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Division of Building Materials

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Contribution to the International Workshop on Freeze-Thaw
and Deicing Salt Scaling Resistance of Concrete
Québec August 30-31, 1993

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Abstract

A theory is presented for the estimation of the service life of concrete exposed to frost action. It is based on a separation of the frost resistance problem in two parts;

(i) one part that is only a function of the material itself and which is expressed in terms of a critical water content or a degree of saturation which is a "fracture value" being almost independent of the outer conditions (except for the lowest temperature and the internal salt concentration). The critical degree of saturation is a consequence of the existence of a critical distance of water transfer during freezing. Some experimental data for the critical distance are given.

(ii) one part that is a function of the wetness of the environment and which is expressed in terms of a time function of the capillary water uptake and the long term water absorption in the air-pore system. It is probably also a function of the salt concentration outside and inside the concrete. It is shown that the long term water absorption in pure water can often be described and extrapolated by simple equations.

The application of the theory is shown by three examples.

Keywords: Frost Resistance, Salt Scaling, Service Life, Capillarity, Water Absorption, Spacing Factor, Air Pore Structure.

1 Destruction mechanisms - the critical size

Water confined in the pore system of a porous material, when freezing, exposes the pore walls to stresses which might, in some cases, cause severe damage to the material. The explanation closest at hand is the 9% increase in volume of water transformed into ice. Excess water is expelled from the freezing site to an adjacent air-filled space that is large enough to accomodate the water. During this flow, which occurs in a very narrow and partly ice-filled pore system, the pore walls are exposed to stresses that are often referred to as hydraulic pressure. The mechanism was for the first

time analyzed theoretically by Powers (1949).

Another destruction mechanism, which should theoretically be of particularly great importance in very dense materials (low w/c-ratios) and/or when freezing occurs in the presence of de-icing salts, is analogous with the mechanism that causes frost heave in the ground. Ice bodies which have already been formed in coarser pores are, due to differentials in free energy between ice and water, able to attract unfrozen water from finer capillary pores and gel pores. Thus, there will be a water transfer towards the freezing site. The ice body will grow and it will thereby expose the pore walls to pressure. The free energy of the ice body will therefore increase at the same time as the free energy of the unfrozen water decreases due to the internal desiccation caused by the water flow. The growth of the icebody will not cease until its free energy is equal to that of the unfrozen water. Considerable pressure, high enough to seriously damage the material, could be built up. The pressure ought to be enhanced when the pore system contains salts; Powers (1956). The mechanism has been treated theoretically by numerous scientists. The first application to concrete was made by Powers & Helmuth (1953). Other references are Powers (1956), (1965).

The relative importance of those two damage mechanisms has not been fully clarified. It is quite clear, however, that the second mechanism, in order to be significant, requires a large fraction of unfrozen water also at rather low temperatures. Therefore, it ought to be most pronounced in materials with low W/C-ratios or other dense concretes.

There are also other destruction mechanisms suggested or modifications of the two mechanisms described above. Such theories have been put forward by Everett (1961), Haynes (1964), Dunn & Hudek (1965), Setzer (1978), Litvan (1972) and others.

One can show theoretically that the hydraulic pressure mechanism as well as the "growing ice body" mechanism predicts that the destructive forces increase with increasing distance between the freezing site and the nearest air-filled space; Powers (1949), Powers & Helmuth (1953). The concrete will be damaged in areas where this distance exceeds a certain critical value. This critical distance will adopt an individual value for each individual concrete and specimen geometry. One such critical distance is the critical thickness being the thickest possible completely water saturated plate of the actual concrete. Another critical distance is the critical shell thickness (or the critical Powers spacing factor) being the thickest possible water saturated cement paste shell surrounding an air-filled spherical cavity having an impermeable outer surface. There is also a critical sphere etc. Simple relations exist between the different sizes; if one of them is known any other can be calculated; Fagerlund (1986).

The relation between the critical thickness DCR and the true

critical spacing factor LCR is:

$$DCR = 2 \cdot LCR \{ 2 \cdot \alpha \cdot LCR / 9 + 1 \}^{1/2} \quad (1)$$

Where α is the specific area of the air-void enclosed by the shell. Thus, for a given concrete the relation between LCR and DCR depends on the specific area of the air-pore system. (Note; strictly speaking, eq (1) is only valid when destruction is caused by the hydraulic pressure mechanism).

2 The fictitious and the true spacing factor

Many investigators have proven experimentally the existence of critical distances of concrete; e.g. Ivey & Torrans (1970) and Bonzel & Siebel (1977). The values seem to depend on the environmental conditions; the critical Powers spacing factor $(L_o)_{CR}$ is often claimed to be about 0,25 mm for freezing in pure water and 0,16 to 0,20 mm for freezing in 3 % NaCl-solution. For very dense concretes the values seem to be higher; Gagne al. (1985). The critical spacing factors are always determined by comparing the results of optical studies of the air-pore structure with results of freeze/thaw experiments of companion specimens. The values $(L_o)_{CR}$ are therefore based on the assumption that all spherical air-pores observed in the specimen are actually air-filled during the freeze/thaw test. This is not the case, however. Therefore, the values $(L_o)_{CR}$ determined in this way are fictitious and considerably smaller than the true values LCR based on the fraction of the air-pore system that is actually air-filled during the freeze/thaw test. The significance of the two different spacing factors is further discussed below.

The spacing factor L of a system of spherical pores in a material matrix is calculated by the Powers equation.

$$L = \{ 1,4 \cdot [V_p/a + 1]^{1/3} - 1 \} \cdot 3/\alpha \quad (2)$$

Where α is the specific area of the pore system the spacing of which is of interest, a is the volume of this pore system and V_p is the material volume within which the actual pore system is located, exclusive of the pores themselves. Normally, in a concrete, V_p is the volume of the cement paste phase inclusive of fine aggregate interfering with the pores.

