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## LUND INSTITUTE OF TECHNOLOGY LUND UNIVERSITY

Division of Building Materials

# A SERVICE LIFE MODEL FOR INTERNAL FROST DAMAGE IN CONCRETE

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## Foreword

The idea behind the service life model presented in this report was published in 1979 (1). It has thereafter been described and developed in a number of reports and papers, e.g. (2-8).

The basis of the model is the observation that a well-defined critical, or maximum allowable, moisture content exists, above which the material is severely damaged by frost, and below which it is unharmed also when freezing is repeated at numerous occasions. This means that there is an analogy between design with regard to frost resistance and design with regard to structural safety. The critical moisture condition corresponds to the fracture load at structural design, whilst the real moisture condition corresponds to the actual load in structural design - the "load effect". This also means that design with regard to frost resistance is to a high extent a "moisture mechanics problem"; one must be able to predict the future moisture variation in all parts of the structure.

The analogy with structural design means that the same theory can be used for calculation of the probability of frost damage as for the risk of structural failure.

The report focuses on the "moisture mechanics part" of the problem; i.e. the "load part". The possibility to predict moisture by theoretical calculation is evaluated, and found to be small. As a substitute to calculations, simplified experimental methods for predicting future moisture levels in a structure are suggested. Principles for how to translate such experimental data to real moisture conditions in the structure are presented. This makes it possible to predict the risk of frost damage as function of exposure time, and therefore also a sort of "potential service life" can be evaluated.

A fundamental idea in the service life model is that a structure can be divided in a number of small representative unit cells, that are uninfluenced of what is going on in neighbouring cells. Each cell, therefore, has its own frost damage risk and its own service life. The frost damage risk and service life of the entire structure is constituted by the sum of the frost damage risk of all the unit cells; some cells located in the more sensitive parts of the structure having bigger influence than others.

The model is developed for internal frost damage. Another type of frost damage is concentrated to the concrete surface, and occurs primarily when the concrete is exposed to weak salt solutions in combination with freezing. Possibly the same theory as described here for internal frost can also be used for this type of damage. Probably a critical moisture level exists also for this type of damage. The actual moisture level depends to a high extent on how freeze-thaw takes place, since this determines the possibility for the concrete to absorb and dry-out water during freeze-thaw. No attempt is made in the present report to cope with this type of frost damage.

Note: The model is applicable not only to concrete but to all types of porous brittle building materials exposed to moisture and freezing temperatures.

The report is supplemented by three APPENDICES.

APPENDIX 1 presents the theoretical background to the service life model. It also gives relations between the material structure and service life. Methods for designing concrete with regard to required service life are presented.

APPENDIX 2 shows how the model can be applied to the problem of assessing the *future service life* of a structure that is already damaged by frost. The text is based on reference (9).

APPENDIX 3 discusses the possibility of using normal freeze-thaw tests for prediction of service life. Traditionally such tests are "open", which means that the specimen is exposed to a rather big number of repeated freezing and thawing taking place in water and/or air making moisture exchange possible. It is shown that such tests cannot be used for service life prediction.

Lund, November 2004

Göran Fagerlund

# 1 Internal frost attack and salt-frost scaling

There are two types of frost attack:

- 1. *Internal frost attack* caused by freezing of moisture inside the concrete. This attack may cause substantial reduction of strength and stiffness. Reductions of the order 80% might occur; see (10).
- 2. *Surface scaling* normally caused by freezing of weak salt solutions in contact with the surface. This destruction is normally limited to the surface while concrete beneath the scaled part is more or less intact.

Probably, both types of attack depend on the same mechanism, namely that too much moisture is present in the material, either inside this, or at its surface part.

Despite this, the salt-frost attack should be treated as a separate problem, because it only occurs during *unsealed* freeze/thaw where the concrete stays in contact with a solution during freezing. Therefore, salt-frost scaling is to a high degree related to the manner by which freeze/thaw takes place; factors like duration of freezing and of thawing, rate of freezing and thawing, lowest temperature reached during freezing have major effects. All these factors affect the moisture level in the surface part, which is the main reason for the observed effects.

Internal frost attack, on the other hand, can take place also when there is no moisture exchange, or moisture contact, between the concrete and its surroundings. This type of freeze/thaw is called *sealed freeze/thaw*. The only pre-condition for damage to take place is that the internal moisture content is sufficiently high when freezing takes place. The amount of frost damage is almost independent on the temperature conditions during freeze/thaw; apart from the minimum temperature reached, that might have a certain effect, because it affects the amount of ice formed in the pores.

The discussion in this report only refers to internal frost damage.

# 2 The isolated representative unit cell

By "representative unit cell" is meant a material volume that is big enough to represent the material in bulk, but not much bigger than that. This means that it shall be big enough to contain the same porosity and the same pore-size distribution as the bulk material. For cement paste this means a volume that might be about  $300 \text{ mm}^2$ ; like a sphere with the radius 4 mm or a cube with a width of about 7 mm. For a coarse aggregate particle with its surrounding mortar belonging to the particle it might be  $30\ 000\ \text{m}^2$ ; like a sphere with the radius 20 mm or a cube with the width 30 mm.

The representative cell is supposed to be *isolated* by which is meant that one does not have to consider moisture movements to or from an adjacent unit cell during freezing.

Furthermore, the cell is so small that moisture and temperature gradients inside it can be neglected.

A freeze-thaw specimen, or a concrete structure, is composed of a very big number of representative cells; Figure 1.



Figure 1: Representative cells on different locations inside a beam (exaggerated size of cells).

## 3 The critical water content of a representative unit cell

## 3.1 Background

One of the unit cells in the beam in Figure 1 is considered in this paragraph.

There are two major frost destruction mechanisms, the *hydraulic pressure* mechanism (11) and the *microscopic ice-lens growth* mechanism (12). Both mechanisms predict the existence of a maximum distance between a place where water freezes and the nearest air-filled space. This distance can be expressed in terms of a "*critical spacing factor*", assuming that all air spaces in the cell being of equal size and arranged in a loose-packed cubic "lattice", (11). A more general way of describing this distance, applicable to air-pore systems of different shape, is by a "*critical flow distance*", which is a measure of the biggest distance that water can flow from a point where freezing occurs to the periphery of the nearest air-filled space without causing damage, (13). The value of this distance depends on how big volume fraction of the saturated matrix that should be "protected", i.e. being on a distance from an air space smaller than the critical distance, (13). The flow distance is visualized in Figure 2. A similar way of expressing the critical spacing is by the "*Philleo spacing factor*", (14).



Figure 2: The flow distance inside a unit cell taken out of the structure.

The flow distance increases with increasing water content since more and more of the previously air-filled pores become water-filled with increasing water content. At low water contents the actual flow distance is below the critical, and consequently there is no frost damage. At high water contents the flow distance is above the critical and frost damage occurs. For a certain, critical, water content the actual flow distance equals the critical distance. No frost damage occurs, but a very small increase in water content makes the flow distance too big and considerable damage occurs at freezing.

The critical water content is individual for each concrete. To some extent it depends on the actual value of the critical flow distance. The amount of air and the size distribution of the airpore system, however, have the most important influence.

The relation between critical flow distance and critical water content is illustrated in Figure 3.



*Figure 3: At a given, critical, water content in a unit cell, the actual flow distance equals the critical value.* 

## 3.2 Experimental determination of the critical water content

The critical water content can be determined experimentally by freezing of a series of specimens that have been pre-conditioned to different water contents before freezing. The specimens are moisture sealed during freeze/thaw in order to keep the initial moisture content constant. Thus, no moisture gain, or loss, during freeze-thaw shall be permitted. Only a few freeze/thaw cycles are required for a safe detection of the critical water content; in many cases only one single cycle is needed. The freezing rate, and the duration of freezing temperature, seems to have marginal effects on the value of the critical water content; (15, 16).

Damage is detected by measurement of dilation during and after terminated freeze/thaw, or by measurement of the dynamic E-modulus determined from the fundamental frequency at transverse vibration. The test method for critical water content is described in (17). An international cooperative test of the method is published in (18). The agreement between the 5 laboratories participating in the test was good.

An example of a determination of the critical water content of a type of concrete, based on determination of E-modulus is shown in Figure 4. In this case the water content is expressed in terms of "*degree of saturation*", S defined:

$$S = V_w / V_p \tag{1}$$

where  $V_w$  is the volume of all evaporable water in the concrete  $[m^3]$ , and  $V_p$  is the total pore volume determined after vacuum-saturation of the pre-dried specimen  $[m^3]$ .

Another example, in which dilation was used for detection of damage, is shown in Figure 5.

In both examples the "*fracture value*",  $S_{CR}$ , is very well defined. A very small transgression of the critical water content gives considerable damage.



Figure 4: Determination of the critical degree of saturation from measurement of dynamic Emodulus. OPC-concrete. Air content 4.5%. w/c=0.45; (19).



*Figure 5: Determination of the critical degree of saturation from measurement of dilation. OPC-concrete. Air content 2.1 %. w/c=0.50; (20)* 

The test method for critical water content is quite laborious, and rather big specimens are used; bigger than the unit cell. Thus, numerous unit cells are tested in the same experiment. Also small variations in pore structure, small moisture variations, and small temperature gradients across the specimen volume might occur, meaning that the value of  $W_{CR}$  or  $S_{CR}$  observed is a mean value for many unit cells. Furthermore, in tests used so far, adjustment of specimens before freeze/thaw is done by *drying* the specimens from almost vacuum-saturated condition to the desired weight, corresponding to the water content desired. Another possibility is to absorb water into pre-dried specimens by using vacuum-treatment. Due to imaginable wetting-drying hysteresis in the high moisture range, one cannot exclude that the critical water content will differ somewhat for the two different ways of pre-conditioning specimens; the drying procedure reasonably giving the highest value, thus being on the "unsafe side", (21). The effect of pre-conditioning method on  $S_{CR}$  has not been investigated.

Ideas of how to refine and rationalize the experimental method, for example by using small specimens with low spread in moisture, temperature and material properties, are given in (21).

## **3.3** Theoretical determination of the critical water content

By knowledge of the air-pore size distribution and the critical distance it is possible to make a theoretical determination of the critical water content. In order to do so it is also necessary to know how water is distributed in air-pores of different size. A reasonable assumption, from a thermodynamic point of view, is that a coarser pore will not be filled until a smaller is completely filled. Having all this information one can calculate theoretically how the flow distance increases with increasing water content (see Figure 3). The critical water content is reached when the actual flow distance (or spacing factor) equals the critical value.

This method gives the lowest possible value of the critical water content.

The theory is described in detail in APPENDIX 1. It has previously been described and applied in references (1, 4, 8).

## 3.4 Effect of the lowest freezing temperature

Theoretically, one might assume that a lower freezing temperature gives higher stresses and therefore a lower value of the critical water content. The reason is that the amount of frozen water increases with lowered temperature. Some measurements also show that considerable dilation might occur at temperature as low as -40°C; (22). One example of measurement of ice formation (and melting) and dilation down to -50°C is shown in Figure 6.



Figure 6: (a) Measurement of ice formed and melted in the temperature range 0 °C to -50 °C. (b) Measurement of dilation. OPC-concrete. w/c 0.40. Air content 2.5%; repeated experiment. (22).

It is not clear how the minimum temperature affects the critical water content. It seems reasonable to assume, however, that the value is reduced with lowered temperature.

In tests of the critical water content made so far the lowest temperature used is about  $-20^{\circ}$ C to  $-25^{\circ}$ C. This should be sufficiently low for most structures. If one believes that even lower temperatures will occur in practice, one can lower the temperature in the test.

## 3.5 Effect of repeated freeze/thaw - fatigue

As long as *moisture isolated* specimens are used the influence of the number of freeze-thaw cycles on the critical moisture content is insignificant. Thus, there is no fatigue effect involved in the critical water content; the "*fracture value*". One example is seen in Figure 4. There are many other tests indicating the same, e.g. (16). In Figure 7 results of tests on cement mortar are shown. It is only when the critical water content is transgressed that a certain fatigue, *directly proportional to the water content*, occurs, but then the concrete is already damaged and fatigue is of no real interest (except for assessment of future damage, see APPENDIX 2); the S<sub>CR</sub>-value serves as a sort of "hinge" for the damage line.



