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Basic principles for frost resistance

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Abstract
A general theory for an estimation of the potential service life of concrete exposed to frost action is presented. The starting point is the critical size which is a measure of the biggest piece of the cement paste that can be frozen in a completely saturated condition without being damaged. In practise a concrete will take up water in its air-pore system. The process is described and found to be a function of the shape and size distribution of the air-pore system and of the diffusivity of dissolved air. The critical thickness in combination with the air-pore size distribution can be used for a theoretical calculation of the critical water absorption in the air-pore system. By combining the water absorption in the practical situation and the critical absorption, the potential service life can be calculated. Examples of such calculations are given.

1. The critical size

1.1 General principles

When a water saturated piece of a porous material freezes some of its pore water is transformed into ice. The lower the temperature, the larger the fraction of frozen pore water. Freezing of water contained in a given pore might occur in situ, or it might occur after transfer of the water to an ice-body already existing in a neighbouring pore. In the first case a hydraulic pressure occurs due to the 9 % increase in volume when ice is transformed into ice and excess water has to move through the partly ice-filled pore system to the surface of the material piece. The mechanism is often referred to as the Hydraulic Pressure mechanism; [1]. In the second case, the driving force for water migration is the free energy differential between unfrozen water and ice; [2]. A mechanical pressure is excerted on the pore wall by the growing ice body. The mechnism is sometimes referred to as the Microscopic Ice Lens Segregation mechanism; [3]. It is equivalent to frost heave in soil which is sometimes called the Macroscopic Ice Lens Segregation mechanism ; [3].

It has never been clarified which of the two mechanisms is the most significant for concrete. Probably both mechanisms act simultaneously, the ice lens segregation mechanism being the most important for very dense concretes and for freezing in the presence of de-icing salts.

Theoretically, both mechanisms predict a reduction of the internal pressure caused by freezing when the size of the water saturated materials piece is reduced; [1], [2]. Thus, there exists a so-called critical size which is a function of the geometry of the saturated piece. One can distinguish between a critical diameter of a sphere, or a critical diameter of a cylinder, or a critical thicknes of a plate. If those critical sizes are transgressed the material piece will be damaged by freezing. If the real size is smaller than the critical no harm occurs because excess water can escape from the piece during freezing without causing damage.

The critical size depends on the destruction mechanism. For the hydraulic pressure the following general equation can be used:

$$f_t=0,09\cdot(dW_f/d\theta)\cdot(d\theta/dt)\cdot(1/K)\cdot f(X_{CR}) \qquad (1)$$

Where, f_t is the tensile strength (MPa), W_f is the freezable water (m^3/m^3 of material), θ is the temperature (°C), $dW_f/d\theta$ is the increase in amount of freezable water when the temperature is lowered by $d\theta$ $[m^3/(m^3\cdot{}^\circ C)]$, $d\theta/dt$ is the rate of temperature lowering (°C/s), K is the permeability $[m^2/(Pa\cdot s)]$, X_{CR} is the critical size (m), $f(X_{CR})$ is a function which depends on the geometry of the materials piece.

Example: for a saturated slice with the thickness D it is valid:

$$f(X_{CR})=(1/8)\cdot D_{CR}^2 \qquad (2)$$

$$D_{CR}=\{8\cdot f_t\cdot K / [0,09\cdot(dW_f/d\theta)\cdot(d\theta/dt)]\}^{1/2} \qquad (3)$$

Formulas for other geometries and a derivation of a general formula for the calculation of critical sizes are given in [4].

1.2 The critical spacing between air-filled pores

A real material is never completely saturated even during very moist conditions, but contains a number of air-filled pores that are bigger than about 10 μm; smaller pores becoming water-filled already during a very short water storage period.

The distance between adjacent air-filled pores is not constant but varies from pore to pore. It is however possible to derive an expression for the average pore spacing taking consideration also to the size distribution of air-filled pores. Such a formula is derived in [5] and is shown in eq (4). It expresses the probability that an arbitrary point in the water-filled part of the material shall be located within the distance L´ from the periphery of the nearest air-filled pore. Thus the average spacing is 2·L´.

$$a\cdot\{1+L'\cdot\alpha+(L')^2\cdot\alpha\cdot[u]_1/[u]_2+1,33\cdot(L')^3\cdot\alpha\cdot[u]_0/[u]_2\}=C \qquad (4)$$

Where, a is the total volume of air-filled pores (m^3/m^3 of material), $[u]_i$ is the i:th statistical moment of the size distribution of air-filled pores, α is the specific area of the air-filled pores; i.e. the total envelope area of all air-filled pores divided by their total volume (m^{-1}). C is a constant that is different for different probabilities that all points in the water-filled matrix shall be within the distance L´ from the nearest air-pore (be protected). For C=1 the probability is 63%; for C=2,3 the probability is 90 %, etc.