3 Direct measurements of the critical true spacing factor

Some attempts have been made to experimentally determine the order of size of the critical true spacing factor of cement paste; Fagerlund (1981), Löfgren & de Scharengrad (1991). In the first study the W/C-ratio varied between 0,3 and 0,8. 3-year old water-cured and completely saturated air-free specimens were pre-dried at +50°C and were then re-saturated by vacuum treatment. They were immersed either in pure water or in 3 % NaCl-solution whereupon they were freeze/thaw tested between room temperature and -20 °C with a rate of temperature lowering of 2,5 °C/h in the interval 0°C to -10°C. The duration of each cycle was 16 hours of freezing and 8 hours of thawing. Since the specimens contained no air, they were fragmented already during the first few cycles. An increasing number of cycles did not decrease the size of the fragments. This size is a measure of the critical thickness. The fragmented specimen was subjected to a sieve analysis on basis of which the critical thickness could be estimated. The results are shown in fig.1. The critical thickness is almost independent of the W/C-ratio and is lowest for freezing in pure water. The following mean values are valid for W/C > 0,40 à 0,45. LCR has been calculated by eq (1) assuming that the specific area is 15 mm⁻¹.

Freeze/thaw in pure water	DCR=1,2 mm; LCR=0,40 mm
Freeze/thaw in 3% NaCl-solution	DCR=1,8 mm; LCR=0,54 mm

Frost damage should therefore occur when the spacing factor between air-filled pores exceeds about 0,40 mm for freezing in pure water and about 0,54 mm for freezing in salt solution. This might seem remarkable since, as mentioned above, the critical fictitious spacing factor is lower for freezing in salt solution. Also, in practice, freezing in salt water involves considerably more severe damage. The explanation closest at hand is that the salt gives rise to a higher moisture content in the concrete surface. The positive effect of the larger critical size is therefore counteracted by an increased water absorption in the air-pore system; see sections 9 and 10. Another remarkable observation is that the critical spacing factors are much higher than the fictitious values.

4 Indirect measurements of the critical true spacing factor

The critical true spacing factor (hereafter called the critical spacing factor) can also be calculated theoretically if the so called critical degree of saturation SCR and the air-pore distribution curve are known. The mathematical procedure is presented in Fagerlund (1979). Calculations made indicate a rather good agreement with the direct measurements presented above.

In Fagerlund (1981) a calculation is made for a concrete with a W/C-ratio of 0,54, a total air content a_0 of 7,1 % and an experimentally determined SCR-value of 0,80; see fig. 3. The air-pore distribution curve was determined by means of the manual linear traverse method. The calculated LCR-value is between 0,37 and 0,42 mm which can be compared with the experimentally determined mean value 0,40 mm; fig. 1. The different values 0,37 and 0,42 mm are based on different definitions of the cement paste volume; 0,42 implies that all aggregate particles smaller than 0,5 mm are included in the "cement paste" phase; 0,37 implies that no aggregate particles are included. According to an analysis performed in Fagerlund (1978) a certain fraction of the finer aggregate ought to be included when calculating the spacing factor. The reason is that the inter-particle spacing of this aggregate fraction is of the same order of size as the air pores.

Some other examples are shown in fig.2. The calculations are based on measurements of the SCR-values and the air-pore distribution curves of 8 concretes containing cement with different amounts of ground granulated blast furnace slag; Fagerlund (1982). Two different concretes with different air contents were tested for each cement type. The two LCR-values differ somewhat. One reason for this is that the the real air-pore distributions were not utilized but merely the standard distribution according to eq (3) adjusted to the measured curve. The agreement between the theoretical and the real distributions is however not perfect.

$$f(r) = n \cdot \ln b/b^r \quad (3)$$

Where r is the pore radius and $f(r)$ is the frequency function of pore radii. n and b are constants adjusted to the measured distribution. The absolute values of the calculated LCR-values are a bit smaller than those found by direct freezing; see section 3.

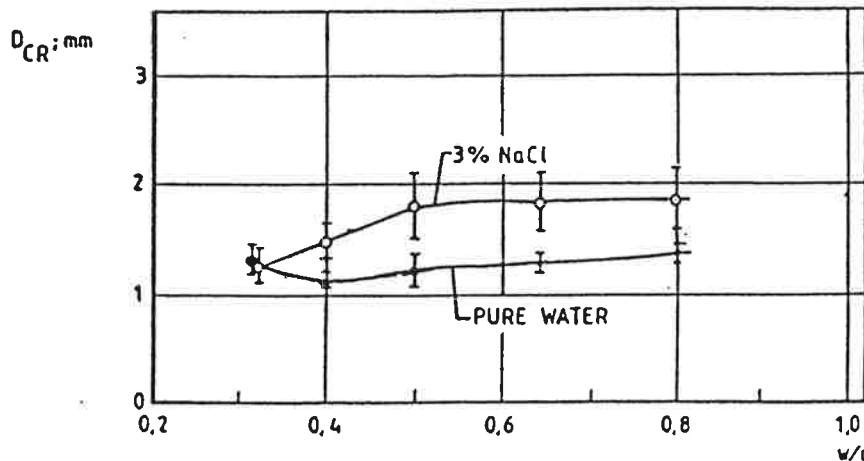


Fig.1. Experimental determinations of the true critical thickness of OPC-pastes which have undergone a drying/wetting cycle; Fagerlund(1981).

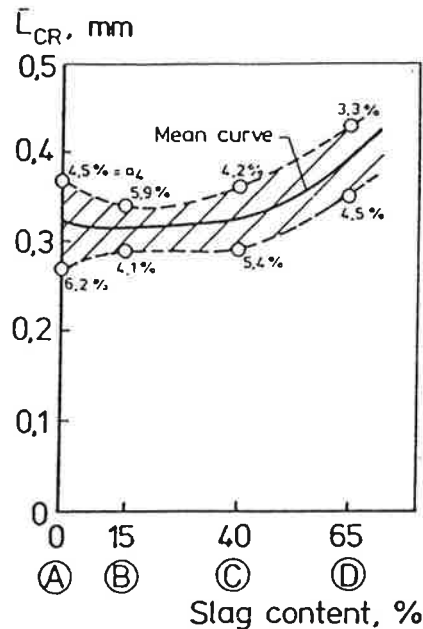


Fig.2. The true critical spacing factor of slag cement concretes. The values are based on experimentally determined SCR-values and air pore distributions; Fagerlund(1982).

