
15. Powers, T.C. (1956) Resistance of Concrete to Frost at Early Ages, In *Winter Concreting*, Proc. of a RILEM Symposium, Copenhagen.
16. Rombén, L. (1973) Test results presented in *Report of Activities 1972/73*, Swedish Cement and Concrete Research Institute, Stockholm.
17. Klamrowski, G. and Neustupny, P. (1984) *Untersuchungen zur Prüfung von Beton auf Frostwiderstand*, Bundesanstalt für Materialprüfung (BAM), Forschungsbericht 100, Berlin.
18. Fagerlund, G. (1972) *Critical Degrees of Saturation at Freezing of Porous and Brittle Materials*, Lund Institute of Technology, Div. of Building Technology, Report 34, Lund. (In Swedish).
19. Fagerlund, G. (1994) *Influence of Environmental Factors on the Frost resistance of Concrete*, Div. of Building Materials, Lund Institute of Technology, Report TVBM-3059, Lund.
20. Fagerlund, G. (1995) *Frost Resistance of Concrete. Estimation of the Future Deterioration*, Div. of Building Materials, Lund Institute of Technology, Report TVBM-3067, Lund.
21. Fagerlund, G. (1992) *Effect of the Freezing Rate on the Frost Resistance of Concrete*, Nordic Concrete Research, Publ. No 11, Oslo
22 Fagerlund, G. (1996) Assessment of the Service Life of Materials Exposed to Frost, In Durability of Building Materials and Components (ed. C. Sjöström), Proc. of the 7:th Int. Conf. Stockholm, May 19-23, E & F Spon, London.
23. Warris, B. (1964) *The Influence of Air-Entrainment on the Frost-Reistance of Concrete*, Swedish Cement and Concrete Research Institute, Proceedings Nr 36, Stockholm.
24. Sandin, K. (1989) Moisture Conditions and Frost Effects in Cavity Brick Walls, *Bygg & Teknik,* Nr 4, Stockholm. (In Swedish)
25. Janz. M. (1997) .*Methods of Measuring the Moisture Diffusivity at High Moisture Levels*, Div. of Building Materials, Lund Institute of Technology, Report TVBM-3076, 1997.