Thus, the value of L´ depends on the size of the portion of the water-filled matrix that shall be protected. In /5/ it is shown that the distance L´ for C=1 (63% probability) is equal to the so-called Philleo spacing factor; [6].

Eq (4) is a general expression giving a sort of *statistical spacing factor L´*. The material is damaged if L´ is transgressed. Hence, the more water in the material, the bigger the distance L´ and the bigger the risk that the material shall be damaged.

The traditional way of defining an average spacing between air-filled pores is to assume that all air-filled pores are of equal size and placed in a loose-packed array, every air-pore being surrounded by a cubic shell consisting of the water saturated matrix (cement paste). The biggest distance water has to be transported during freezing corresponds to the distance betwwn the corner of the cube and the periphery of the air-pore. This distance is called the *Powers´spacing factor*; /1/. The Powers spacing factor L is calculated by[1] :

$$L=\{3/\alpha\}\cdot\{1{,}4[Vp/a+1]^{1/3}-1\} \qquad (5)$$

Where V_p is the volume fraction of the water saturated matrix (cement paste), no air-filled pores included (m^3/m^3)

Geometrical relations exist between the critical spacing factor and other critical sizes; see [4]. The relation is probably to a certain extent depending on the major destruction mechanism. In the following only the hydraulic pressure mechanism is regarded. Then, the relation between the critical thickness of a slice, D_{CR} -Eq(3)- and the critical spacing factor, L, is:

$$D_{CR}=2\cdot L_{CR}\{2\cdot\alpha\cdot L_{CR}/9+1\}^{1/2} \qquad (6)$$

Thus, the relation is also a function of the size of the air-filled pores which is expressed in terms of the specific area α.

It is reasonable to assume that D_{CR} and L_{CR} are functions of the w/c-ratio. An approximative relation between D_{CR} and the w/c-ratio can be derived assuming simple relations for the effect of the w/c-ratio on the freezable water, the tensile strength and the permeability.

Assumption 1: The tensile strength is inversely proportional to the w/c-ratio:

$$f_t=Const/(w/c) \qquad (7)$$

Assumption 2: The freezable water at any given temperature is supposed to be a certain fraction γ of the capillary porosity. The value of γ increases with lowered temperature.This assumption is based on measurements of the freezable water of cement paste that have underwent a drying-resaturation cycle; [7]. For a more general discussion of the freezable water in concrete refer to [8].

$$dW_f/d\theta=const\cdot\gamma\cdot P_{cap} \qquad (8)$$

The capillary porosity P_{cap} is; [10]:

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[1] In the original formulation by Powers /1/ all air-pores were included in the values α and a. Thus Powers assumed that all so-called air-pores (i.e. pores bigger than about 10 μm) always stayed air-filled. This leads to an under-estimation of the true spacing between pores that are actually air-filled during natural conditions. Powers´ definition gives a *fictitious spacing factor* whilst eq (5) gives a *true spacing factor*. The difference in the two values is significant ; [9].

$$P_{cap}=(w/c-0{,}39\cdot\kappa)/(w/c+0{,}32) \qquad (9)$$

The degree of hydration κ can only become complete for w/c-ratios above 0,39. For lower w/c-ratios the maximum possible degree of hydration is:

$$\kappa_{max}=(w/c)/0{,}39 \quad \text{for } w/c < 0{,}39 \qquad (10)$$

The degree of hydration is supposed to be a fraction β of the maximum possible the freezable water. Then, the degree of hydration is:

$$\kappa=\beta\cdot(w/c)/0{,}39 \quad \text{for } w/c<0{,}39 \qquad (11)$$

$$\kappa=\beta \quad \text{for } w/c>0{,}39 \qquad (12)$$

Inserting eq(9), (11) and (12) in eq(8) gives the following relations for the freezable water:

$$dW_f/d\theta=\text{const}\cdot\gamma\cdot(w/c)(1-\beta)/(w/c+0{,}32) \quad \text{for } w/c < 0{,}39 \qquad (13)$$

$$dW_f/d\theta=\text{const}\cdot\gamma\cdot(w/c-0{,}39\cdot\kappa)/(w/c+0{,}32) \quad \text{for } w/c > 0{,}39 \qquad (14)$$