5 The critical degree of saturation

The existence of a critical size implies the existence of a critical water absorption in the air pore system and the existence of a critical degree of saturation of the concrete as a whole; Fagerlund (1979). For a given value of L_{CR} , the critical air pore absorption and therefore the SCR-value will be different for different air pore distribution curves and air contents. Thus, the SCR-value is individual for each concrete despite the fact that the value of L_{CR} is the same. This was first pointed out by Warris (1964). Degree of saturation is defined:

$$S = W_e / \epsilon \quad [\text{volume/volume}] \quad (4)$$

Where W_e is the total evaporable water volume in the concrete and ϵ is its total pore volume (porosity) including all compaction pores, air pores and aggregate pores. In almost all cases, the occurrence of the moisture level SCR implies that a certain fraction of the air pore system is water-filled. This is the reason why the experimentally determined true L_{CR} -values presented above are considerably larger than the fictive (L_0) $_{CR}$ -values (0,25 mm and 0,16 to 0,20 mm) on which a certain agreement has existed for a long time. These "tra-

ditional values" are valid for the entire air pore system and imply that no part of this is water-filled during a freeze/thaw test. Therefore, in determining $(L_0)_{CR}$ by the Powers equation (2) the specific area of the air-pore system has always been assumed to be α_0 which is valid for the "dry" air pore system although, in reality, one should use a much smaller value α_r valid for the part of the air pore system that is actually air-filled; see Fig 12. The smallest air pores are water-filled at first -Fagerlund (1993)- and since they are numerous they contribute very much to the value of α_0 . Therefore the difference between α_0 and α_r is often big. Besides in calculating the value of $(L_0)_{CR}$ the total air content a_0 is used and not the real volume a_r that is actually air-filled. The real spacing factor L between air-filled pores in a specimen that is freeze-tested should of course be calculated by eq (2) using the values α_r and a_r which are valid for the actual specimen considering its actual water absorption.

The SCR-value can be calculated theoretically when the air content a_0 , the radius distribution of the air pore system $f(r)$ and the true value L_{CR} are known; eq (5). The method of calculation is shown in detail in Fagerlund (1979). The only assumption made is that a smaller air pore is water-filled before a larger pore which is a very reasonable assumption from a thermodynamical point of view.

$$SCR = f\{a_0; f(r); L_{CR}\} \quad (5)$$

Inversely, the L_{CR} -value can, as said above, be calculated when the SCR-value and the pore size distribution are known.

$$L_{CR} = g\{a_0; f(r); SCR\} \quad (6)$$

6 Experimental determination of SCR

The SCR-value can be determined experimentally by methods described in Fagerlund (1977). A number of specimens are adjusted to individual degrees of saturation by drying from a vacuum-saturated condition or by absorbing water after vacuum treatment of the dry specimen to a certain residual pressure. They are immediately sealed from moisture gain or loss and freeze/thaw-tested during one cycle only or during a few cycles. Damage is measured by means of expansion or dynamic E-modulus. A plot of damage versus degree of saturation reveals the SCR-value. Examples of determinations of SCR of concrete and other materials can be found in many reports i.a. Fagerlund (1972), (1975), (1977), (1978), (1982), Studer (1979), (1980), Stehno (1979), Klamrowski and Neustupny (1984). One example is seen in fig.3.

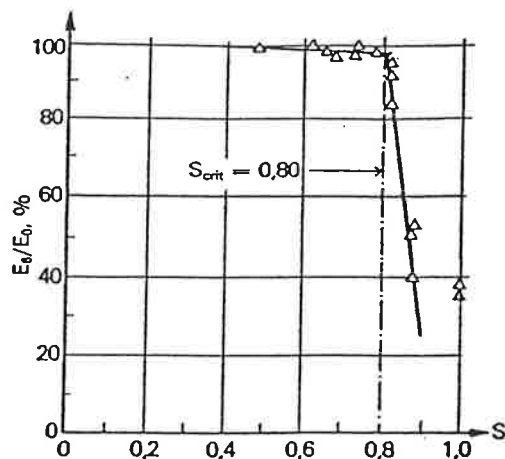


Fig.3. Example of an experimental determination of the critical degree of saturation of an OPC-concrete with $W/C=0,54$ and air content 7,1 %. E_n is the dynamic E-modulus after n freeze/thaw cycles; Fagerlund(1981).

The number of freeze/thaw cycles seems to have a negligible effect on the SCR-value which means that there is almost no effect of fatigue. One example is shown in fig.4. The SCR-value determined by the onset of expansion is well-defined already after 1 freeze/thaw cycle; Klamrowski & Neustupny (1984). This fact has also been demonstrated in other tests; Fagerlund (1972), (1980). This negligible effect of repeated freeze/thaw cycles depends on the fact that the specimen is sealed. In an unsealed test there is normally increasing damage with increasing number of cycles -e.g in the traditional salt scaling test. But, this is probably to a large extent depending on the fact that moisture flows into the specimen during the test. This gradually increases its degree of saturation.

The SCR-value is also almost independent of the freezing rate. One example is seen in fig.5 showing the effect of the freezing rate on the expansion of specimens with different but constant degrees of saturation; Klamrowski & Neustupny (1984). Another example is shown in fig.6 which shows the result of a comparative international investigation of the so called SCR-method; Fagerlund (1977). An analysis performed in Fagerlund (1992a) explain this behaviour theoretically. In normal freeze-testing, an effect of the freezing rate is often found. The results are however not unambiguous; in some tests an increased freezing rate bring about an increase of the damage -e.g. Nischer (1976), Pigeon, Prévost & Simard (1985). In other tests, the opposite is the case - e.g. HRB (1959). The most plausible explanation is that different test procedures effect in different ways the possibility of the specimen to take up or give away moisture.

Thus, SCR seems to be little affected by normal variations in the environmental conditions. It can therefore be regarded as a true material property, a fact that is utilized in the the proposed method for service life prediction.