Figure 7: Effect of the number of freeze-thaw cycles on damage. Non-air-entrained cement mortar. w/c 0.40; (23)

For the data in Figure 7 the amount of damage (D) as function of number of freeze-thaw cycles N can be described by:

 $S \le S_{CRIT}$ : D=0 (2a)  $S > S_{CRIT}$ : D= K<sub>N</sub>·(S-S<sub>CRIT</sub>) = K<sub>N</sub>·(S-0.77) (2b)

where the "coefficient of fatigue", K<sub>N</sub> is:

$$K_{N}=1.2 \cdot N/(4+N)$$
 (3a)

Or, expressed in more general terms, valid for any concrete type:

$$K_{N} = A \cdot N / (B + N) \tag{3b}$$

"Damage" is then defined as relative reduction in E-modulus:  $D=\Delta E/E_o$  where  $E_o$  is E before freeze-thaw. Damage can also be defined by loss of strength, or by permanent expansion. Then, the coefficients A and B obtain other values.

Equations (2b) and (3) show that a maximum amount of damage,  $D_{\infty}$ , can occur irrespectively of the number of freeze-thaw cycles. For the data in Figure 7 this "*fatigue limit*" is:

$$\begin{array}{ll} S \leq S_{CRIT}: & D_{\infty} = 0 \\ S > S_{CRIT}: & D_{\infty} = A \cdot (S - S_{CRIT}) = 1.2 \cdot (S - S_{CRIT}) \end{array}$$

The fatigue limit is therefore described by the coefficient A. For the cement mortar in Figure 7, the value of A is low. For concrete the value of A is much higher. Values of the order 17 are frequent, which means that the fatigue limit is 1 (100% destruction) already at a very small transgression of the  $S_{CR}$ -value; reference (24).

In traditional "open" freeze/thaw tests, during which the specimen stays in contact with liquid water during parts of the cycle, there seems to be a "fatigue effect" since the extent of damage often increases with increasing number of cycles. The reason is, however, that each new cycle is performed with higher moisture content than the cycle before due to moisture uptake during that. Moreover, for damage to occur at all during an open freeze/thaw test, the specimen has to be saturated above the critical value. If not, there should not be any damage irrespectively of the number of freeze/thaw cycles.

The seemingly occurring "fatigue effect" during open freeze/thaw is discussed in more detail in reference (24) and in APPENDIX 3.

## 3.6 Effect of the concrete age

Theoretically, the amount of freezable water decreases with increasing concrete age, due to continued hydration, and the strength increases. Both factors ought to be favourable, increasing the value of the critical distance, and thereby increasing the value of the critical water content. On the other hand, the concrete also becomes more dense and impermeable with time. This is a negative factor reducing the values of critical distance and critical water content.

Some limited tests indicate that the positive factors are dominant. One example is shown in Figure 8. By increasing concrete age from 5 days to 26, the critical degree of saturation is increased from 0.75 to 0.90. The air-pore system is unchanged, which means that the only reasonable explanation for the favourable effect of age lies in favourable changes in the micro-structure of the cement paste.

In reality, a concrete structure is seldom exposed to severe frost until it is at least one month old. Since rather marginal changes occur after one month, a value of the critical water content determined when the concrete is at least one month old ought to be valid also for the older concrete. The value is on "the safe side".



Figure 8: Effect of age on the critical degree of saturation.  $E_3/E_o$  is the dynamic E-modulus after 3 isolated F/T-cycles related to the E-modulus before freeze/thaw;(21).

## 3.7 Conclusions – critical water content

For each concrete there exists one distinct value of the critical water content with regard to frost. The value is different for different concretes and can be regarded a characteristic "fracture value" with regard to frost. Below the critical water level no frost damage occurs irrespectively of the number of freeze-thaw cycles.

The critical water content is almost independent of the rate of temperature lowering, but is probably somewhat dependent on the minimum freezing temperature reached; a lower temperature reducing the value.

The concrete age, when this is higher than 1 month, has small influence on the critical water content.

The critical water content can be determined experimentally by well-tried technique. This might be developed further, however, in order to facilitate the work.

In theory, the critical water content can also be calculated purely theoretically provided information is at hand as regards the critical spacing between air-filled spaces inside the concrete, and the size distribution of these spaces; see APPENDIX 1.

The critical water content forms the basis for the service life prediction.

## 4 The actual water content of a representative unit cell

## 4.1 Background

Within a real structure there will be a time-dependent moisture field. Some parts of the structure will be moister than other parts due to different outer moisture conditions. The wetter the environment, the higher is the moisture level in the structure. In a structure that is constantly exposed to liquid water (when unfrozen), like a hydraulic structure below the water level, there will be a steadily increasing moisture level over time. In a structure that is exposed to more dry conditions between times of exposure to water, the moisture field might reach "steady state" conditions.

The moisture field in a structure is illustrated by Figure 9. Each unit cell will obtain its own individual moisture-time field, or actual water content,  $W_{ACT}$ . A unit cell close to the air-exposed surface in the hydraulic structure shown in Figure 9a will normally reach lower and more variable water content than a unit cell in the interior. For other structures, like a façade periodically exposed to rain, Figure 9b, the reverse is valid; the surface cell is normally more moist than the interior cell.



Figure 9: The actual moisture level in unit cells within the structure is different in different cells depending on their location and it varies over time. (a) Hydraulic structure constantly sucking water. (b) Façade element periodically exposed to rain.

If the actual water level in a given unit cell exceeds the critical value immediately before freezing of this, considerable damage will occur in the cell. Therefore, *for a service life prediction of a given unit cell, the moisture-time variations in the cell must be predicted.* 

## 4.2 Theoretical calculation of water-time field in concrete--principles

The moisture level in concrete might be divided into three ranges depending on the major mechanism for water absorption; Figure 10:



Figure 10: Different moisture ranges as regards the basic water absorption mechanism.

### Range 1: The "hygroscopic range" (0% RH to about 98% RH).

Within this range, water absorption can occur by capillary condensation of water vapour (but also by capillary suction). The amount of water taken up by concrete at a given RH (or left in concrete at drying at the same RH) is given by the *sorption isotherms* of the actual concrete; Figure 10 and 12. Sorption isotherms are dependent on the type of cement used. Isotherms for OPC-concrete are published in (25).

Moisture transport in the hygroscopic range (when there is no temperature gradient) can be calculated by a transport equation in which vapour concentration (or vapour pressure, or RH) is the driving potential:

$$q = -\delta_c (dc/dx) \tag{4}$$

where q is the water flux  $[kg/(m^2 \cdot s)]$ ,  $\delta_c$  is the transport coefficient  $[m^2/s]$ , and dc/dx is the vapour concentration gradient  $[kg/m^3 \cdot m]$ .  $\delta_c$  is a function of the RH-level. Data for different OPC-concrete qualities can be found in (26). In that report a suitable experimental technique for determination of  $\delta_c$  is also described and used.

### Range 2: The "capillary range" (up to 100% RH).

Within this range, water absorption normally takes place by water absorption from a free water surface. Absorption stops more or less completely when all through pores are water-filled. A typical water uptake-time curve for a thin piece of an initially unsaturated

material, with one flat surface in contact with a water surface, is shown in Figure 11. The first steep line (in square-root scale) represents the rising water front when all through pores below the front have become water-filled and pores above the front are still unfilled. The "*breaking-point*" represents the stage when the water front has reached the top surface. After that, the absorption rate is very low and depends on another mechanism than capillary forces (see range 3 below).

The breaking-point in a test of type Figure 11, at which the concrete has free access to liquid water represents the *upper limit* of the capillary range. No more water can be taken up by capillary forces; concrete has reached "*capillary saturation*".



Figure 11: A capillary absorption test of a thin slab. The steep line corresponds to moisture ranges 1 and 2. The breaking point corresponds to capillary saturation in Figure 10. The slow absorption after the breaking-point corresponds to moisture range 3.

Note

The division of moisture level into a hygroscopic and a capillary range is fictitious and made for practical reasons. In reality, the hygroscopic range and the capillary range overlap; viz. each RH in the hygroscopic range corresponds to a certain capillary pressure, or "suction" in the capillary range. The suction is inversely proportional to the radius of the water menisci in the pore system.

$$\Delta p = k/r = -K \cdot \ln(RH) = -K \cdot \ln(c/c_0)$$

(5)

Where  $\Delta p$  is the capillary pressure [Pa]. r is the pore radius for cylinder-shaped pores and hydraulic radius for an arbitrary pore shape. k and K are temperature dependent coefficients.  $c_o$  is the saturation vapour concentration

At the breaking point, all water menisci inside the concrete are plane, and therefore "suction" is zero.

Since equation (5) is valid, there is no real difference between the hygroscopic range and the capillary range. Therefore, theoretically also the amount of water taken up at equilibrium within the capillary range can be described by the sorption isotherm. This is unsuitable, however, since it is practically impossible to resolve RH in the range 98% to 100%. Therefore, the moisture level at equilibrium is instead related to suction. This equilibrium curve is called the "*capillary equilibrium curve*". This can be determined by the pressure plate method; (27). The relation between the sorption isotherm and the capillary absorption curve is illustrated by Figure 12.



Figure 12: Sorption isotherm and capillary equilibrium curve. Each RH corresponds to a certain capillary pressure (suction). The values given in the figure are valid for +20C and cylinder-shaped pores.

Water transport in the capillary range can be described by equation (4). Thus, also within this range, moisture transport (when there are no temperature gradients) is governed by the gradient in vapour concentration (or vapour pressure, or RH). Normally, however, the gradient is expressed in terms of water content w  $[kg/m^3]$ . Then, the transport equation becomes:

$$q = -\delta_w (dw/dx) \tag{6}$$

Theoretically, the transport coefficient  $\delta_w$  [m<sup>2</sup>/s] is related to  $\delta_c$ . Thus, if any of the two coefficients is known, the other can be calculated by knowledge of the moisture equilibrium curve.

Transport data in the capillary range can be determined by a method described in (27).

Note

Equation (6) indicates that moisture is always moving from a higher moisture content to a lower. In reality this is not necessarily the case, due to drying-wetting hysteresis in the moisture equilibrium curves. Therefore, the formulation in equation (4) is superior to equation (6).

#### Range 3: The "over-capillary range".

During capillary water uptake, air-bubbles will be enclosed in some coarse pores surrounded by a web of finer pores. The mechanism is described in APPENDIX 1. See also (1, 8, 28). Therefore, when the breaking point in a free capillary absorption has been reached, there are pores that are still not water-filled. In concrete such pores are entrained air-pores and compaction pores, but also coarse pores in light-weight aggregate.

Since the material (the cement paste) is "saturated" in range 3 (suction=zero) there is no gradient in moisture that can make these air-filled pores take up water. Consequently they might stay air-filled for all time. In reality however slow water absorption occurs. An

example is shown in Figure 13. Slabs with 30mm thickness are sucking water. The breaking point ("nickpoint") occurs after about 6 hours. At that point, rapid suction stops almost immediately. There is a small slope in the absorption curve also after the breaking-point. Absorption never stops completely during the 1 month the test lasted.



Figure 13: Results of a capillary absorption test. 30 mm thick slices. OPC-concrete, w/c=0.45, different air contents in different slices. The upper and the lower part of the figure show the first 5 days and the last weeks of water uptake, respectively; (19). (The same concrete as in Figure 4)

Tests of this type have been run for many years and concrete never ceases to take up water. There are two possible reasons:

1: Continued cement hydration. Chemically bound water has lower specific volume than bulk water. Therefore, due to hydration a certain part of the capillary pore space will be emptied, and suction will appear. The water sucked in will fill the capillary pore space but not enter the air-pores.

2: Dissolution of enclosed air in pore water surrounding the air pores and gradual diffusion of the dissolved air to the surface, and replacement of dissolved air by water from outside.

The first mechanism is almost negligible as shown by the following example.

#### Example

An OPC-concrete with w/c=0.45, cement content 400 kg/m<sup>3</sup>, air content 6%. The continued hydration after 1 month corresponds to an increase in degree of hydration of maximum 20%. Thus, the amount of air-filled capillary pore space created by hydration, and the corresponding water absorption, is about 5 litres/m<sup>3</sup>. This shall be compared with the breaking-point absorption (at capillary saturation) that is 125 litres/m<sup>3</sup>. Test results show that the real long-term absorption after *1 month* of water storage in this type of concrete is often more than 20 litres/m<sup>3</sup>. After 1 year it might be 30 litres/m<sup>3</sup>; (19).

For slag cement concrete with the same w/c-ratio, the long-term absorption is even higher. Values as high as 35 litres/m<sup>3</sup> have been observed after 1 month water storage, which means that more than 50% of the air pores system has become water-filled; (19).

The dissolution-of-air mechanism therefore seems to be the main reason for the long-term absorption. This conclusion is strengthened by the fact that the long-term absorption increases with increased air content. This can be seen in Figure 13.

Air-bubbles enclosed in coarse isolated pores are exposed to an over-pressure  $\Delta P$ , which is inversely proportional to the bubble radius:

 $\Delta P = 2 \cdot \sigma / r \tag{7}$ 

Where  $\sigma$  is the surface tension between air and water.