Assumption 3: The permeability K of the matrix (the cement paste) is assumed to be reduced when ice is formed. The residual permeability at a certain temperature is supposed to be directly proportional to the non-freezable water. Thus, pores containing ice are not supposed to take part in the transport process. Then it is valid:

$$K=\text{const}\cdot(w_{nf}/c)\,/(w/c+0{,}32)=\text{const}\cdot(w_e/c-w_f/c)\,/(w/c+0{,}32) \qquad (15)$$

Where, w_{nf} is the non-freezable water (kg), w_e is the total evaporable water (kg), w_f is the freezable water (kg), c is the cement content (kg).

The total evaporable water is supposed to correspond to the total pore volume in the matrix and, as said above, the freezable water is a fraction γ of the capillary water. Then, the following relations are valid:

$$w_e/c=w/c-0{,}19\cdot\kappa \qquad (16)$$

$$w_f/c=\gamma\cdot(w/c-0{,}39\cdot\kappa) \qquad (17)$$

Where κ is the degree of hydratation.

The permeability of the frozen cement paste therefore is:

$$K=\text{const}\cdot\frac{w/c-0{,}19\cdot\kappa-\gamma\cdot(w/c-0{,}39\cdot\kappa)]}{(w/c+0{,}32)} \qquad (18)$$

Finally, after inserting equations (7), (13), (14) and (18) in (3) the following relations are obtained for the critical thickness, D_{CR}:

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

$$D_{CR} = \text{const}\cdot\left\{\frac{w/c\cdot(1-\gamma)+\beta\cdot(0{,}39\cdot\gamma-0{,}19)}{\gamma\cdot w/c\cdot(w/c-0{,}30\cdot\beta)}\right\}^{1/2} \qquad (20)$$

Those equations can be used for a calculation of the effect of the w/c-ratio on the critical size. Calculations are made for a degree of hydration that is 75% of the maximum possible (i.e. $\beta=0{,}75$). The amount of freezable water is supposed to be 75% of the capillary porosity (i.e. $\gamma=0{,}75$). This corresponds to a temperature of about -20°C ; see [8]. The critical spacing factor L_{CR} is calculated from the critical thickness by eq(6). The specific area of the air pore system is assumed to be 30 mm^{-1} corresponding to a pore diameter of 200 µm. D_{CR} and L_{CR} are supposed to be 1 at the w/c-ratio 0,40.The result of the calculations is shown in Table 1.

Table 1: Calculated effect of the w/c-ratio on the critical size of cement paste ($\gamma=0{,}75$, $\beta=0{,}75$, $\alpha=30$ mm^{-1}).

w/c	D_{CR}	L_{CR}
0,70	0,46	0,53
0,60	0,55	0,63
0,50	0,69	0,73
0,40	1,00	1,00
0,35	1,11	1,07
0,30	1,20	1,10
0,25	1,32	1,20
0,20	1,47	1,30

Thus, according to the theory presented, the critical size increases with decreasing w/c-ratio. The critical size can be calculated from measurements of the critical water absorption and utilizing the air-pore size distribution. The calculation is the inverse of the calculation of the critical water absorption from the critical size; see paragraph 4 below. Preliminary calculations -/9/- indicate that a normal value of the critical spacing factor L for concretes with w/c-ratio of about 0,45 is of the order of size 0,35 mm[2]. This means that the variation in the critical spacing factor might be from about 0,50 mm for a very dense cement paste (w/c=0,20) to about 0,20 mm for a porous paste (w/c=0,70).

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[2] This is the critical true spacing factor. The critical fictitious spacing factor assuming all air-pores always being air-filled is of the order of size 0,25 mm for freezing in pure water and about 0,16 to 0,20 mm for freezing in presence of de-icing salts; [9].

3. The water absorption in the air pore system

During a capillary water uptake process air bubbles will always be entrapped in coarse pores surrounded by finer continuous pores. This process of enclosing air bubbles in pores is described in [11]. The air bubble is exposed to an over-pressure caused by the curved meniscus between the air bubble and the water. The bubble will therefore be compressed.The relation between the volume of the compressed air bubble and the total volume of the empty pore can be described by Boyle´s law. The following relation is valid; [11]:

$$(V_1/V_0)^{1/3}\cdot(V_0/V_1-1)=2\cdot\sigma/(10^5\cdot R) \qquad (21)$$

Where, V_0 is the pore volume (m^3), V_1 is the volume of the compressed air bubble inside the pore (m^3), R is the radius of the empty pore (m), σ is the surface tension between air and water (N/m), 10^5 is the atmospheric pressure (Pa).