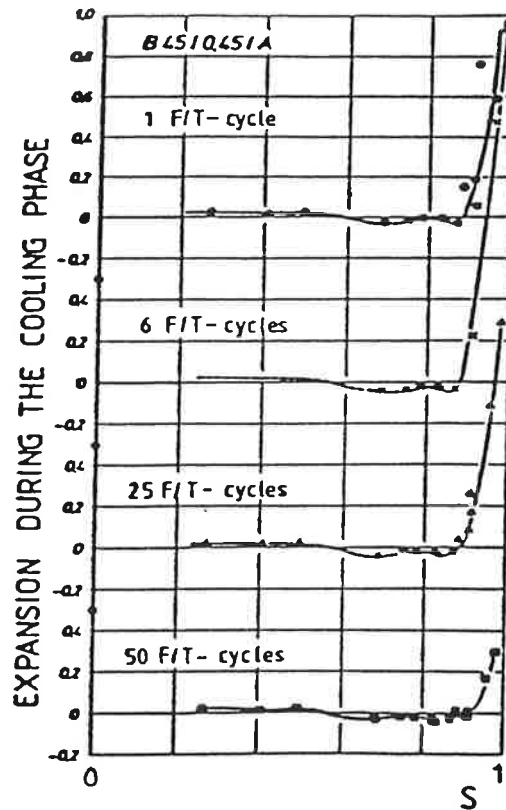


Fig. 4. Effect of the degree of saturation and the number of freeze/thaw cycles on the expansion of a concrete during freezing; Klamrowski and Neustupny (1984).

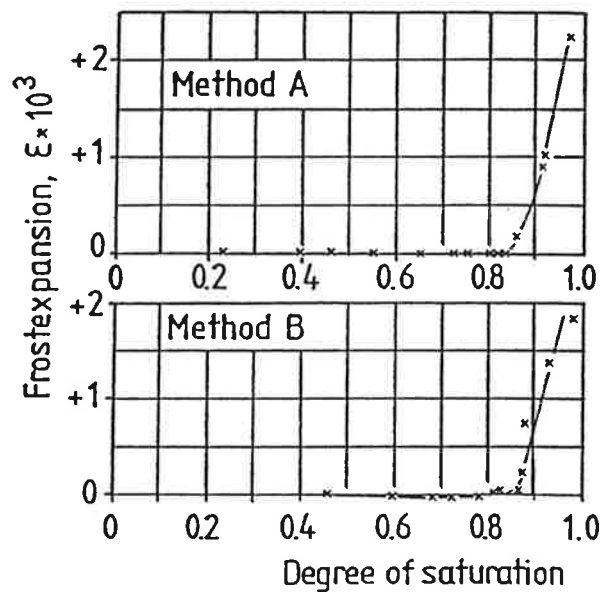


Fig. 5. Effect of the degree of saturation and the freezing rate on the expansion of a concrete during freezing (Method A, 6°C/hour; Method B, 12°C/hour); Klamrowsky and Neustupny (1984).

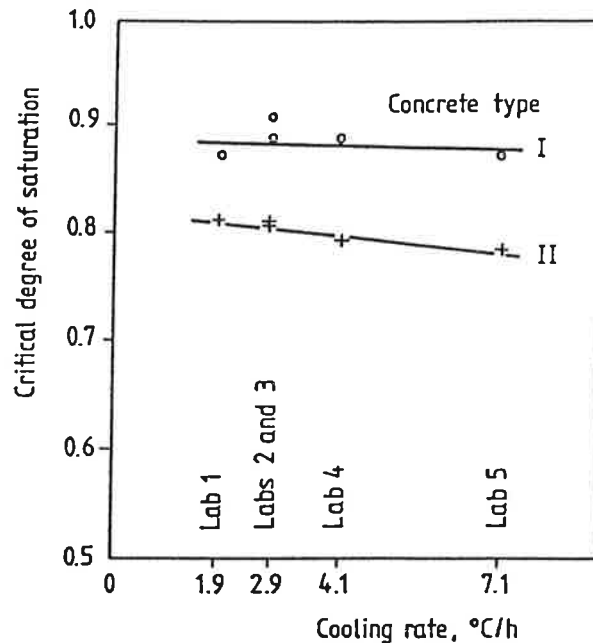


Fig.6. Effect of the freezing rate on the critical degree of saturation of two OPC-concretes; Fagerlund(1992a).

It might be that the SCR-value is a function of the salt concentration of the pore water and that a lowest value is obtained for a certain pessimum concentration; Fagerlund (1992b). The effect of salt water in the pores on the critical degree of saturation therefore has to be clarified.

One can also expect that the SCR-value depends on the lowest temperature employed. Thus, it has been found that a lowest freezing temperature of -22°C causes considerably more scaling in a traditional salt scaling test than the temperatures -8°C and -14°C ; Lindmark (1993).

7 The actual degree of saturation - the service life

In fig.7 the behaviour of a representative volume inside the concrete is shown. The SCR-value can be regarded constant after the first few months provided there is no change of the air pore structure, such as deposition of crystals in the "active air pores", pores that are coarse enough not to become readily water-filled during normal conditions. The actual degree of saturation, SACT, of the unit volume and the temperature changes with changes in the outer climate conditions. At point B the unit volume freezes at the same time as the SACT-value of the unit volume exceeds its SCR-value. This causes considerable destruction of the unit volume. One can always assume that a large number of adjacent unit volumes are damaged at the same time giving a measurable reduction of the serviceability of the entire structure.