The air solubility is directly proportional to the pressure (Henry's law). Therefore, there will be a higher concentration of dissolved air around a small air-bubble than around a big. Consequently dissolved air will move from small to big bubbles. It can be proven that this process leads to a reduction in total air-filled volume which causes a suction of water from outside; (1, 28) and APPENDIX 1. This process goes on simultaneously in all parts of the air-pore system. Therefore, long-term water uptake will not occur as a moving boundary process, but a certain volume adjacent to the water source (bigger than the unit cell) will be filled more or less uniformly. If the water uptake specimen is thin, this means that the water taken up in the experiment can be assumed to be distributed homogeneously in air-pores across the entire specimen volume.

The water absorption process is illustrated by Figure 14. Figure 14(a) shows a system consisting of two air-bubbles. The bubbles are connected by a water-filled capillary. If the difference in bubble size is big enough, water will move from pore 1 to pore 2 until pore 1 has lost all its air and is completely filled by water. Figure 14(b) shows a material volume (bigger than the unit cell) in contact with water. The process shown in Fig 14(a) will occur between all adjacent bubbles over the entire volume. The net effect of this redistribution of air is a gradual water uptake from outside. Figure 14(c) shows the absorption which can be assumed to occur simultaneously across the entire material volume when this is not too big.



Figure 14: The long-term water absorption process in air-pores.

The process has been theoretically analysed in (8, 28). A thorough presentation is also given in APPENDIX 1. The analysis shows that the process is governed by the diffusivity of dissolved air in the saturated matrix (cement paste), and that the size distribution of the air-pore system plays a fundamental role.

The analysis indicates that the long-term absorption in air-pores can be described by:

 $w=c \cdot t^d$  (8)

Where w is water taken up  $[kg/m^2]$  at time t. c and d are material dependent coefficients. c depends mainly on the diffusivity of dissolved air. The exponent d is to a high degree determined by the bubble size distribution (i.e. the air-pore size distribution). d<0.5, i.e. the long-term water absorption is retarded.

#### Note

There are also other mechanisms for water uptake than the three major mechanisms described above. Examples are:

- 1. Some water can probably be absorbed (or desorbed) during thawing of structures in contact with liquid water. This mechanism is of low significance, however, since a new freezing seldom occurs directly after thawing (except for in an "open" cyclic freeze-thaw test). Before the new freezing occurs, the concrete normally has the possibility to dry out this sucked-in water.
- 2. Under some conditions water might be absorbed by a mechanism similar to that causing frost heave in soil. This can occur in a low quality concrete member with one surface exposed to frost and the other side for long time exposed to unfrozen water; like a dam, or water reservoir wall. Then, under some conditions as regards water permeability and temperature, water can be attracted by big icelenses formed at an immobile "zero-degree front" inside the member. This is a very rare situation, however. It might possibly be accompanied by big destruction of the member. This type of destruction is not treated in this report. It is not even known if the mechanism exists in concrete.
- 3. The mechanisms, and the calculation methods described above, assume that there are no temperature gradients in the structure. Water might, however, move under temperature gradients also when there are no gradients in moisture level as expressed in vapour pressure or suction. How such moisture movement occurs is not fully understood, and transport coefficients for this type of transport in concrete are non-existing. Probably such transport is negligible compared with transport driven by gradients in moisture level.

## 4.3 Theoretical calculation of water-time field in concrete--possibilities

Even if theoretical possibilities exist, as described above, it seems impossible in practice to predict the future moisture-time field in a given unit cell in the structure with the precision required for a prediction of the exact risk of frost damage in the cell. The reasons are obvious:

- 1: The critical water content is almost always above the "hygroscopic range", and normally also above the "capillary absorption range". A certain fraction of the air pore system, therefore, has to be water-filled for frost damage to occur. Theories for calculating water uptake in range 3 are almost non-existing although some attempts to derive a theory have been made as described above. This theory is insufficiently verified. Some verification that seems fairly promising can be found in (28). More information is required however on how the absorption process in air-voids proceeds on different distance from the outer water source. Such information might possibly be obtained by computer modelling the dissolution-diffusion process within a web of numerous air-pores generated by the computer. The analysis of a two-pore model treated in (28) and APPENDIX 1 might be used as the basis for such a modelling.
- 2: Calculations of moisture transport within the *hygroscopic* and *capillary* ranges can be made since theories are available. Furthermore, experimental methods for determination of necessary material data for transport coefficients and moisture fixation exist. Despite this the calculations are uncertain since re-distribution of moisture at varying outer "moisture load" requires information of absorption-desorption hysteresis phenomena in moisture transport and fixation. Such information is lacking.
- 3: The biggest complication is that it is impossible to accurately predict the future fluctuation in outer moisture conditions. Even if "historic" weather statistics for the location where the structure is standing is available it will be impossible to predict exactly how the microclimate around all parts of the structure, i.e. the *boundary conditions*, to be used in the moisture calculation, will look like during the intended future service life of the structure.

Approximate calculations can however be made for simulated moisture conditions. Some examples are given in Figure 15-17.

### Moisture range 1:

Figure 15 shows the calculated RH-distribution in the concrete cover of a concrete exposed to regular variations in outer RH. It is interesting to see that the concrete "feels" changes in the outer moisture conditions only on the outermost few centimetres. The equilibrium RH on big depth in the concrete is higher than the average outer RH which depends on the fact that the sorption isotherm is non-linear.

### Moisture ranges 1+2:

Figure 16 shows the effect of exposing the same concrete as in Figure 15 for periodic rain and drying. Now, the moisture level is higher and fluctuations occur on a higher depth from the surface

### Moisture range 3:

Figures 17 and 18 give the result of a calculation of the water absorption in the air-pore structure of a concrete with two different types of size distribution of air-pores;  $S_a$  is the

volume fraction of water-filled air-pores. The calculation shows that the absorption characteristics are different for the two distribution types despite the fact that the average air-pore size as described by the specific surface  $\alpha_0$  is unchanged.



*Figure 15: Concrete w/c=0.40 exposed to cyclic variation in outer RH between* 60% and 90% RH; (29).



Figure 16: Concrete w/c=0.40 exposed to cyclic rain and drying; (29).



Figure 17: Calculated water absorption in the air-pore system of concrete; S<sub>a</sub> is the volume fraction of water-filled air-pore system. Diffusivity of dissolved air is assumed to be either 10<sup>-11</sup> or 10<sup>-12</sup> m<sup>2</sup>/s. The air-pore size frequency curve is described by f(r)=k·lnb/b<sup>r</sup> where k and b are constants and r is pore radius. The specific surface of the empty air-pore system is varying from 10 mm<sup>-1</sup> to 50 mm<sup>-1</sup> (average pore radius 0.3 mm to 0.06 mm); (28).



Figure 18: Calculated water absorption in the air-pore system of concrete. The air-pore size frequency curve is described by  $f(r)=k(1/r^b+1/r_{max}^b)$  where k and b are constants and r is pore radius. The air diffusivity and the specific surface of the air-pore system are the same as in Figure 17; (28).

# 4.4 Experimental determination of capillary water uptake in concrete

Instead of basing the prediction of the future moisture level on a highly uncertain theoretical calculation, one can base it on a simple water absorption test of the type shown in Figure 11. An example of the result of such a test is shown in Figure 13.

It is important to use as thin specimen as possible, partly in order to obtain a well-defined breaking-point, partly to obtain homogeneous long-term air-pore absorption across the entire specimen volume. The thickness must of course be bigger than the representative cell, but since this is thinner than a few millimetres, this is not a problem.

#### Short-term absorption

The first steep absorption line before the breaking-point describes the rising water front. The absorption after the breaking-point describes the gradual absorption in the air-pore system.

The rising front is described by:

$$W/A=k \cdot t^{1/2}$$
 (9)  
 $t=m \cdot z^2$  (10)

where W is the absorbed water [kg], A is the area of the surface in contact with water  $[m^2]$ , k is a capillarity coefficient  $[kg/(m^2 \cdot s^{1/2})]$ , z is the depth of the penetrating water front [m], and m expresses the resistance to penetration of the water front  $[s/m^2]$ .

The coefficients k and m can be calculated from the experiment; Figure 11:

$$k = [(W_b - W_o)/A] \cdot (1/t_b^{1/2})$$
(11)

$$m = t_b / H^2$$
(12)

where  $W_o$  is the water content when the test starts [kg],  $W_b$  is the water content at the breaking-point [kg],  $t_b$  is the suction time at the breaking point [s], A is the area in contact with water [m<sup>2</sup>], and H is the specimen thickness [m].

Data of m and k for OPC-concrete can be found in (30). The coefficient m is fairly independent of the initial water content:

$$m \approx (1-2 \cdot P_{CAP}) \cdot 11 \cdot 10^7 \text{ kg/(m}^2 \cdot \text{s}^{1/2})$$
 (13)

where  $P_{CAP}$  is the capillary porosity of the cement paste ( $P_{CAP}=(w/c-0.39\alpha)/(w/c+0.32)$ ); i.e.

$$m \approx [1 - 2(w/c - 0.39 \cdot \alpha)/(w/c + 0.32)] \cdot 11 \cdot 10^7 \text{ kg}/(m^2 \cdot s^{1/2})$$
(14)

where  $\alpha$  is the degree of hydration.

The coefficient k depends on the initial water content when capillary absorption starts. For concrete pre-conditioned to equilibrium with 50% RH the following expression might be used, (30):

$$k \approx C \cdot (w/c - 0.27)/m^{1/2}$$
 (15)

where C is the cement content  $[kg/m^3]$ .

#### Example

OPC-concrete with w/c=0.50. Pre-conditioned at 50% RH before suction starts. Degree of hydration 75%. According to Equation (14),  $m\approx 5\cdot 10^7$  s/m<sup>2</sup>.

1. A unit cell of thickness 3 mm located at the surface. The entire cell has reached capillary saturation after  $t_b=5\cdot10^7\cdot0.003^2=450$  s (7.5 minutes)

2: The same unit cell but located on a distance 5 cm from the surface. The cell starts to absorb water after  $5 \cdot 10^7 \cdot 0.050^2 = 1.24 \cdot 10^5$  s (34.5 hours) The entire cell has reached capillary saturation after  $t_b = 5 \cdot 10^7 \cdot 0.053^2 = 1.40 \cdot 10^5$  s (39 hours)

The example shows that it takes 35 times as long time to reach capillary saturation in a 3 mm thick cell that is located 5 cm form the surface than in an equal cell at the surface. The deep cell will not "feel" water at the surface until many hours or days have passed. Short exposure to water (like rain) will therefore only affect the outermost representative cells.

#### Long-term absorption

The breaking-point in the absorption curve corresponds to a state where all capillary pores are water-filled but the isolated air-pores are still air-filled (apart from some small absorption needed for creating an air-bubble inside the air-pore; see Figure 14 (a). A theoretical analysis made in APPENDIX 1 shows that also some of the smallest air-pores become water-filled already during the first rapid absorption process. This depends on that air-bubbles enclosed in small air-voids are almost completely compressed due to the over-pressure caused by the surface tension between air and water; (1,28) and APPENDIX 1. The total volume of such small air-pores is normally marginal.

An example of the good correlation between the measured air content of the hardened concrete and the air content calculated as the difference between total pore volume and water-filled pore volume at the breaking-point is shown in Figure 19. The air content is calculated from the breaking point as follows.

$$V_{a,b} = V_p - V_{w,b} \tag{16}$$

$$a = V_{a,b} / V \tag{17}$$

where  $V_{a,b}$  is the air content left in the specimen at the breaking point [m<sup>3</sup>],  $V_p$  is the total pore volume (including all air-pores and other pores in the concrete) [m<sup>3</sup>],  $V_{w,b}$  is the volume of pores water-filled at the breaking point [m<sup>3</sup>], a is the air content of the concrete [m<sup>3</sup>/m<sup>3</sup>] and V is the specimen volume [m<sup>3</sup>].



Figure 19: Correlation between the measured air-content in 8 types of concrete  $(a_{measured})$ , and the air-content calculated from the breaking-point absorption using Equation (17)  $(a_b)$ ; (19).

After the breaking-point there is always a slow continued water absorption that occurs in airpores *inactivating* these. If the specimen is thin, the observed water absorption can be assumed to be almost evenly distributed across the entire specimen thickness. Thus, water taken up in the air-pore system is; see Figure 11:

$$w_a = W_a / (A \cdot H) \tag{18}$$

where  $w_a$  is the water content absorbed in air-pores in 1 m<sup>3</sup> of concrete [kg/m<sup>3</sup>],  $W_a$  is the measured long-term water taken up by air-pores in the specimen [kg], A is the surface exposed to water [m], and H is the specimen thickness [m].