Some relations between the pore radius and the relative volume V_1/V_0 are given in Table 2.

Table 2: Relation between the pore radius and the relative volume of the compressed air-bubble.

R (µm)	V_1/V_0
0,05	0,006
0,10	0,018
1	0,32
10	0,87

This means that pores that are smaller than 0,1 µm will be almost completely compressed already during the first capillary uptake process. Such pores are therefore almost always saturated during normal moist conditions. Bigger air-pores stay air-filled for some time but the over-pressure inside the air bubble makes air gradually dissolve in the surrounding pore water.

The process described implies that when a piece of airentrained cement paste is placed in water all the gel pores and the capillary pores become completely water-filled already after a very short time. An isolated air-pore with diameter above about 1 µm surrounded by cement paste will however stay air-filled for a certain time, the length of which depends on the size of the bubble and on the diffusivity of dissolved air through the cement paste.

The solubility of air increases linearily with increased pressure. At +20°C the solubility of air in water is $2{,}5\cdot10^{-7}\cdot P$ kg/m^3 where P is the air pressure. This is given by the Laplace law:

$$P=10^5+2\cdot\sigma/r \qquad (22)$$

Where 10^5 is the normal atmospheric pressure in Pa and r is the radius of the air bubble. The bubble will be dissolved rapidly if the amount of pore water surrounding the bubble is big enough to dissolve all the air. In such a case no diffusion of dissolved air to the surface of the specimen or to distant coarser pores is needed. An approximative expression for the size of the bubble that can dissolve locally can be calculated; [11].

$$t > \{[1+\frac{42(1+105\cdot r/(2\cdot\sigma))}{P_{tot}}]^{1/3}-1\}\cdot r \qquad (23)$$

Where, t is the required thickness of the cement paste shell immediately surrounding the air bubble (m), r is the radius of the bubble that can dissolve (m), P_{tot} is the total porosity of the cement paste matrix (m^3/m^3)

$$P_{tot}=(w/c-0,19\cdot\kappa)/(w/c+0,32) \qquad (24)$$

Where κ is the degree of hydration. The thickness t is evidently half the distance between adjacent air-pores. For small pores this is a bit smaller than the average Powers´ spacing factor L (i.e. $t < L$). Eq (23) shows that in a cement paste with the w/c-ratio 0,40 and a spacing of 0,15 mm between small pores all air pores with a diameter of less than about 30 μm will dissolve very rapidly in the surrounding pore water.

One can evidently conclude that air-pores with diameter bigger than about 20 to 30 μm will contain air bubbles even after a certain time of water storage. There will however be a gradual and slow transfer of air from every bubble to adjacent coarser air bubbles. The driving force for this transport of air is the difference in air pressure and hence in the solubility of air. The smaller the bubble the bigger the pressure and solubility. Consequently, there will be a complicated network of inter-pore diffusion of air. It can be shown that this interdiffusion causes a net reduction in air volume; [11]. Therefore it causes a water uptake in the cement paste even if no air is transferred to the surface of the paste. In reality, there is also a transfer of air to the surface making the water uptake still bigger. Principally, after long time, the total volume of water uptake is equal to the total air volume transferred to the surface and leaving this.

The inter-pore air diffusion between two adjacent air-bubbles-one small and one big- can be described by:

$$q=\delta\cdot[1+1/\varepsilon]\cdot 4\pi\cdot s\cdot 2\cdot\sigma \qquad (25)$$

Where, q is the flow (kg/s), δ is the diffusivity of dissolved air in pore water (m^2/s), ε is the assumed constant ratio between the inter-pore distance and the radius of the smallest pore (m/m), s is the solubility of air in water [$kg/(m^3\cdot Pa)$], σ is the surface tension between air and water (N/m)

The following values on the constants are used below: $\varepsilon=5$, $s=2,4\cdot 10^{-7}$, $\sigma=0,074$ N/m. Then eq(25) can be written:

$$q=5,6\cdot 10^{-7}\cdot\delta \qquad (26)$$

The diffusivity of air in bulk water at room temperature is $2\cdot 10^{-9}$ m^2/s. In pore water it ought to be 2 or three decades lower; i.e 10^{-11}-10^{-12} m^2/s. A very important consequence of eq (26) is that the diffusion rate can be regarded independent of the pore size.