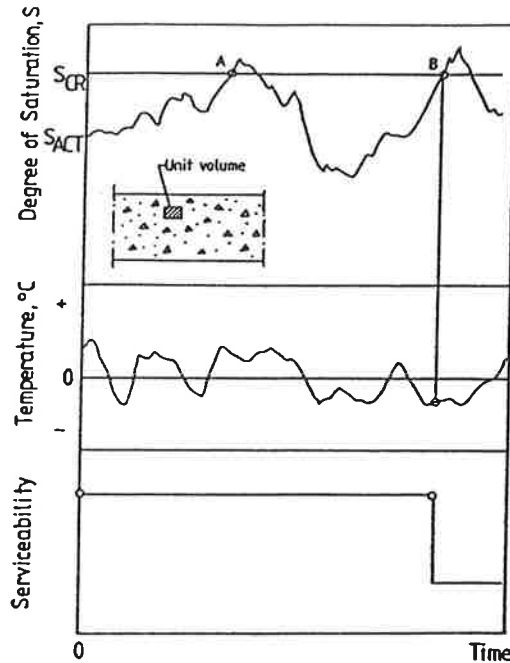


Fig.7. Hypothetical time functions of the actual degree of saturation, S_{ACT} , the critical degree of saturation, S_{CR} and the temperature inside a unit volume in a concrete member.

The frost resistance problem is a good example of the statistical nature of durability. The unlucky combination of excess of water and low temperature might occur during the first year as well as after many decades. Therefore, it is very difficult -or even impossible- to make an exact prediction of the service life of concrete exposed to natural frost action. It is evident, however, that a long service life implies that the concrete is designed in such a way that the probability is very low that S_{ACT} will ever exceed S_{CR} .

8 The potential service life - the capillary absorption

Instead of trying to analyze or simulate the real environment, which is practically impossible but, if successful, should give the true service life, one can utilize a "standard environment" and obtain a sort of "potential service life". One possibility is to use a long-term water absorption test and measure the capillary degree of saturation, $SCAP$ as function of the suction time. Thus, the true and fluctuating value S_{ACT} is replaced by the gradually increasing value $SCAP$. The potential service life t_{ps} is implicitly defined by.

$$SCAP(t_p) = SCR$$

(7)

Where $SCAP(t_p)$ is the degree of saturation after the time t_p of continuous capillary water uptake. In theory, the time function $SCAP(t)$ could be calculated by means of advanced moisture mechanics and a detailed knowledge of the air pore system. Such a theory is worked out in detail in Fagerlund (1993). Examples of an application of the theory are shown in fig.8 where the degree of water-filling S_a of the air pore system is plotted as function of time. $S_a=0$ and $S_a=1$ correspond to an empty and a completely water saturated air pore system respectively. Thus, water in the capillary pores and gel pores are not included in S_a . The assumed frequency function of the air pores is.

$$f(r) = n \cdot \{ 1/r^b - 1/r_{max}^b \} \quad (8)$$

Where n and b are constants, b being a function of the specific area α_o of the entire air pore system. r_{max} is the radius of the coarsest air pore. The theoretical solution -see eq (13) below- is performed for two different values of the diffusivity of dissolved air through pore water. With a diffusivity of 10^{-12} m²/s and a specific area of 30 mm⁻¹ the time needed to fill 50 % of the air pore system is about 30 years. The finer the pore system, the more rapid is the rate of water-filling and the shorter is the service life. With a specific area of 50 mm⁻¹ it only takes 1 year to fill 50 % of the air pore system. The theoretical calculation was compared with experimental tests yielding fairly good agreement.

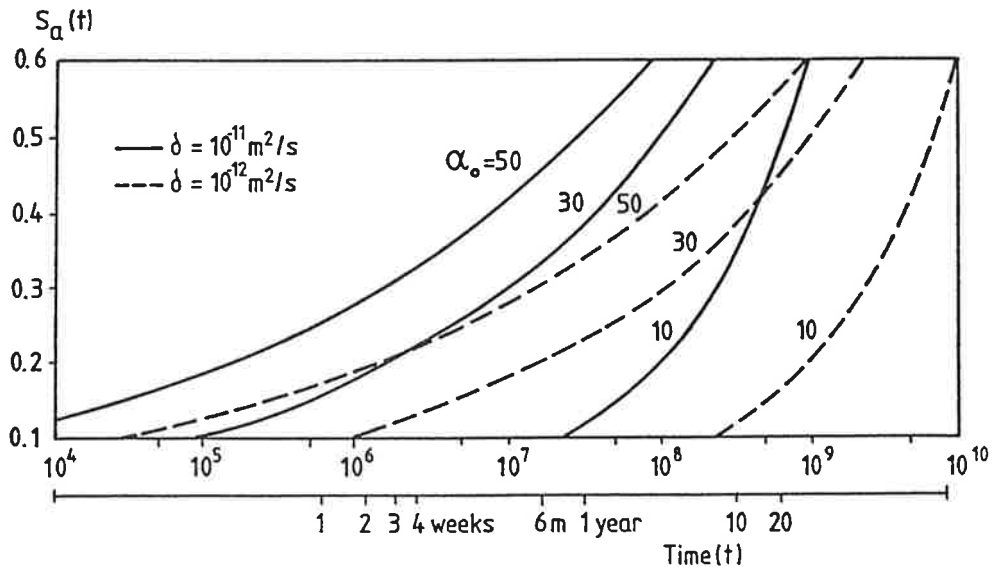


Fig.8. Calculated degree of saturation of the air pore system of concretes permanently stored in water and with air pore systems that are described by eq (8); Fagerlund(1993).

A practical, experimental method for determination of SCAP is a capillary absorption test using thin concrete plates (about 20 mm) that are completely immersed in water for a long time or that are sucking water from one side which is put in contact with the surface of water contained in a vessel that is sealed in order to protect the top surface of the specimen from evaporation. The thickness of the plate must be small so that the measured water absorption can be assumed to have occurred homogeneously over the entire material volume. Typical absorption-time curves are shown in fig.9. The nick-point in the diagram -at point $(t_n; S_n)$ - corresponds to the stage where all capillary pores and gel pores are completely water-filled while no air pores are filled. Thus the quantity $(1-S_n) \cdot \epsilon$ is equal to the total air content a_0 of the concrete. The good agreement between those two quantities is seen in fig.10.

The water absorption that occurs after the nick-point is the gradual water-filling of the air pore system. This is caused by dissolution in the pore water of air contained in the pores and transfer of this air by diffusion to coarser air pores and to the specimen surface. The water absorption process after the nick-point absorption can be described by an equation of type (9).