The total water content in the concrete after the breaking point has been reached is:

$$W_{cap} = W_b + W_a = W/(A \cdot H) = (W_b + W_a)/(A \cdot H)$$
 (19)

where  $w_{cap}$  is the total water content in the specimen taken up during a capillary absorption experiment [kg/m<sup>3</sup>],  $w_b$  is the water content at the breaking point [kg/m<sup>3</sup>], W is total water sucked up by the specimen [kg], and  $W_b$  is the water sucked up at the breaking-point [kg].

It is not possible to follow the long-tem water absorption for more than a couple of months. In practice the concrete might be sucking water for decades. Theoretical analysis and test results indicate, however, that the long-term absorption might be extrapolated as; (28) and APPENDIX 1:

$$\mathbf{w}_{cap} = \mathbf{w}_b + \mathbf{c} \cdot (\mathbf{t} - \mathbf{t}_b)^d \approx \mathbf{w}_b + \mathbf{c} \cdot \mathbf{t}^d \tag{20}$$

where c and d are material coefficients; see paragraph 3.2 moisture range 3. Since the time  $t_b$  at the breaking point is normally short compared with the total water uptake time t, it can

normally be neglected; i.e. absorption in air-pores is assumed to start immediately. This simplification is quite acceptable for unit cells close to the surface. For cells deep in the structure the time  $t_b$  can be quite big and then the simplification is more dubious, unless the structure is sucking water for months or decades, like hydraulic structures.

Since it is normally only the cement paste phase that is vulnerable to frost, and it is only the cement paste that is porous, it is more convenient to express water content in terms of degree of saturation. For definition see equation (1). Then, the water absorption process can be described by:

$$S_{cap} = S_b + e \cdot t^d \tag{21}$$

Where  $S_b$  is the degree of saturation reached at the breaking-point. e is a material coefficient that can be easily calculated from the coefficient c in equation (8) by knowing the water content at complete saturation,  $w_{sat} [kg/m^3]$ :

 $e=c/w_{sat}$  (22)

#### Note

In the analysis made above of long-term absorption, it is assumed that the water absorption process proceeds in the same manner irrespectively of the thickness of the structure. In reality the thickness ought to influence the absorption process for the following reasons:

- 1. When the water front is penetrating the concrete, air must be expelled from the previously air-filled capillaries. This makes a hinder to water ingress. A thicker structure means bigger hindrance; i.e. the coefficients m ought to be higher and k ought to be lower the thicker the concrete member.
- 2. Absorption in air-pores requires that dissolved air is transported by diffusion in pore water to the surface. The thicker the member, the bigger the resistance to this transport.
- 3. On big depth from the surface the supply of water from outside might be lower than the potential transport of dissolved air from the air-pores. In this case the long-term absorption will be obstructed.

All three effects cause the long-term water absorption to be slower the thicker the concrete member. This means that water absorption calculated from an absorption experiment with thin specimens according to the theories above are on the "safe side".

## 4.5 The equivalent capillary absorption time

The simple capillary absorption experiment might be used as a substitute to the real absorption in practice. Each real environment is assumed to correspond to a certain capillary absorption time. This can be called an "*equivalent capillary absorption time*",  $t_{equiv}$ . It is illustrated in Figure 20.



Figure 20: Examples of equivalent capillary absorption time.
(a) Façade alternately exposed to rain and drying. One unit cell at the surface (cell 1), and one at the bottom side (cell 2).
(b) A road surface alternately exposed to rain ,de-icing salt, drying. One unit cell at the upper surface (cell 3).
(c) A pillar constantly in water. No drying possible. One unit cell in the interior (cell 4).

(a) A *façade element* is sometimes exposed to rain. Sometimes it dries outwards. Sometimes the sun shines on the surface forcing the drying process. Unit cells at the surface might reach a maximum moisture content corresponding to 1 week of rain (more in some climates). Cells at the far end of the element will probably not reach higher moisture content than that corresponding to the breaking-point absorption in the experiment.

Cell 1:  $t_{equiv} = 1$  week Cell 2:  $t_{equiv} = t_b$ 

(b) A *road surface* is sometimes exposed to rain and melting snow. Sometimes it dries. Water might also be taken up from the ground. During winter the surface might be exposed to deicing salt that keeps the surface moist also when there is freezing temperatures. Maybe unit cells at the surface will reach a moisture content corresponding to 4 months of capillary water uptake.

Cell 3:  $t_{equiv} = 4$  months.

(d) A structure standing in water from casting until its service life is ended will constantly absorb water. A unit cell in the interior will reach a moisture content that is equal to capillary absorption during the whole service life of the structure (provided the effect of self-desiccation is neglected which is reasonable for very long absorption times).

Cell 4: t<sub>equiv</sub>= required service life.

The moisture content in Cells 3 and 4 must be based on extrapolation of capillary suction tests. The extrapolation can be based on equation (20) or (21). The coefficients  $w_b$ ,  $S_b$ , c, e and d are evaluated from the test. The longer the duration of this, the safer is the extrapolation.

## 4.6 Field investigations of the equivalent capillary absorption time

In order to find values of  $t_{equiv}$  for different types of structures one can make field investigations of real variations in moisture level *during winter-time* in typical structures. These values are compared with the result of capillary absorption tests performed on specimens taken from the same structure. The principles are illustrated by Figure 21.



Figure 21: Evaluation of the equivalent capillary absorption time from field investigations of the moisture state in a real structure.

- (a) A bridge deck. Moisture is determined on three levels in the structure. Measurements are made on different occasions. Specimens for capillary absorption experiment are taken out.
   (b) Moisture variations in the structure during a certain period.
  - (c) A capillary absorption curve extrapolated to long time. The maximum moisture level obtained in the field determines the equivalent capillary absorption time.
# 4.7 Conclusions – actual water content

Theories for a theoretical calculation of the future moisture-time field in a concrete structure exist. However, such theories cannot be used for a precise enough prediction of moisture levels that are of importance for frost damage. The moisture level of interest is above the hygroscopic range, and normally also above the capillary range. Theories and material data for these very high moisture ranges are lacking. It is not possible to predict the boundary moisture condition many decades in advance with the precision needed for a useful calculation of the future moisture state in all parts of the structure.

The best possibility is to use simple capillary absorption tests and from them extrapolate reasonable moisture conditions in different types of structures by using the concept "equivalent capillary absorption time". This can be determined by field investigations, or be based on "qualified reasoning".

# 5 The service life of a representative cell

# 5.1 Principles

Consider a representative unit cell in a structure; Figure 22. The critical moisture content of the cell, suitably expressed in terms of degree of saturation, has been determined either theoretically or by experiment. The critical degree of saturation  $S_{CR}$  might be a function of concrete age and is also a function of the minimum temperature. An example of  $S_{CR}$  is shown in Figure 22. More water is needed to destroy the cell when the minimum freezing temperature is high.

The actual moisture content in the cell  $S_{ACT}$  varies over time. The only important moisture contents are such that occur immediately before freezing takes place. An example of the  $S_{ACT}$ -variation before freezing is shown in Figure 22. It is supposed to be independent of the freezing temperature.

The cell is almost totally destroyed if the critical degree of saturation is transgressed once; see Figure 5. Thus, damage D is 100% when  $S_{ACT}>S_{CR}$ .

For the cell in Figure 22 service life is ended when, at time  $t_{-25}$ , the minimum temperature goes down to -25 °C, and it ends at time  $t_{-10}$  when the temperature only reaches -10 °C.

Therefore, in theory, service life is not only a function of the amount of water in the structure, but also of the minimum temperature. Normally, for safety reasons this can be neglected, and service life be based on the lowest temperature likely to occur.



Figure 22: The critical and actual degrees of saturation in a representative cell inside a structure. Total destruction (D=100%) is assumed to occur when the value of  $S_{CR}$  is transgresses once.

In prediction of service life with regard to frost there is a direct analogy with structural design:

- The *critical moisture content* corresponds to the *fracture load* at structural design.
   The *actual moisture content* corresponds to the *actual load* at structural design.

# 5.2 Stochastic prediction of the risk of frost damage

In Figure 22 both  $S_{CR}$  and  $S_{ACT}$  were assumed to be defined by unique values for each exposure time, i.e. calculation of service life is *deterministic* giving one single value. In reality both the critical moisture content and the actual moisture content of the representative cell should be treated as *stochastic variables*; see Figure 23. Therefore, also service life will be a stochastic variable.

The frequency function (f) and distribution function (F) of  $S_{CR}$  and  $S_{ACT}$  for a given exposure time are:

$$f(S_{CR})$$
 and  $f(S_{ACT})$   
 $F(S_{CR})$  and  $F(S_{ACT})$ 

Principally  $S_{ACT}$  is also a *time function*. In reality it is, however, not possible to predict *when* a certain value of  $S_{ACT}$  will occur; it might occur during the first year after erection of the structure, as well as during the 50:th year. Therefore, one can only calculate the *risk* of frost damage, but not exactly when this will occur. The distribution for  $S_{ACT}$  above shall therefore include the time variation of  $S_{ACT}$ .

The probability that frost damage shall occur is calculated by:

$$P\{\text{frost damage}\} = P\{S_{ACT} > S_{CR}\} = \int_{0}^{\infty} F(S_{CR}) \cdot f(S_{ACT}) \cdot dS$$
(23)

When the time functions of  $S_{CR}$  and  $S_{ACT}$  are known one can also use Equation (23) to calculate how the probability of frost damage changes with time. Values of  $F(S_{CR})$  and  $f(S_{ACT})$  valid for different age of the structure are introduced in the equation. Examples are given in paragraph 5.4.



Figure 23: Frequency and distribution functions of critical and actual degrees of saturation. Areas under the frequency curves are 1.

#### Example

Both  $S_{CR}$  and  $S_{ACT}$  are supposed to be normal distributed. The mean value and standard deviations are estimated to be (based on tests or calculations):

S <sub>CR</sub> :	Mean value $= 0.82$	Std. deviation = $0.03$
S <sub>ACT</sub> :	Mean value $= 0.76$	Std. deviation $= 0.08$

The probability of frost damage in the cell, completely destroying this, is 23 %.

#### Example

The uncertainty in  $S_{ACT}$  is higher, while the mean value is unchanged. The distribution of  $S_{CR}$  is unchanged. The following distributions are valid:

S <sub>CR</sub> :	Mean value $= 0.82$	Std. deviation $= 0.03$
S <sub>ACT</sub> :	Mean value $= 0.76$	Std. deviation = $0.15$

The probability of frost damage is increased to 33 %.

If a deterministic approach had been used in the two examples above, at which only the mean values were used, frost resistance should have been excellent since  $S_{CR,mean}$  was never transgressed by  $S_{ACT,mean}$  in any of the examples.

# 5.3 Deterministic prediction of service life based on capillary water absorption (potential service life)

The frost damage risk as function of time might be assessed from a capillary absorption experiment. Absorption is described by equation (21). This means that the value  $S_{ACT}$  increases with water absorption time. Consequently, the frost damage risk increases with increased absorption time.

The concrete is no longer frost resistant when the following condition is fulfilled:

$$S_{ACT} > S_{CR}$$
 (24)

Introducing Equation (21) in this equation gives the following *maximum* (*potential*) service *life* at uninterrupted water uptake.

$$t_{\text{life,pot}} = \left[ (S_{\text{CR}} - S_b)/e \right]^{1/d}$$
(25)

This potential service life can be compared with the equivalent absorption time,  $t_{equiv}$ ; see Figure 24. There are two possibilities:

- $t_{life,pot} > t_{equiv}$ : Damage can never occur; i.e. service life= $\infty$
- t<sub>life,pot</sub><t<sub>equiv</sub>: Damage will occur. It is not possible to say when this happens, but the service life will be short.



Figure 24: A structure in an environment which gives a certain equivalent capillary absorption time. Two types of concrete; one type (1) with "eternal" service life; one type (2) with short service life.

Example

A concrete façade element is considered.

The absorption test gave the following result:  $S_b=0.79$ .  $e=4.5 \cdot 10^{-3}$ . d=0.5. (The absorption time in days)

A freezing test gave the following value of the critical degree of saturation:  $S_{\text{CR}}{=}0.85$ 

The potential service life is:  $t_{\text{life,pot}} = [(0.85 - 0.79)/4.5 \cdot 10^{-3}]^{1/0.5} = 178 \text{ days}$ 

Frost damage will probably never occur, since it is very unlikely that a façade obtains a moisture content that can be reached first after  $\frac{1}{2}$  year of continuous water absorption.

# 5.4 Stochastic prediction of service life based on capillary water absorption

The stochastic approach can be applied to the capillary water experiment, which makes a more safe service life prediction possible than that obtained by the deterministic approach in the present paragraph.