The diffusivity is probably a function of the w/c-ratio. The following simple expression is suggested as a first approximation:

$$\delta = \text{const} \cdot (w/c)^2 \qquad (27)$$

The constant is not known. One possibility is to assume that the diffusion coefficient is the same as for diffusion in bulk water ($2 \cdot 10^{-9}$ m^2/s) when the w/c-ratio is 10 corresponding theoretically to a porosity of 95% at full hydration.Then the diffusivity for other w/c-ratios is:

$$\delta = 10^{-11} \cdot (w/c)^2 \qquad (28)$$

Thus for the w/c-ratios 0,80, 0,60 and 0,40 the diffusion coefficients are $6{,}4 \cdot 10^{-12}$, $3{,}6 \cdot 10^{-12}$ and $1{,}6 \cdot 10^{-12}$ m^2/s respectively.

In a real air-pore system there are numerous air-pores and a very complicated diffusion pattern. A detailed theoretical analysis of the total process has been performed in [11]. The starting point is the pore size distribution and the fact that the diffusivity can be regarded as independent of the pore size; eq (26). There are two main models for the water absorption process:

Model 1: A coarser air bubble does not start to fill by water until all smaller bubbles have become completely water-filled.

Model 2: All air bubbles start to absorb water with the same rate, right from the beginning of water storage, the smaller bubbles being saturated before the larger due to the fact that they contain less air.

In reality the process is probably a mixture of the two models. Model 1 is however the most plausible one from a theoretical point of view. It is used in the following.

In [11] an analysis is made of the water absorption process in an arbitrary air-pore system. A degree of saturation of the air-pore system is introduced and is defined:

$$S_a = w_a / a_0 \qquad (29)$$

Where, w_a is the water absorbed in the air pore system (m^3), a_0 is the total air-pore volume when the diffusion process starts (m^3)

In a_0 are not included air-pores that collapse already during the very first absorption period; i.e, pores smaller than about 20 μm (see above).

Two types of air-pore size distributions are analysed:

1: *Exponential function*

$$f(r) = \ln(b)/b^r \qquad (30)$$

Where, $f(r)$ is the frequency function of pore radii, b is a constant determining the fineness of the pore system, r is the pore radius (m)

The coefficient b is coupled to the specific area of the empty air-pore system, α_0 (valid when all air-pores are actually air-filled):

$$b = \exp(\alpha_0) \qquad (31)$$

2: *Power function*

$$f(r)=1/(r)^{b} - 1/(r_{max})^{b} \tag{32}$$

Where, b is a constant determining the fineness of the pore system, r_{max} is the radius of the biggest air-pore (m).
The coefficient b is related to the specific area of the entire air-pore system by the following equation:

$$\alpha_o= \{4\cdot(4^{-b})/(3^{-b})\}\cdot\{r_{max}^{3-b} - r_{min}^{3-b}\}/\{r_{max}^{4-b} - r_{min}^{4-b}\} \tag{33}$$

Where r_{min} is the radius of the smallest air-pore.
The analysis of the time process of the water absorption in the air-pore system gives the following relations for a degree of saturation of the air-pore system (S_a) between 0,1 and 0,6:

a) *Exponential function*

$$S_a(t)=39,6\cdot\alpha_o^{2,36}\cdot[q\cdot t]^{0,51} \tag{34}$$

Where, t is the water absorption time (s), q is the rate of water inflow in a pore given by eq(26) (kg/s).

Inserting eq(26) gives:

$$S_a(t)=2,56\cdot 10^{-2}\cdot\alpha_o^{2,36}[\delta\cdot t]^{0,51} \tag{35}$$

Where α_o is in mm^{-1}.