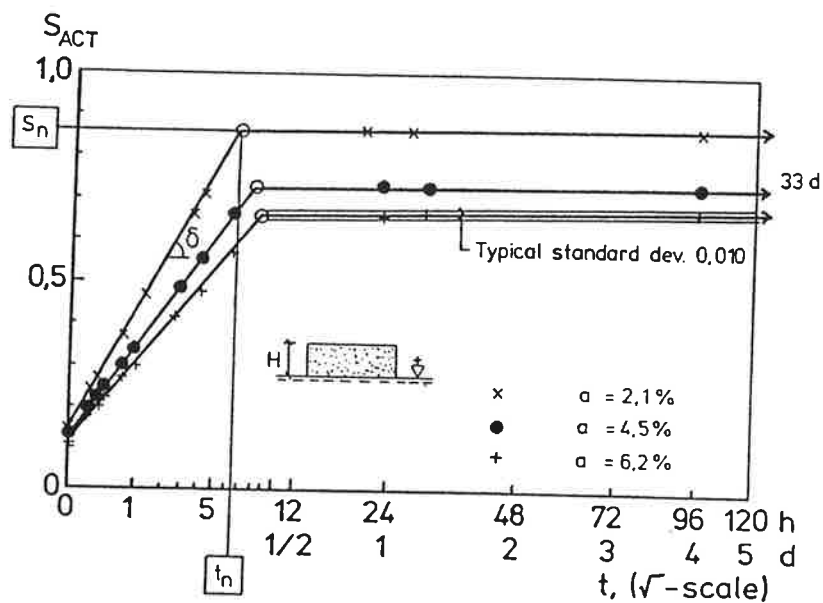


Fig.9. Examples of the water absorption curves of OPC-concrete slices with one surface put in contact with water (a is the air content of the hardened concrete); Fagerlund(1982).

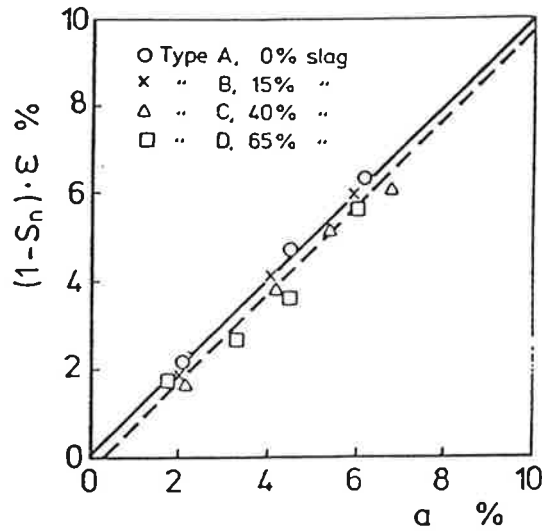


Fig.10. Relation between the parameter $(1-S_n) \cdot \epsilon$ and the total air content a of concretes made with different types of cement and with $W/C=0,45$; Fagerlund(1982).

$$SCAP(t) = [1/\epsilon] \cdot \{\epsilon_0 + f[a_0; W/C; \text{cem.type}] \cdot g[f(r); t]\} \quad (9)$$

Where ϵ_0 is the porosity exclusive of air pores. The total porosity is $\epsilon = \epsilon_0 + a_0$. The first term within the second parenthesis, $\epsilon_0/\epsilon \approx S_n \cdot \epsilon$ therefore is the rapid absorption in the gel- and capillary pores up to the nick-point and the other term determines the absorption in the air pores. The function f describes the rate of water absorption in the air pores and the function g describes the shape of the time-curve of this process.

Our knowledge of the two functions f and g is limited although some estimates can be made as seen in fig.8. One possibility is to extrapolate the result of a water absorption test which is run for some time (weeks or months). The most simple extrapolation is a lin-log relation.

$$SCAP(t) = A + B \cdot \log t \quad (10)$$

Where A and B are constants which are adjusted to the test results and where t is the suction time expressed in a suitable unit (normally hours). The coefficient A is almost the same as the quantity $\epsilon_0/\epsilon \approx S_n \cdot \epsilon$ and B is determined by the rate by which air in the air pores can dissolve and be replaced by water. Eq (10) can therefore be written.

$$SCAP(t) = [1/\epsilon] \cdot \{\epsilon_0 + B \cdot \epsilon \cdot \log t\} \quad (11)$$

Where the coefficient B involves all the material parameters that are implicit in eq (9). Some examples of measured

values of the coefficient B are shown in fig.11. B increases with increasing air content which is reasonable since the diffusivity of gases increases with increasing air content; Fagerlund (1993). B also increases with increasing amount of ground granulated blast furnace slag in the cement. The reason is not fully known. It was found, however, that the specific area of the air pore system increased substantially with increasing slag content. This should theoretically give the observed effect on the coefficient B; see fig.8.

Combination of eq (7) and (10) gives the following relation for the potential service life.

$$t_p = 10^{(SCR-A)/B} \quad (12)$$

A theoretical analysis indicates that a lin-log extrapolation might overestimate the service life; viz. the real long-term absorption seems to be more rapid than that predicted by eq (10); Fagerlund (1993). A relation of the following type seems to be more realistic for the degree of saturation S_a of the air pore system itself, provided $S_a < 0,5$.

$$S_a(t) = C \cdot \alpha_o^D \cdot (\delta \cdot t)^E \quad (13)$$

Where C and D are general constants, E is a constant which also depends on the specific area of the air pore system and δ is the diffusivity of dissolved air.

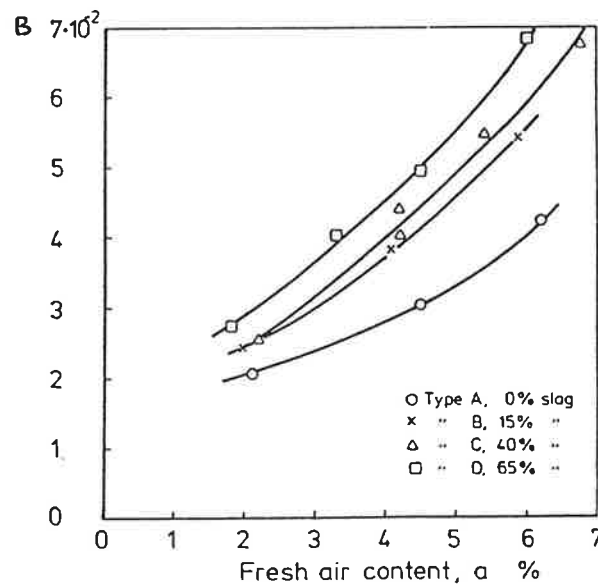


Fig.11. Examples of experimental determinations of the coefficient B in eq (10) as function of the air content and cement type. (W/C=0,45); Fagerlund(1982).