The critical degree of saturation is assumed to increase somewhat with time. The capillary degree of saturation increases with increased absorption time. It may be described by Equation (21).

Both  $S_{CR}$  and  $S_{CAP}$  are stochastic variables that can be described by mean value and standard deviation. The actual distributions are determined experimentally at the two types of test made; i.e. a freeze-thaw test for  $S_{CR}$  and an absorption test for  $S_{CAP}$ .

The calculation is made by Equation (23). The method is illustrated by the example in Figure 25.



Figure 25: Example of a calculation of a stochastic service life calculation based on capillary absorption experiments.

The frost damage risk increases with increasing concrete age: The following values are obtained:

1 month:	8 %
1 year:	11%
10 years:	23%
50 years:	46%

These data are plotted in Figure 26. This figure can be used for calculation of the potential service life of a structure permanently in contact with water. Service will depend on the acceptable risk. If 20% risk is accepted, the potential service life will be about 5 years.



Figure 26: The example in Figure 24. Damage risk versus the capillary exposure time.

A calculation of the type performed can also be used for assessment of *the damage risk at the equivalent absorption time*, t<sub>equiv</sub> (see paragraph 4.6).

*The example above* The damage risk is 8% if the equivalent absorption time is 1 month. The damage risk is 23% if the equivalent absorption time is 10 years

# 5.5 Conclusions – service life

Service life of a given unit cell is ended when the real water level in the cell exceeds the critical water level once.

Service life can therefore be calculated if the future moisture-time field in the cell can be predicted with high precision. This is not possible, however due to lack of data concerning boundary conditions and transport data for the over-capillary range.

A capillary water absorption experiment can be used as substitute for the real moisture conditions. If the water content obtained at the equivalent absorption time does not transgress the critical water content, the cell will have high potential frost resistance. If the critical water content is transgressed at absorption times shorter than the equivalent absorption time the cell is likely to become damaged in practice.

The risk of frost damage can be calculated if the statistical distributions of the critical and real water contents are known. By defining a highest acceptable risk a potential service life can be calculated.

Using the same stochastic approach the damage risk for a given equivalent capillary absorption time can be assessed.

# 6 The service life of the structure

A structure is composed of numerous unit cells; see Figure 1. Each cell will have its own service life which depends on its critical and real water contents. When a certain cell is lost due to frost, the structure will loose part of its function (like load-carrying capacity). The residual function depends on the location of the cell lost. The process is illustrated by Figure 27.

Each cell has its own moisture-time field which depends on the boundary conditions for the cell. The critical water content is probably almost the same in all parts of the structure, provided the whole structural member is made of concrete from the same batch. One cannot exclude, however, that separation phenomena makes the value differ.

Cell 1 being directly exposed to outer moisture is lost at time  $t_1$  which is the first time that the real water content transgresses the critical. Then, total destruction of cell occurs.

Cell 2 is lost at time  $t_2$ .

Thereafter, more and more cells are lost until there are no more cells that can be critically saturated.

The gradual loss of unit cells weakens the structure. The effect can be calculated by methods used in traditional structural design. The effect of frost damage on destruction of concrete (loss in E-modulus, compressive strength, tensile strength and bond strength) has been studied, (10). Damage can be very big.



*Figure 27: The service life of the structure is determined by service life of individual unit cells in the structure.* 

# 7 The required air content for given service life and frost damage risk

The air content is a decisive factor both for the critical and the actual water contents. Therefore, the air content also determines the frost damage risk. Theoretically, both  $S_{CR}$  and  $S_{ACT}$  (or  $S_{CAP}$ ) diminish with increased air content. The reduction is  $S_{ACT}$  is dominant, however, which means that the frost damage risk is markedly decreased with increased air content. This fact is proven theoretically in APPENDIX 1.

Principal effects of the air content is illustrated by Figure 28.



Figure 28: Principal effects of the air content on the critical and actual water contents and on the probability for frost damage to occur. Determination of the minimum air content for obtaining a highest acceptable frost damage risk.

A certain  $S_{ACT}$ -curve in the figure is supposed to be valid for a given exposure time  $t_1$  (service life  $t_1$ ). Thus, the figure shows the frost damage risk at time  $t_1$  for different air contents. For a maximum acceptable damage risk  $P_{max}$  the required air content is  $a_{min,t1}$ .

If another, longer, exposure time is selected ( $t_2$ ) the value of  $S_{ACT}$  will normally be higher (at least if  $S_{ACT}$  is replaced by the uninterrupted capillary absorption  $S_{CAP}$ ). Thus, for *a given air content* the frost damage risk is increased. Alternatively, a higher air content ( $a_{min,t2}$ ) is required for the same damage risk  $P_{max}$ .

A diagram of type Figure 28 is therefore a sort of service life diagram that can be used for selection of the required air content for given service lives and frost risks. The diagram will be different for different types of concrete. The air-pore size distribution plays a fundamental role.

Exactly how changes in the air content affects the critical and actual degrees of saturation is not easy to predict in a precise way, since changes in air content also might cause changes in the-pore size distribution. Moreover, it is not known exactly how the water absorption process in the air-pore system takes place.

Theoretical methods for calculation of relations between air content, and the values of  $S_{CR}$  and  $S_{ACT}$  are presented in APPENDIX 1.

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## **Comment:**

Most references are to the author himself. For this seemingly self-glorifying reference list he should reasonably make his apologies. There is a reason, however, and that is that the service life model was developed by the author, and that most of the theoretical and experimental background work needed for developing and verifying the model were performed by the author. In order to be able to present the model in fairly condensed form reference to this background work must be made.

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# **APPENDIX 1**

# Theoretical calculation of service life and required air content

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# A1.1 Introduction and summary

As described in Chapter 7 the frost damage risk is determined by the air content; see Figure 28. The required air content can be calculated theoretically under some conditions:

- 1: The critical flow distance -see Figure 2- must be known.
- 2: The size distribution of air-pores must be known.
- 3: The absorption process in the air-pore system must be understood and be possible to quantify.
- 4: The relation between the outer moisture conditions -the boundary moisture conditionsand the time-process of water uptake in the air-pore system must be known.

Conditions 1-3 are required for a calculation of the effect of air on the critical water content,  $S_{CR}$ .

Condition 4 is required for a calculation of the effect of air on the time-development of the actual water content,  $S_{ACT}$  or  $S_{CAP}$ .

In Chapter A1.2 theoretical methods for calculating the value of  $S_{CR}$  are described and exemplified. Theoretical and experimental methods for determination of the critical flow distance are given.

In Chapter A1.3 a theoretical background to the mechanism behind long-term water uptake in the air-pore system is presented. On basis of this theory, values of  $S_{ACT}$  are calculated for concrete with different air-pore systems and air contents.

In Chapter A1.4 deterministic and probabilistic methods for estimation of the frost damage risk are presented and exemplified.

In Chapter A1.5 the relation between air content and service life is treated theoretically and exemplified. It is shown that the traditional concept Powers spacing factor cannot be used for calculation of required air content and service life since it does not consider water uptake in air-pores.

In Chapter A1.6 methods for experimental determination of material parameters required for analysis of service life are presented.

# A1.2 Calculation of the critical moisture content; $S_{CR}$

# A1.2.1 Principles

The air-pore system is described by a frequency function of pore radii, f(r); Figure A1.1.



Figure A1.1: Frequency curves for the air-pore radius.

## Totally air-filled air-pore system

The specific surface  $\alpha$  of the *totally air-filled* air-pore system is  $\alpha_0 (m^{-1})$ . Specific surface is defined:

$$\alpha = s/a$$
 (A1.1)

Where s is the total envelope surface of all pores considered (m<sup>2</sup>) and a is the total volume of these pores (m<sup>3</sup>). Thus, the specific surface is a measure of the fineness of the air-pore system; the higher the value of  $\alpha$ , the finer the pore system.

At the *breaking-point* in a capillary absorption experiment -see Figure 11 and 13- all air-pores are actually air-filled, see Figure 19. Then, the air-volume is  $a_0$  (m<sup>3</sup>), which is equal to the total air content, and the surface area is  $s_0$  (m<sup>2</sup>). The specific surface is  $\alpha_0$  (m<sup>2</sup>/m<sup>3</sup>=m<sup>-1</sup>).

$$\alpha_0 = s_0 / a_0$$
 (A1.1')

When the air-pore system is empty the actual flow distance, D (m), from a place where water freezes and the nearest air-filled pore -see Figure 2- is the shortest possible:

 $D=D_0$  (A1.2)

D can be calculated in different ways as described in paragraph 3.1. For simplicity the *spacing factor* described by Powers is used, (11) (although only actually *air-filled pores* are considered, and not all air-pores like in Powers original use of the spacing factor; see also paragraph A.5.1). All air-filled pores are assumed to be of equal size (which is not correct) and located in a loose-packed cubic array inside the cement paste (not correct either).

However, this simplification is acceptable for a description of the calculation technique. The spacing factor depends on the air volume and the specific surface of the air-filled pores:

$$\mathbf{D} = (3/\alpha) \cdot \{1.4(1/a)^{1/3} - 1\}$$
(A1.3)

The factor 1/a is the relation between  $1m^3$  of the material including air, and the air volume  $a_0$  in the same  $1m^3$  of the material.

Thus, D at the breaking point in a capillary absorption experiment is:

$$D_0 = (3/\alpha_0) \cdot \{1.4(1/a_0)^{1/3} - 1\}$$
(A1.3')

In deriving this equation, only the cement paste is considered. Thus, the flow distance is the distance inside the cement paste. This means that  $a_0$  is the air content of the cement paste and not of the concrete.

#### Partially water-filled air-pore system

When water gradually enters the air-pore system the residual air content and the surface area gradually decrease. It is assumed that a small air-pore is water-filled before a bigger pore. This means that, after certain water absorption, *all air-pores with radii smaller than*  $r_w$  *are water-filled*. Then, the residual air volume  $a_a$ , the residual surface area  $s_a$ , the residual specific surface  $\alpha_a$ , and the new flow distance  $D_a$  are:

$$a_a = \int_{r_w}^{r_{max}} f(\mathbf{r}) \cdot (4/3)\pi r^3 d\mathbf{r}$$
(A1.4)

$$s_a = \int_{r_w}^{r_{max}} f(r) \cdot 4\pi r^2 dr$$
(A1.5)

$$\alpha_a = s_a/a_a \tag{A1.6}$$

$$D_{a} = (3/\alpha_{a}) \cdot \{1.4(V/a_{a})^{1/3} - 1\}$$
(A1.7)

Where V is the total, frost sensitive, volume considered  $(m^3)$  (including air pores), and a is the air volume in the entire material volume.

In normal concrete only the cement pate phase is porous and frost sensitive. D is the flow distance inside the cement paste: Thus, for this case equation (A1.7) can be written:

$$D_{a} = (3/\alpha_{a}) \cdot \{1.4(V_{p}/a_{a})^{1/3} - 1\}$$
(A1.7')

Where  $V_p$  is the volume of cement paste (including the air pores) (m<sup>3</sup>/m<sup>3</sup>), and a is the volume of air in the *concrete* (m<sup>3</sup>/m<sup>3</sup>).

The more water in the air-pore system, the bigger the value of  $r_w$ , the lower the values of  $a_a$  and  $\alpha_a$ , and the bigger the value of  $D_a$ . When the pore system is completely filled,  $r_w=r_{max}$ ,  $a_a=0$ , and  $D_a=\infty$ .

The principal effects of air-pore absorption are illustrated by Figure A1.2.



Figure A1.2: Effect of a gradual water-filling of the air-pore system on the residual air content, the residual specific surface and the residual flow distance ("spacing factor").

After a certain (critical) water absorption the flow distance equals the critical flow distance. Then, all pores with radius smaller than  $r_{w,CR}$  are filled. If absorption continues, the concrete will be harmed by frost. This means that  $a_{CR}$  corresponds to a critical degree of saturation of the cement paste.

The critical degree of saturation of the *cement paste*  $(S_{CR,p})$  can be calculated by (definition of S in equation (1):

$$S_{CR,p} = (P_p - a_{CR,p})/P_p = 1 - a_{CR,p}/P_p$$
 (A1.8)

Where  $P_p$  is the total pore volume of the cement paste including air-pores (m<sup>3</sup>), and  $a_{CR,p}$  is the critical air content in the cement paste (m<sup>3</sup>).

#### Note:

The critical *degree of saturation of the concrete* ( $S_{CR,c}$ ) is the same as for the *cement paste*, provided there are no other pores that can be water-filled than pores in the cement paste; i.e. the cement paste is the only frost sensitive phase in the concrete. This statement can be easily proven. Let  $P_p$  be the pore volume in 1 m<sup>3</sup> cement paste, i.e.  $P_p$  in equation (A1.8) is the cement paste porosity (m<sup>3</sup>/m<sup>3</sup>), and let  $a_{CR,p}$  in equation (A1.8) be the critical air content in 1 m<sup>3</sup> cement paste; i.e.  $a_{0,p}$  is the total air content expressed in m<sup>3</sup> per m<sup>3</sup> of the cement paste.