This expression is plotted in Fig 1 for the two diffusivities $\delta=10^{-11}$ and $\delta=10^{-12}$ m^2/s. It is quite clear that the rate by which the air-pore system becomes inactivated is a function of the fineness of the air-pore system; the finer the air-pore system the more rapid the inactivation.

b) *Power function*

$$S_a(t)=4,47\cdot 10^{-10}\cdot\ \alpha_o^{4,49}\ [q\cdot t/(10^{-18}\cdot\rho_o)]^{2,08\cdot\alpha_o^{-0,65}} \tag{36}$$

Where α_o is in mm^{-1}, ρ_o is the density of air (1,25 kg/m^3). q is given by eq (26). Thus eq(36) can be written:

$$S_a(t)=4,47\cdot 10^{-10}\cdot\alpha_o^{4,49}\ [4,48\cdot 10^{11}\cdot\delta\cdot t]^{2,08\cdot\alpha_o^{-0,65}} \tag{37}$$

This expression is plotted in Fig 2 for the same two diffusivities as in Fig 1. A comparison with Fig 1 shows that the rate by which the air-pore system is filled by water is not only dependent of the specific area but also on the general shape of the pore size distribution. The power function gives a considerably slower water filling than the exponential function at the same specific area.

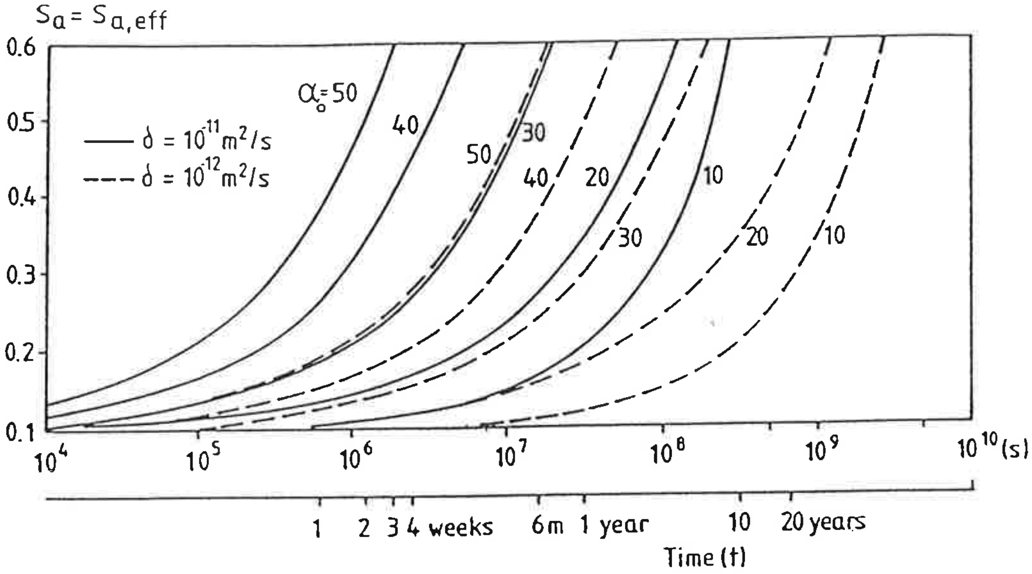

Fig. 1. The degree of saturation of the air-pore system as a function of the water absorption time. Exponential frequency function.

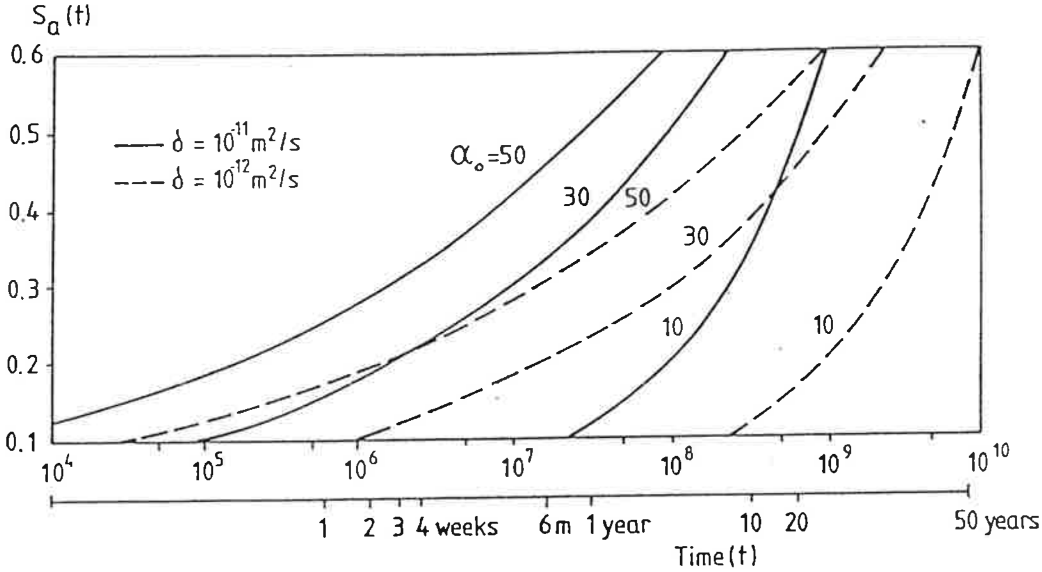

Fig. 2. The degree of saturation of the air-pore system as a function of the water absorption time. Power frequency function.