The capillary degree of saturation of the total concrete is.

$$SCAP(t) = [1/\epsilon] \cdot \{\epsilon_0 + S_a(t) \cdot a_0\} \quad (14)$$

Inserting eq (13) gives.

$$SCAP(t) = [1/\epsilon] \cdot \{\epsilon_0 + C \cdot \alpha_0^D \cdot a_0 \cdot (\delta \cdot t)^E\} \quad (15)$$

This can also be formulated.

$$SCAP(t) = A + F \cdot t^E \quad (16)$$

Where the constant $F = C \cdot \alpha_0^D \cdot a_0 \cdot \delta^E / \epsilon$ is individual for each concrete. A is the same as in eq (10). The potential service life is.

$$t_p = \{(SCR - A) / F\}^{1/E} \quad (17)$$

Provided one has information on how different concrete technology parameters such as W/C-ratio, cement type, curing, moisture history etc, affects the functions f and g in eq (9) and the critical distance LCR(or DCR) it should be possible to make a purely theoretical calculation of the potential service life of a concrete stored in water and then frozen. Neither a freeze/thaw test nor a time consuming water absorption test would be necessary. The only information needed concerns the air pore structure. Then, one can calculate the SCR-value according to the principles described in section 5 and the SCAP-function by eq (15). A combination yields the potential service life.

It is quite clear that by using the SCR-concept one can from a theoretical point of view obtain quantitative information of the expected service life and not only a rough qualitative durability level as that obtained by a traditional freeze/thaw test. One can also, by making parameter studies, investigate the sensitivity with regard to frost resistance of different material parameters such as pore size distribution, air content, W/C-ratio, diffusivity (permeability), etc.

9 The required air content for a given service life

The required total air content a_{0is} is normally calculated by the Powers equation eq (1) expressed in the following form based on the specific area α_0 of the empty (dry) air pore system and the fictitious critical spacing factor $(L_0)_{CR}$.

$$a_0 = V_p / \{0,364 \cdot [(L_0)_{CR} \cdot \alpha_0 / 3 + 1]^3 - 1\} \quad (18)$$

As said above, from a theoretical point of view, no value of $(L_o)_{CR}$ can exist. A certain fraction of the air pore system will always become water-filled during natural conditions. The fact that certain researchers seem to have found rather well-defined values of $(L_o)_{CR}$ for normal types of concrete most likely depends on the fact that pore systems in such concretes are often of similar shape. Therefore, possibly there exists a fairly constant relation between the fictitious value $(L_o)_{CR}$ and the true value L_{CR} . This relation will probably no longer exist for air pore systems of divergent appearance such as extremely fine-porous systems or extremely coarse-porous systems. In the first case, the air requirement calculated by means of eq (18) will be underestimated due to an underestimation of the substantial water absorption in such pore systems. In the second case the air requirement will be overestimated because such pore systems do not absorb much water; more or less all pores will stay air-filled even during very moist conditions.

A more realistic value of the required air content should be calculated by the following equation.

$$a_o = a_w + a_{CR} + a_b \quad (?)$$

Where a_w is the water-filled air pore volume, a_{CR} is the air pore volume needed in order that the spacing L_{CR} should not be exceeded when a_w is reached in the pore system and a_b is an "air-buffer" or a safety margin. The value a_{CR} is calculated by the Powers equation (2) using the true value L_{CR} and the value α_{CR} which is the specific area of the air-filled part of the air pore system when the residual spacing of this is exactly L_{CR} .

$$a_{CR} = V_p / \{0,364 \cdot [L_{CR} \cdot \alpha_{CR} / 3 + 1]^3 - 1\} \quad (20)$$

The value a_w is depending on the environmental conditions. The wetter the environment, the higher is the value of a_w and the bigger is the size of the largest water-filled air pore. Therefore, the value of the "residual" specific area α_{CR} is reduced when the environment becomes wetter and according to eq (20) the required air volume a_{CR} is increased. Therefore, according to eq (19), in order to compensate for a wetter environment the total air content a_o of the concrete must be increased. This is not considered when the air requirement is calculated by eq (18) since neither the value of $(L_o)_{CR}$ nor the value of α_o are dependent of the wetness of the environment.

The ideas presented are illustrated by fig.12 showing the effect of a gradual water-filling of the air pore system on the residual values L_r , α_r and a_r of the parameters L , α

and a. A water-filling that corresponds exactly to the residual spacing factor L_{CR} also gives the residual specific area α_{CR} and the residual air content a_{CR} . All pores with a diameter smaller than Φ_{CR} are then water-filled. In the real case, only pores smaller than Φ_w are water-filled, where $\Phi_w < \Phi_{CR}$. This gives an air-buffer Δb which is a sort of safety margin against the occurrence of exceptionally moist conditions. The air-buffer will increase with increasing air content under the assumption that the shape of the air pore system is unchanged. A long service life requires an air-buffer which is large enough never to be fully utilized even during very moist conditions.