Then:	
$P_c = V_p \cdot P_p$	(A1.9′)
$a_{0,c} = V_P \cdot \dot{a}_0$	(A1.9'')
$a_{CR,c} = V_p \cdot a_{CR}$	(A1.9''')

Where  $V_p$  is the volume fraction of cement paste in the concrete including air-pores (m<sup>3</sup>/m<sup>3</sup>), P<sub>c</sub> is the porosity of the concrete (m<sup>3</sup>/m<sup>3</sup>), , a<sub>0,c</sub> and a<sub>CR,c</sub> are the total air content and the critical air content in the concrete (m<sup>3</sup>/m<sup>3</sup>).

The critical degree of saturation of the concrete is by definition:

$S_{CR,c} = (P_c - a_{CR,c})/P_c = 1 - a_{CR,c}/P_c$	(A1.10)
Inserting equations (A.1.9') and (A1.9''') in equation (A1.10) gives:	
$\mathbf{S}_{\mathbf{CR},\mathbf{c}} = 1 - \mathbf{V}_{\mathbf{P}} \cdot \mathbf{a}_{\mathbf{CR},\mathbf{p}} / \mathbf{V}_{\mathbf{P}} \cdot \mathbf{P}_{\mathbf{p}} = 1 - \mathbf{a}_{\mathbf{CR},\mathbf{p}} / \mathbf{P}_{\mathbf{p}} = \mathbf{S}_{\mathbf{CR},\mathbf{p}}$	(A1.8)

### A1.2.2 Examples of calculation of S<sub>CR</sub>

The effect of a gradual water-filling of the following two types of air-pore systems will be calculated

1. The exponential type of pore size distribution

$$f(r) = k \cdot \ln b / b^r \tag{A1.10}$$

Where k is a coefficient that is only dependent of the material volume considered; e.g. b is 1000 times bigger when 1  $m^3$  of concrete is considered than when 1 litre is considered. b is a coefficient that is dependent on the fineness of the air-pore system. It is related to the specific surface of the empty pore system:

$$b = \exp(\alpha_0) \tag{A1.11}$$

2. The power type of pore size distribution

$$f(r) = \lambda \{ 1/r^{c} - 1/r_{max}^{c} \}$$
(A1.12)

Where  $\lambda$  has the same function as k. c is related to the fineness of the entire air-pore system by the following equation:

$$\alpha_0 = [4(4-c)/(3-c)] \cdot (r_{\max}^{3-c} - r_{\min}^{3-b}) / (r_{\max}^{4-c} - r_{\min}^{4-c})$$
(A1.13)

The different types of size distribution are shown in Figure A1.3.



Figure A1.3: Frequency functions of different air-pore size distributions.  $(r_{min}=10\mu m, r_{max}=1000\mu m=1mm)$ 

The effect of water absorption on the residual air content is calculated by equation (A1.4) The result is shown in Figure A1.4. It is assumed that  $r_{min}=10\mu m$  and  $r_{max}=1$  mm.

The figure shows clearly that for the same specific surface of the empty air-pore system ( $\alpha_0$ ) and a given size of the biggest water-filled pore, a much smaller fraction of the air-pore

system is water filled in a pore system of power type. This depends on the fact that most airpore space is located in big pores for this type of distribution; see Figure A1.3.

The effect of water absorption on the residual specific surface is calculated by equation (A1.6). The result is shown in Figure A1.5.

The figure shows that the reduction in specific surface of the residual air-filled part of the airpore system occurs much more rapidly for the power distribution. This is a consequence of the big number of very small air-pores for this type of distribution; see Figure A1.3.



*Figure A1.4: Effect of water absorption on the volume fraction of filled air-pores.* 



*Figure A1.5: Effect of water absorption on the residual specific surface.* 

Figure A1.4 and A1.5 can be used for a calculation of  $S_{CR}$ . The calculation procedure will be shown by some examples.

Example A1.1: Exponential air-pore distribution	
Assumptions: $\alpha_0=30 \text{ mm}^{-1}$ . D <sub>CR</sub> =0.40 mm. 1m <sup>3</sup> of the concrete is considered. Air content in concrete, $a_0=4.5\%$ . Cement paste volume including air, V <sub>p</sub> =32.5%. Total porosity, 16.5%.	
The calculation is made "graphically" using figures A1.4 and A1.5. a) Assume $r = 140 \text{ um}$	
According to Figure A1.4 the water-filled pore volume is 62% of the total air-pore volume. Thus $a_{=}(1-0.62)45\%=1.71\%$	
According to Figure A1.5 $\alpha_a = 16 \text{ mm}^{-1}$ . The spacing factor D=(3/16){1 4(32.5/1.71)^{1/3}-1}=0.51 \text{ mm}^{-1}	
This is bigger than $D_{CR}$ . Thus, a too big water-filled pore was assumed.	
b) Assume $r_w=120 \ \mu m$ . According to Figure A1.4 the water-filled pore volume is 48% of the total air-pore volume. Thus $a_a=(1-0.48)4.5\%=2.34\%$	
According to Figure A1.5 $\alpha_a$ =19 mm <sup>-1</sup> . The spacing factor D=(3/19){1.4(32.5/2.34) <sup>1/3</sup> -1}=0.37 mm This is smaller than D <sub>CR</sub> .	
Interpolation gives the critical air content $a_{CR}$ =2.25%. (corresponds to $r_{w,CR}$ =124 µm)	
The critical degree of saturation of the concrete is according to equation (A1.10):	
$S_{CR} = (16.5 - 2.25)/16.5 = 0.86$	

#### Example A1.2: Power distribution of air pores

Assumptions: The same as Example A1.1: Thus,  $\alpha_0=30 \text{ mm}^{-1}$ . D<sub>CR</sub>=0.40 mm. Air content  $\alpha_0=4.5\%$ . Cement paste volume including air, V<sub>p</sub>=32.5%. Total porosity, 16.5%.

The calculation is made "graphically" using figures A1.4 and A1.5. a) Assume  $r_w=100 \mu m$ . According to Figure A1.4 the water-filled pore volume is 15% of the total air-pore volume. Thus  $a_a=(1-0.15)4.5\%=3.83\%$ According to Figure A1.5  $\alpha_a=12 \text{ mm}^{-1}$ . The spacing factor D=(3/12){1.4(32.5/3.83)<sup>1/3</sup>-1}=0.46 mm This is bigger than D<sub>CR</sub>. Thus, too big water-filled pore was assumed.

b) Assume  $r_w=70 \mu m$ .

According to Figure A1.4 the water-filled pore volume is 10% of the total air-pore volume. Thus  $a_a=(1-0.10)4.5\%=4.05$ According to Figure A1.5  $\alpha_a=14 \text{ mm}^{-1}$ . The spacing factor D=(3/14){1.4(32.5/4.05)^{1/3}-1}=0.39 \text{ mm} This is somewhat smaller than D<sub>CR</sub>.

Interpolation gives  $a_{CR}$ =4.3%. This means that almost no air-pores can be allowed to become water-filled. ( $r_{w,CR}$ =74 µm)

The critical degree of saturation of the concrete is according to equation (A1.10):

 $S_{CR} = (16.5 - 4.3)/16.5 = 0.74$ 

These two examples show some interesting things:

- 1: The critical water-filling is highly dependent on the shape of the air-pore structure. The smaller the volume of small pores, the smaller the allowable water-filling and the lower the value of  $S_{CR}$ .
- 2: The critical degree of saturation is a function of the *shape* of the air-pore system, and not only on the specific surface  $\alpha_0$  and air-content  $a_0$ , as is predicted by the Powers spacing factor applied to the empty air-pore system; c.f. paragraph A1.5.1.
- 3: Since the time it takes to fill a pore of fixed size is probably fairly independent of the shape of the air-pore system (see paragraph A1.3.1), also the value of S<sub>ACT</sub> for a given water absorption time is fairly independent of the pore system shape. This means that *the frost damage risk is highly dependent of the shape of the air-pore system* and not only of the total air content and specific surface; pore systems reducing the value of S<sub>CR</sub> increase the frost damage risk, and reduce the service life.

#### Example A1.3: Power distribution of air pores

Assumptions: The same as Example A1.2: Thus,  $\alpha_0=30 \text{ mm}^{-1}$ . D<sub>CR</sub>=0.40 mm. Porosity excluding air pores, 16.5-4.5=12%. Cement paste volume excluding air pores 32.5-4.5=28%. The air content is however now unknown and shall be calculated.

**To be calculated:** the air content needed in order to sustain frost attack when the biggest waterfilled pore is the same as in Example A1.1; i.e. when the water absorption time has been the same as that needed for causing frost damage in the concrete in Example A1.1.

The calculation is made graphically using figures A1.4 and A1.5. a) According to Example A1.1  $r_{w,CR}$ =124 µm. According to Figure A1.4 the water-filled pore volume is 19% of the total air-pore volume. Thus  $a_{CR}$ =(1-0.19) $a_0$ %=0.81 $a_0$ According to Figure A1.5  $\alpha_a$ =10 mm<sup>-1</sup>. The spacing factor D=(3/10){1.4[(28+a\_0)/0.81a\_0]^{1/3}-1}=0.40 mm (The critical value D<sub>CR</sub>) **This gives the required air content 10.2%**!

The critical degree of saturation is now very low. Assuming the same total amount of pores except the air- pores as in Example A1.1 (i.e. 16.5-4.5=12%) the total porosity is 12+10.2=22.2%. The critical air content is  $0.81\cdot12=9.7\%$ 

S<sub>CR</sub>=(22.2-9.7)/22.2=0.56.

This example shows that much more air is needed in an air-pore system of the power type than in a pore system of the exponential type despite the fact that the specific surface of the empty air-pore system is the same. *This shows the very big drawback of using the Powers spacing factor as it is normally used. This is further discussed in paragraph A1.5.1.* 



A comparison with Example A1.1 shows that an increase in fineness of the air-pore system leads to an increase in the  $S_{CR}$ -value.

## A1.2.3 Estimation of variations in $S_{CR}$

In the examples above it was assumed that the air-pore system could be expressed by an exact frequency function and that the critical flow distance had a distinct value. In reality there is an uncertainty in the shape of the air-pore system, and this might vary from one unit cell to the other. There is also an uncertainty in the critical flow distance. Also the total air content has a certain variation. This means that the calculated value of  $S_{CR}$  will be defined within a certain interval. The principles are shown in Figure A1.6.



*Figure A1.6: Principles for calculation of the critical degree of saturation as a stochastic variable.* 

The variation in air-pore structure is supposed to be expressed by a	
variation in the specific surface $\alpha_0$ . Therefore also, the frequency	
function f(r) of the pore radius will have a certain variation.	
Therefore, according to equation (A1.4) the relation between the	
biggest water-filled air-pore r <sub>w</sub> and the residual air content a <sub>a</sub> must be	
a stochastic variable.	
Moreover, application of equation (A1.6) gives the variation in the	
residual specific surface $\alpha_a$ valid for given values of $r_w$ .	
The total air content $a_0$ is not constant but is supposed to have a	
certain variation.	
Combining Figure A1.6(b), A1.6(c) and A1.6(d) using equation	
(A1.7) gives the variation in flow distance D.	
The critical flow distance D <sub>CR</sub> has a certain variation.	

Figure A1.6(g): Combining Figure A1.6(d) and A1.6(e). and using Figure A1.6(c) for the value of the air content  $a_a$  that corresponds to the value of D being equal to  $D_{CR}$ , gives the variation in the critical degree of saturation.