The analysis shows that the water absorption in the air pore system can be described by the following type of expression:

$$S_a(t)=A \cdot t^B \tag{38}$$

Where the coefficients A and B are functions of the diffiusivity of dissolved air in pore water and of the fineness and shape of the air-pore system.

4. The critical water absorption

The absorption process described in 3 above causes changes in the residual specific area and the residual air content of that part of the air pore system that is still air-filled. It is assumed that model 1 of water absorption is valid; viz. a coarser pore does not start to fill by water until all smaller pores are completely water-filled.

The residual total envelope area of all air-filled pores A_r is:

$$A_r= \int_{r_{a,min}}^{r_{max}} f(r) \cdot 4 \cdot \pi . r^2 \cdot dr \tag{39}$$

Where, f(r) is the frequency functuion of pore radii, r_{max} is the radius of the coarsest air-pore (m), $r_{a,min}$ is the radius of the smallest air-filled air-pore (m)

The residual air-filled pore volume a_r is:

$$a_r= \int_{r_{a,min}}^{r_{max}} f(r) \cdot (4 \cdot \pi/3) \cdot r^3 \cdot dr \tag{40}$$

The residual specific area α_r is:

$$\alpha_r=A_r/a_r \tag{41}$$

Then, according to eq (5) the residual spacing factor L_r is:

$$L_r=(3/\alpha_r) \cdot \{1{,}4(V_p/a_r+1)^{1/3}-1\} \tag{42}$$

This means that the gradual water absorption in the air-pore system makes the spacing between air-pores bigger and bigger. At a certain critical degree of saturation of the air-pore system, $S_{a,CR}$, the residual spacing equals the critical. If this water content is transgressed frost damage will occur. The time needed for this to happen depends on the air-pore distribution, the total air content, the shape of the air-pore system and the w/c-ratio; the latter determining the critical spacing factor and the diffusivity of dissolved air.

Two examples of the changes in the spacing factor due to water absorption are seen in Fig 3. The air-pore system is supposed to be of the exponential type described by eq(30) but of different fineness; one fine with the total specific area α_0=30 mm^{-1} (b=1,031 when r is expressed in µm); one coarse with the total specific area α_0=20 mm^{-1} (b=1,020 when r is in µm). The total air content a_0 is assumed to be 4 %. The critical spacing factor is supposed to be 0,40 mm for both concretes (i.e. the w/c-ratio is the same).

The mutually connected values α_r, a_r and L_r calculated by eq (41), (40) and (42) are shown in Fig 3. The smallest air-filled (biggest water-filled) pore when $S_{a,CR}$ is reached is called r_{CR}. The corresponding residual specific areas and air contents are called α_{CR} and a_{CR} respectively. The values listed in Table 3 are valid for the two air pore systems.

Table 3: Values corresponding to the critical absorption in the pore-systems in Fig 3.

Parameter	Coarse-porous; α_0=20 mm^{-1}	Fine-porous; α_0=30 mm^{-1}	
r_{CR}	105 µm	r_{CR}	115 mm
α_{CR}	15 mm^{-1}	α_{CR}	18 mm^{-1}
a_{CR}	3,3 %	a_{CR}	2,25 %
$S_{a,CR}$	1-3,3/4=0,175	$S_{a,CR}$	1-2,25/4=0,438

The calculations show that much more water must be absorbed in the finest air-pore system before a frost damage can occur. This is a positive factor. On the other hand, the analysis presented in paragraph 3 shows that the water absorption is more rapid the finer the air-pore system. Therefore it is not necessarily so that the finest air-pore system gives the highest service life. This fact is treated further in the next paragraph.