The increased air requirement when freezing occurs in the presence of salt can possibly be understood by the theory just presented. The extra need of air is normally explained by the fact that salt apparently reduces the critical fictitious factor $(L_o)_{CR}$ from about 0,25 mm to about 0,16 to 0,20 mm for normal concrete. Inserted in eq (18) this decrease in the $(L_o)_{CR}$ -value gives a substantial increase in the required air content. The following reasoning is however just as plausible. The presence of salt increases the water content in the air pore system of the surface part of the concrete, e.g. by attracting water from the interior of the concrete or by prolonging the periods of wetness of the concrete surface. Thus the value a_w increases as well as the size Φ_w of the largest water-filled air pore. This means that the specific area of the air-filled part of the pore system decreases. Then according to eq (20) the required air content a_{CR} of the portion of the air pore system that has to stay air-filled either increases or decreases depending on the effect of salt on the true spacing factor L_{CR} . The decrease in the specific area α_{CR} might be more or less compensated for by the possible increase in the true L_{CR} -value that was found in the tests described in section 3. The combined effect of the changes in a_w and a_{CR} is such, however, that the total air requirement increases.

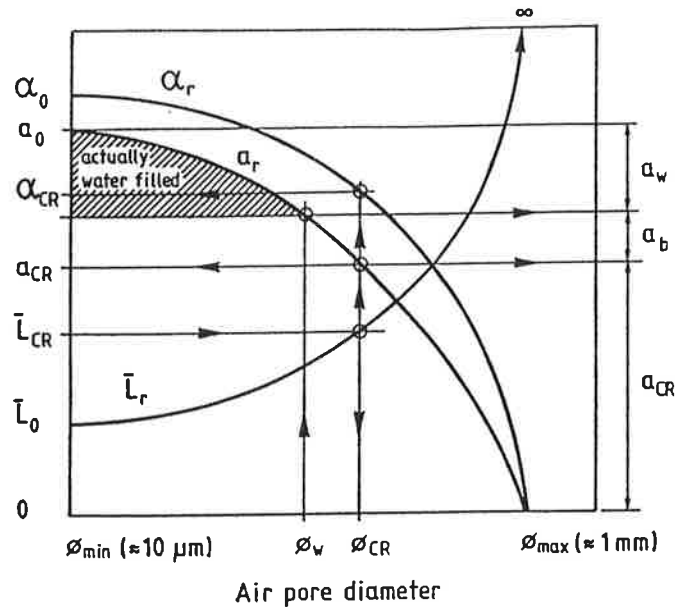


Fig.12. Illustration of the principles behind the concepts residual specific area α_r , residual air content a_r , residual spacing factor \bar{L}_r , water-filled air pore volume a_w , critical air pore volume a_{CR} and air buffer a_b .

10 Numerical examples

The application of the theory is shown by some examples. In all examples the following concrete is assumed: The cement paste fraction (including "interfering" fine aggregate) is $0,37 \text{ m}^3/\text{m}^3$, the air void system is described by eq (3) with the constant $b=1,03$ when the pore radius is expressed in μm . This corresponds to a specific area of the empty pore system of 30 mm^{-1} . The calculations of the relations between the water absorption a_w , the corresponding pore diameter ϕ_w and the residual specific area α_r are based on formulas presented in Fagerlund (1979).

The true critical spacing factor is assumed to have the values that were found experimentally (section 3); $0,40 \text{ mm}$ for freezing in water and $0,54 \text{ mm}$ for freezing in salt.

Example 1: No salt. Short storage in water

All pores with diameter smaller than $140 \mu\text{m}$ are assumed to be water-filled. This corresponds to a residual specific area $\alpha=23 \text{ mm}^{-1}$ and a degree of water-filling S_{aof} of the air pore system of 16 %. The required amount of air-filled pores is; eq (20).

$$acr = 0,37 / \{0,364 \cdot [0,40 \cdot 23/3 + 1]^3 - 1\} \cdot 100 = 1,6 \%$$

The required minimum total air content is; eq (19).

$$(ao)_{min} = Sa \cdot (ao)_{min} + acr = 0,16 \cdot (ao)_{min} + 1,6 = 1,9 \%$$

Example 2: No salt. Long storage in water

The amount of water in the air pore system is higher than in example 1. All pores with diameter smaller than 200 μm are assumed to be water-filled. This corresponds to a residual specific area of 19,5 mm^{-1} and a degree of water-filling Sa of the air pore system of 34 %. The required amount of air-filled pores is.

$$acr = 0,37 / \{0,364 \cdot [0,40 \cdot 19,5/3 + 1]^3 - 1\} \cdot 100 = 2,3 \%$$

The required minimum total air content is:

$$(ao)_{min} = Sa \cdot (ao)_{min} + acr = 0,34 \cdot (ao)_{min} + 2,3 = 3,5 \%$$

Thus, the air content must be increased by 1,6 % when the concrete is more moist.

Example 3: With salt. Long storage in water as in example 2

The water absorption is assumed to increase when salt is used. All pores with diameter smaller than 300 μm are assumed to be water-filled. This corresponds to a residual specific area of 15 mm^{-1} and a degree of water-filling Sa of the air pore system of 65 %. The true critical spacing factor is now assumed to be increased to 0,54 mm. The required amount of air-filled pores therefore is.

$$acr = 0,37 / \{0,364 [0,54 \cdot 15/3 + 1]^3 - 1\} \cdot 100 = 2,1 \%$$

This is almost the same value as for freezing in pure water; the decrease in α is compensated for by the increase in LCR. The required minimum total air content is:

$$(ao)_{min} = Sa \cdot (ao)_{min} + acr = 0,65 \cdot (ao)_{min} + 2,1 = 6 \%$$

Thus, the required air content might be higher when freezing occurs in the presence of salt despite the fact that the true critical spacing factor might be increased.

11 Suggestions for future research

In order to verify the theory and make it more applicable also when salts are involved the following experimental studies -among others- should be made.

- * Determination of the true critical spacing factors from measurements of SCR-values of concretes containing salt water of different concentrations and with different air pore structures. The evaluation is made according to the principles described in section 4.
- * Determination of the long term water absorption in air pore systems of different shape and during different outer conditions; varying temperature, interrupted and resumed water absorption, variable salt concentration etc.
- * Determination of the "micro-flow" of salt and water in the surface part of a concrete during a freeze/thaw cycle and between the surface and the surrounding medium; pure water or salt water.

Much of the work deals with moisture flow which is natural because the frost resistance problem is to a very large extent a "moisture mechanics problem". One will never obtain a good theory for the service life with regard to frost attack if the moisture mechanics of the problem is not understood.

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