## Example A1.5 In order to get an idea of the magnitude of variations in $S_{CR}$ a calculation is made for a concrete with the following quite big variations: • The air-pore structure is described by the exponential frequency function (A1.10) • The specific surface $\alpha_0$ varies between 30 mm<sup>-1</sup> and 40 mm<sup>-1</sup>. • The total air content varies between 5.0% and 5.5%. • The critical spacing factor varies between 0.35 mm and 0.40 mm. • The porosity exclusive of air-pores P<sub>gel+capillaries</sub> varies between 12.1 and 12.8%. • The cement paste volume excluding air pores is constant 28% The maximum value of $S_{CR}$ is obtained for $\alpha_0=40 \text{ mm}^{-1}$ , $a_0=5.0\%$ , $D_{CR}=0.40 \text{ mm}$ , P<sub>gel+capillaries</sub>=12.8%, P<sub>tot</sub>=12.8+5.0=17.8%. V<sub>p</sub>=28+5=33% The *minimum* value of S<sub>CR</sub> is obtained for $\alpha_0$ =30 mm<sup>-1</sup>, $a_0$ =5.5%, D<sub>CR</sub>=0.35 mm, P<sub>gel+capillaries</sub>=12.1%, P<sub>tot</sub>=12.1+5.5=17.6%. V<sub>p</sub>=28+5.5=33.5%. Calculation of maximum $S_{CR}$ : The calculation is made "graphically" using Figures A1.4 and A1.5. a) Assume $r_w = 100 \mu m$ . According to Figure A1.4, for $\alpha_0$ =40mm<sup>-1</sup>, the water-filled pore volume is 55% of the total airpore volume. Thus $a_a = (1-0.55)5.0\% = 2.25\%$ According to Figure A1.5 $\alpha_a=21.5 \text{ mm}^{-1}$ . The spacing factor $D=(3/21.5)\{1.4(33/2.25)^{1/3}-1\}=0.34$ mm This is smaller than $D_{CR}=0.40$ mm. Thus, a too small water-filled pore was assumed. b) Assume r<sub>w</sub>=120 μm. According to Figure A1.4 the water-filled pore volume is 70% of the total air-pore volume. Thus a<sub>a</sub>=(1-0.70)5.0%=1.5% According to Figure A1.5 $\alpha_a = 19.5 \text{ mm}^{-1}$ . The spacing factor $D=(3/19.5)\{1.4(33/1.5)^{1/3}-1\}=0.45 \text{ mm}$ This is bigger than $D_{CR}$ .

Interpolation gives the critical air content  $a_{CR}=1.6\%$ . (corresponds to  $r_{w,CR}=110\mu m$ )

The critical degree of saturation of the concrete is according to equation (A1.10):

S<sub>CR</sub>=(17.8-1.6)/17.8= 0.910

# Calculation of minimum S<sub>CR</sub>:

The calculation is made "graphically" using figures A1.4 and A1.5. a) Assume  $r_w=110 \ \mu m$ . According to Figure A1.4, for  $\alpha_0=30 \text{ mm}^{-1}$ , the water-filled pore volume is 41% of the total airpore volume. Thus  $a_a=(1-0.41)5.5\%=3.25\%$ According to Figure A1.5  $\alpha_a=18.5 \text{ mm}^{-1}$ . The spacing factor D=(3/18.5){1.4(33.5/3.25)^{1/3}-1}=0.33 \text{ mm} This is smaller than D<sub>CR</sub>=0.35 mm. Thus, a too small water-filled pore was assumed.

#### Example A1.5 Continued

b) Assume  $r_w=120 \ \mu m$ . According to Figure A1.4 the water-filled pore volume is 49% of the total air-pore volume. Thus  $a_a=(1-0.49)5.5\%=2.80\%$ According to Figure A1.5  $\alpha_a=18 \ mm^{-1}$ . The spacing factor D=(3/18){1.4(33.5/2.80)^{1/3}-1}=0.37 \ mm This is bigger than D<sub>CR</sub>. Interpolation gives the critical air content  $a_{CR}=3.0\%$ . (corresponds to  $r_{w,CR}=115\mu m$ ) The critical degree of saturation of the concrete is according to equation (A1.10):  $S_{CR}=(17.6-3.0)/17.6= 0.830$ 

According to this example the uncertainty in  $S_{CR}$  might be rather big;  $\pm 0.04$  (mean value 0.87). It must be noticed, however, that a very big variation in the air-pore structure was assumed. Normally, the variations are much smaller.

If the limiting  $S_{CR}$ -values obtained in the example are supposed to correspond to the upper and lower 5% fractiles, the standard deviation in  $S_{CR}$  is 0.02, a value that is somewhat smaller than that (0.03) used in the example shown in Figure 25.

### A.1.2.4 The critical flow distance

#### (A) The critical thickness versus the critical spacing factor

The critical flow distance  $D_{CR}$  is important for the value of  $S_{CR}$ .

 $D_{CR}$  is determined mainly by properties of the cement paste. As said in paragraph 3.1 there are many ways of defining a critical flow distance. One possibility is to use the concept *critical thickness* which is the thickest slice of the cement paste that will not be harmed by frost even if it is completely saturated; excess water formed at the 9% increase in volume when pore water freezes can escape through the surfaces without causing damage. The critical thickness is shown in Figure A1.7(b).

The following formula can be used for calculation of the critical thickness, provided damage is caused by hydraulic pressure appearing when water is forced away from the site of ice formation<sup>1</sup>:

$$\mathbf{d}_{\mathrm{CR}} = \left\{ 2 \cdot \mathbf{f}_{t} \cdot \mathbf{K} / \left[ 0.09 \cdot (\mathbf{d}\mathbf{w}_{\mathrm{f}}/\mathbf{d}\theta) \cdot (\mathbf{d}\theta/\mathbf{d}t) \right] \right\}^{1/2}$$
(A1.14)

Where  $d_{CR}$  (m) is *half* the critical thickness.  $f_t$  is the tensile strength of the cement paste (Pa). K is the permeability to displaced water (m<sup>2</sup>/(Pa·s)). K is defined by equation (A1.15).  $dw_f/d\theta$  is a material characteristic describing the increase in amount of frozen water per degree temperature lowering (m<sup>3</sup>/(m<sup>3</sup>·s)); see Figure A1.8.  $d\theta/dt$  is the rate of temperature lowering of the unit cell considered. It depends on the outer temperature conditions, and is different for different unit cells depending on their location inside the structure; the closer to the outer surface and the more rapid the lowering of outdoor air, the higher the value of  $d\theta/dt$ .

$$q_w = K \cdot dP/dx \tag{A1.15}$$

Where  $q_w$  is the volume flux of displaced water (m<sup>3</sup>/(m<sup>2</sup>s)), dP/dx is the hydraulic pressure gradient (Pa/m).

Previously, in paragraph A1.2, the critical flow distance has been expressed in terms of the *critical spacing factor*. The definition of spacing factor is shown Figure A1.21 and in Figure A1.7(a). It is the thickness of a fictive spherical shell surrounding a spherical air-pore with radius  $r_{mean}$ . There is a relation between these two different measures of the critical flow distance is (the derivation is made in the report in footnote 1):

$$d_{CR} = L_{CR} (2 \cdot \alpha \cdot L_{CR} / 9 + 1)^{1/2}$$
(A1.16)

Where  $\alpha$  is the specific surface of the air-pore located at the centre of the shell;  $\alpha = 3/r_{mean}$ . The relation is valid provided hydraulic pressure is the cause of destruction.

The difference between the critical spacing factor (or critical shell thickness) and the critical thickness is illustrated by Figure A1.7. The critical thickness is a more natural material property than the critical spacing factor since it is independent on the shape of the air-pore system. The value of  $L_{CR}$ , on the other hand, depends on the shape of the air-pore system

<sup>&</sup>lt;sup>1</sup>) Fagerlund, G.: *The critical distance in connection with freezing of porous materials*. Cementa AB. Technical Report T86039, Danderyd, Sweden, 1986.

through the parameter  $\alpha$ . The relation between d<sub>CR</sub> and L<sub>CR</sub> as defined by equation (A1.16) is illustrated by Example A1.6.



Figure A1.7: Critical flow distances. (a) The critical spacing factor,  $L_{CR}$  (see also Figure A1.21). (b) The critical thickness,  $d_{CR}$ .



*Figure A1.8: Definition of the parameter*  $dw_{f}/d\theta$  *in equation (A1.14)* 

**Example A1.6** The critical thickness for a certain type of cement paste is **1.2 mm**; see Figure A1.10. Thus, half the critical distance,  $d_{CR}$ =0.6 mm. (a) For a certain specimen made of the actual cement paste it is assumed that the specific surface  $\alpha_{CR}$  is 20 mm<sup>-1</sup> when  $S_{CR}$  is reached. Equation (A1.16) gives:  $0.6=L_{CR}(2\cdot20\cdot L_{CR}/9+1)^{1/2}$ . This gives the critical spacing factor  $L_{CR}$ =0.370 mm. (b) For another specimen made of the same cement paste but with another air-pore structure  $\alpha_{CR}$ =15 mm<sup>-1</sup> Equation (A1.16) gives:  $0.6=L_{CR}(2\cdot15\cdot L_{CR}/9+1)^{1/2}$ . This gives the critical spacing factor  $L_{CR}$ =0.395 mm. (c) For a third specimen  $\alpha_{CR}$ =10 mm<sup>-1</sup> Equation (A1.16) gives:  $0.6=L_{CR}(2\cdot10\cdot L_{CR}/9+1)^{1/2}$ . This gives the critical spacing factor  $L_{CR}$ =0.430 mm.

The example shows that one cannot expect that the value of the critical spacing factor is constant. It depends to a certain extent on the characteristics of the air-pore structure. The variation is not so big, however. In the Examples A1.1-A1.4 the value of  $\alpha_{CR}$  varies between 10 mm<sup>-1</sup> to 18 mm<sup>-1</sup>. Thus the variation is d<sub>CR</sub> is limited to about ±0.025 mm.

### (B) Theoretical calculation of the critical thickness

Equation (A1.14) can be used for a theoretical calculation of the critical thickness since all parameters except the rate of temperature lowering are determined by properties of the cement paste. Such calculations have been made in reference (1). These calculations are presented below. A somewhat revised calculation, also covering concrete with very low w/c-ratio, has been performed in the report in  $^2$ .

Each of the parameters in equation (A1.14) is discussed below.

1. *Tensile strength*  $f_i$ : This is supposed to be inversely proportional to the w/c-ratio:

 $f_t = constant_1 \cdot (w/c)^{-1}$ 

(A1.17)

2. *Permeability K:* This is a complicated parameter since one might assume that permeability is not constant but is reduced with increased ice formation due to the fact that ice can be assumed to block pathways for water transport. A "reasonable assumption" is that permeability is proportional to the square of the non-freezable water; viz. it is only in "unfrozen pores" that water can be transported:

<sup>&</sup>lt;sup>2</sup>) Fagerlund, G.: Frost resistance of high performance concrete – Some theoretical considerations. Sommer, H. (Editor): Proc. RILEM International Workshop "*Durability of High Performance Concrete*", Vienna, Febr. 14-15, 1994.Cachan, 194.

$$K = K_0 (w_{nf}/w_e)^2$$
 (A1.18)

Where  $K_0$  is the permeability of the unfrozen material; i.e. when  $w_{nf}=w_e$ .  $w_{nf}$  is the unfrozen pore water  $(m^3/m^3)$ .  $w_e$  is the total evaporable water before freezing  $(m^3/m^3)$ .

 $K_0$  is a function of the w/c-ratio<sup>3</sup>:

$$K_0 = \text{constant}_2 \cdot (w/c)^7 \tag{A1.19}$$

The evaporable water for a saturated pore system, excluding air pores, is:

$$w_e/c=w/c-0.19\cdot\beta$$
 (A1.20)

Where  $\beta$  is the degree of hydration.

The non-freezable water is:

$$w_{nf}/c = w_e/c - w_f/c$$
 (A1.21)

Where the freezable water  $w_f$  depends on the temperature. Often the biggest expansion occurs at the lowest temperature. This therefore determines the value of the critical thickness. The freezable water at low temperature is<sup>4</sup>:

$$w_{f}/c = w_{e}/c - 0.25\beta$$
 (A1.22)

Inserting equations (A1.19) to (A1.22) in equation (A1.18) gives the following relation for the permeability at low temperature:

$$K = constant_2(w/c)^7 [0.25\beta/(w/c-0.19\beta)]^2$$
(A1.23)

3. Amount of ice formed  $dw_f/d\theta$ : This varies with temperature. It might be reasonable to assume that it is proportional to the amount of freezable water.

$$dw_f/d\theta = constant_3(w_f/c)$$
 (A1.24)

Where the constant depends on temperature. The lowest temperature could probably be used.

Inserting equation (A1.22) and (A1.20) gives:

<sup>&</sup>lt;sup>3</sup>) Based on experimental data in Powers, T.C., Copeland, L.E., Hayes, J.C., Mann, H.M.: *Permeability of portland cement paste.* Proc. American Concrete Institute. 51, 1954-1955.

<sup>&</sup>lt;sup>4</sup>) Based on experimental data in Powers, T.C., Brownyard, T.L.: *Studies of the physical properties of hardened portland cement paste.* Research Laboratories of the Portland Cement Association. Bulletin no 22, Chicago 1948.

A similar observation was made in Vuorinen, J.: *On determination of effective degree of saturation of concrete*. Concrete and Soil Laboratory, Imatran Voima OY, Oulo. Manuscript 1973. According to this work the maximum amount of freezable water was about equal to the amount of water in capillary pores; i.e.