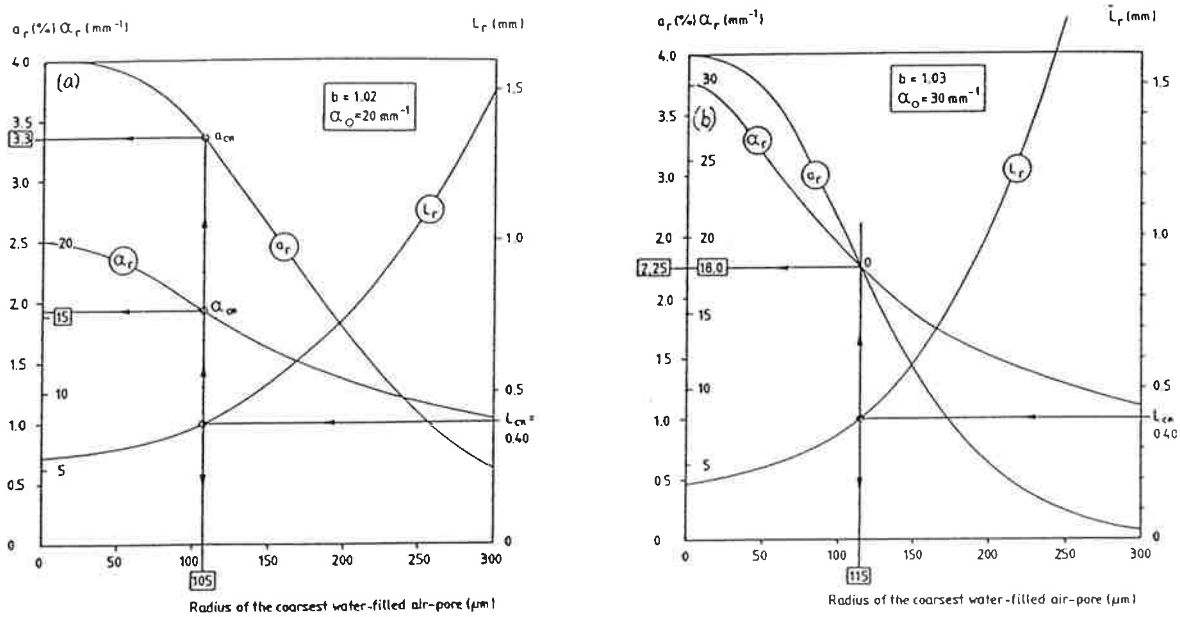

Fig. 3. Example of a calculation of the critical water absorption in the air-pore system. (a) Coarse-porous, (b) Fine-porous.

5. The potential service life

The potential service life can be defined; [12]:

$$S_{a,CR}=S_a(t_p) \tag{43}$$

Where, $S_{a,Cr}$ is the critical degree of saturation of the air-pore system, $S_a(t_p)$ is the real degree of saturation of the air-pore system after time t_p of uninterrupted water absorption, t_p is the potential service life

According to what is said in paragraphs 3 and 4 the two paramers $S_{a,CR}$ and $S_a(t)$ are functions of the pore shape and size distribution and of the w/c-ratio.

$S_{a,CR}=f\{\text{air-pore system; } L_{CR}\}$	[see paragraph 4]
$L_{CR}=f\{w/c\}$	[see eq (19), (20)]
$S_a(t)=f\{\text{pore structure; diffusivity}\}$	[see eq(34), (36)]
$\text{Diffusivity}=f\{w/c\}$	[see eq (27)]

As an example is calculated the potential service life for the two concretes with the air-pore systems shown in Fig 3. The w/c-ratio is supposed to be 0,50. This means that the diffusivity is assumed to be $2{,}5\cdot 10^{-12}$ m^2/s [Eq(28)]. The water absorption in the air-pore system is given by Eq (34).

$$S_a(t)=2{,}56\cdot 10^{-2}\cdot\alpha_o^{2,36}[2{,}5\cdot 10^{-12}\cdot t]^{0,51} \tag{34´}$$

Then the potential service lives are:

- Coarse-porous air-pore system; $\alpha_o=20$ mm^{-1} [$S_{a,CR}=0{,}175$ (Table 3)]

  $t_p=1{,}65\cdot 10^7$ seconds = 190 days
- Fine-porous air-pore system; $\alpha_o=30$ mm^{-1} [$S_{a,CR}=0{,}438$ (Table 3)]

  $t_p = 1{,}53\cdot 10^7$ seconds = 177 days

The finest air-pore system gives the highest tolerable water absorption but in this case not the longest service life, which depends on the more rapid water absorption in the finest pore system. Similar parameter studies can be made for other pore systems, other air contents, other w/c-ratios and other critical spacing factors.

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