 $w_f/c=w/c-0.39\beta$ . Inserting the relation (A1.20) gives  $w_f/c=w_e/c-0.20\beta$ ; i.e. a bit higher amount of freezable water than that given by equation (A1.22). Then, it must be noted that the specimens used by Vuorinen were dried at +105°C before being re-saturated and tested for freezable water.

 $dw_f/d\theta = constant_3(w/c-0.44\beta)$ 

- (A1.25)
- 4. *The rate of temperature lowering d\theta/dt:* This depends on the outer temperature conditions and on the location of the unit cell considered. The most rapid freezing rate observed in structures is about 3°C/h.

Inserting equations (A1.17), (A1.23 and (A1.25) in equation (A1.14) gives the following expression for the critical distance:

$$d_{CR} = \text{constant}_4 \cdot (w/c)^3 \cdot \{0.25\beta/(w/c-0.19\beta)\} \cdot \{[1/(w/c-0.44\beta)] \cdot (1/d\theta/dt)\}^{1/2}$$
(A1.26)

Where,

$$constant_4 = [constant_1 \cdot constant_2/constant_3]^{1/2}$$
 (A1.27)

Equation (A1.26) can be used for a calculation of absolute values of the critical thickness, provided the values of the three constants are known. Evaluation of the constants can be done from tests of tensile strength (constant<sub>1</sub>), permeability of unfrozen cement paste (constant<sub>2</sub>) and amount of frozen water as function of temperature lowering (constant<sub>3</sub>).

No attempt is made here to evaluate these constants. Instead the *relative effect* of the w/c-ratio on the critical thickness is calculated in Example A1.7.

```
Example A1.7
It is assumed that half the critical thickness is d_{CR}=0.6 mm for w/c=0.50. This value is based on
some observations, see Figure A1.10.
According to equation (A1.26) this gives the following value for the constant parameter in the
equation:
  constant<sub>4</sub>/(d\theta/dt)^{1/2}=3.21 when d<sub>CR</sub> is in mm.
The degree of hydration is assumed to correspond to about 2 à 3 months of hydration. The
following values are used:
  \beta = 0.80 for w/c>0.50
  \beta = 0.75 for w/c=0.40
  \beta = 0.60 for w/c=0.30
The calculated values of d_{CR} become:
  w/c=0.30: d<sub>CB</sub>=0.49 mm (0.83 mm if the degree of hydration is increased to 65%)
  w/c=0.40: d<sub>CB</sub>=0.60 mm
  w/c=0.50: d<sub>CB</sub>=0.60 mm
  w/c=0.60: d<sub>CR</sub>=0.62 mm
  w/c=0.70: d<sub>CR</sub>=0.68 mm
```

The calculations indicate that *the effect of w/c-ratio on the critical distance is fairly small*. The reason is that the negative effects of an increased w/c-ratio caused by increased amount of freezable water and reduced strength are almost totally counteracted by the positive effect of the higher permeability. Similar results were also

obtained at the calculations made in the report in footnote 2 using a somewhat different expression for permeability.

The calculated values of  $d_{CR}$  can be used for calculating the critical spacing factor  $L_{CR}$  using equation (A1.16). The value depends on the size of the air-pore inside the hole-sphere; see Figure A1.7(a) and Example A1.6. The calculation indicates that  $L_{CR}$  is even more independent of the w/c-ratio than  $d_{CR}$ ; see Figure A1.9.

The calculated values of d<sub>CR</sub> and L<sub>CR</sub> are plotted in Figure A1.9.



Figure A1.9: Calculated critical thickness  $d_{CR}$  as function of the w/c-ratio(Example A1.7) Critical spacing factor calculated by equation (A1.16) for two different values of the specific surface of the air-pore at the centre of the hole-sphere; see Figure A1.7(a).

The critical thickness is inversely proportional to the freezing rate; i.e. a reduction in freezing rate by 50% (e.g. from 3°C/hour to 1.5°C/hour) will increase the critical thickness by a factor  $\sqrt{2}=1.4$ .

### (C) Experimental determination of the critical thickness

An attempt to determine the critical thickness by direct experiments is presented in<sup>5</sup>. More than 3 year old water-stored OPC-paste specimens were predried at  $+50^{\circ}$ C, and re-saturated by vacuum. The specimens were frozen and thawed when immersed in pure water or in 3% NaCl-solution.

The freeze-thaw made the specimens fracture into small fragments that reached the final size after only a couple of cycles. The size of the fragments was determined by a sieve analysis. The fragment size is a measure of the critical thickness. The results are presented in Figure A1.10.

<sup>&</sup>lt;sup>5</sup>) Fagerlund, G.: *Principles of frost resistance of concrete*. Nordisk Betong, Nr 2, 1981. (In Swedish with English summary).


Figure A1.10: Measurements of the critical thickness  $(2d_{CR}, mm)$  based on size of fragment caused by freezing of saturated cement paste; see footnote 5.

Some interesting observations are made:

- 1. The size of the fragments is almost independent of the w/c-ratio. This strengthens the theoretical derivation made above.
- 2. The critical size at freezing in pure water is of the order 1.2 mm which corresponds to:

#### d<sub>CR</sub>≈0.6 mm

This is a value that was also used in Examples A1.6 and A1.7.

- 3. A critical thickness of 2.0.6=1.2 mm corresponds to a critical spacing factor of about L<sub>CR</sub>≈0.38 mm; see Example A1.6.
- 4. The critical size is bigger when freeze-thaw takes place in salt solution. This might seem contradictory to frequent observations that salt solution increases frost damage. The most probable explanation is that open freeze-thaw in salt solution considerably increases the water uptake compared to when open freeze-thaw takes place in pure water. Consequently, the aggravated effect of salt is not due to a decrease in S<sub>CR</sub> -on the contrary, it increases due to the bigger critical size- but to a big increase in S<sub>ACT</sub>.

#### (D) Experimental determination of the critical spacing factor

In contrast to  $d_{CR}$ ,  $L_{CR}$  is not a pure material coefficient since it is also dependent on the airpore size distribution; see equation (A1.16).

There are two methods to determine  $L_{CR}$ .

#### Method 1: Based on determination of the critical thickness

The experimentally determined  $d_{CR}$ -values shown in Figure A1.10 can be used for calculation of the critical spacing factor  $L_{CR}$ . The calculation is made with equation (A1.16).

The measured value of  $d_{CR}$  is about 0.6 mm. According to Example A1.6 this corresponds to:

# L<sub>CR</sub>=0.37 à 0.43 mm

### Method 2: Based on the critical degree of saturation, S<sub>CR</sub>

The calculation is the reverse to calculation of  $S_{CR}$  (paragraph A1.2.1). The  $S_{CR}$ -value corresponds to a certain size of the biggest water-filled pore,  $r_{w,CR}$ . This corresponds to a certain residual specific surface  $\alpha_{a,CR}$  and a certain residual air-filled pore volume  $a_{a,CR}$ . The relations between  $r_{w,CR}$  and the parameters  $\alpha_{a,CR}$  and  $a_{a,CR}$  depend on the shape of the pore size distribution, f(r).

The critical spacing factor is calculated by equation (A1.7'). In this equation the flow distance  $D_{CR}$  is equal to  $L_{CR}$ .

The method of calculating  $L_{true,CR}$  from  $S_{CR}$  is illustrated by the following example.

Example A1.8
A concrete with air content $a_0=6\%$ , specific surface $\alpha_0=30$ mm <sup>-1</sup> , total porosity 18.5%, exponential type of air-pore distribution, cement paste volume including air-pores 32%, experimentally determined S <sub>CR</sub> =0.83
The critical air content is calculated from equation (A1.10): $a_{a,CR}=P(1-S_{CR})=18.5(1-0.83)=3.1\%$
The volume fraction of water-filled pores is: (6-3.1)/6=0.48=48%
According to Figure A1.4 the biggest water-filled pore for this degree of water-filling is 120µm.
According to Figure A1.5 the specific surface of air-filled pores at this pore radius is: $\alpha_{a,CR}=18 \text{mm}^{-1}$ .
The critical spacing factor can now be calculated by equation (A1.7'):
$L_{true,CR} = (3/18) \cdot \{1.4(32/3.1)^{1/3} - 1\} = 0.34$ mm

The result of some calculations for concrete with w/c-ratio 0.45 produced with OPC, or with slag cements with different amount of slag are shown in Figure A1.11.



Figure A1.11: Calculated true critical spacing factors from determinations of  $S_{CR}$  and airpore distribution; (19). (The figures at the curves give the air content)

The spread in calculated values is quite big:

OPC:	L <sub>CR</sub> =0.28-0.38 mm	(mean 0.33 mm)
15% slag:	L <sub>CR</sub> =0.29-0.34 mm	(mean 0.32 mm)
40% slag:	L <sub>CR</sub> =0.29-0.36 mm	(mean 0.33 mm)
65% slag:	$L_{CR}$ =0.35-0.42 mm	(mean 0.39 mm)

It is very interesting to note that the order of size of  $L_{CR}$  is the same as that calculated from experimental determination of the critical thickness; see Example A1.6.

# A1.3 Calculation of the actual moisture content; $S_{ACT}$

# A1.3.1 Mechanism of long-term water absorption

The value of  $S_{CR}$  says nothing of the frost damage risk or service life. A pore system that produces a high value of  $S_{CR}$  like an exponential pore system with high fineness (see Example A.4 above) does not necessarily give a long service life, or a low frost damage risk, simply because such a pore system might be rapidly water-filled in practice. A theory of how this water absorption might occur will be described in this paragraph.

When water enters a porous material like concrete, containing pores with a wide size spectrum, there is a great possibility that air becomes enclosed in coarser pores surrounded by a web of very fine pores. The mechanism is visualised in Figure A1.12.



Figure A1.12: The mechanism behind enclosure of air-bubbles in isolated coarser pores; (1).

- When the specimen is placed in contact with water, pore A directly starts to absorb water.
- When the water front reaches pore B (level 1) this also starts to take up water. Pore A continues to take up water since the capillary under-pressure is high and of the same order as in pore B.
- When the water front in pore A reaches pore D (level 2) suction is immediately reduced due to the increase in pore radius (meniscus radius). Suction (capillary under-pressure) in pore B (the "bifurcation pore") is maintained on a high level. Therefore, water continues to penetrate this pore.
- When the water front in pore B reaches pore C (level 3) the water front starts to penetrate this upwards and downwards.
- When the water front in pore C reaches the periphery of pore D an air bubble is enclosed.

This process will go on simultaneously in numerous places in the material. Air-entrained concrete is a typical material in which the process occurs. Pores A, B and C correspond to the capillary pores. These have radii smaller than 0.1µm and are therefore rapidly filled with water. Pore D corresponds to the air pores.

The enclosed air-bubble is exposed to an over-pressure,  $\Delta P$ :

$$\Delta P = 2\sigma/r \tag{A1.28}$$

Where  $\sigma$  is the surface tension water-air (N/m) and r is the bubble radius (m).

The surface tension causes the bubble to contract. The relation between radii and volumes of the bubble and the pore (assuming this be spherical) is:

$$r/R = (V_1/V_0)^{1/3}$$
 (A1.29)

Where r and  $V_1$  are the bubble radius and volume after compression. R and  $V_0$  are the radius and the volume of the pore itself.

At constant temperature Boyle's law gives:

$$V_0 \cdot P_0 = V_1 (P_0 + 2\sigma/r)$$
 (A1.30)

Where  $P_0$  is the atmospheric pressure (10<sup>5</sup>Pa).

Inserting equation (A1.29) gives the following relation between the bubble and pore volumes:

$$(V_1/V_0)^{1/3}(V_0/V_1-1) = 2\sigma/(10^5 R)$$
(A1.31)

Combination of equation (A1.29) and (A1.31) gives the following relation between the pore radius and the bubble radius:

$$\mathbf{R} = [\mathbf{r}^2 (\mathbf{r} + 2\sigma/10^5)]^{1/3} \tag{A1.32}$$

The total pressure in the air-bubble is:

$$P=10^{5}+(2\sigma/r)=10^{5}+2\sigma/[R\cdot(V_{1}/V_{0})^{1/3}] \quad (Pa)$$
(A1.33)

The second term on the right hand side gives the *over-pressure*.

This means that bubbles enclosed in small pores will become almost completely compressed and vanish almost completely. Examples of the relation between pore size and bubble size are shown in Table A1.1.

Pore radius	Relative bubble radius	Relative bubble volume	Over-pressure in bubble
(µm)	r/R	$(V_1/V_0)$	(Pa)
0.05	0.18	0.006 (>1%!)	$16.3 \cdot 10^6$
0.10	0.26	0.018 (2%!)	$5.64 \cdot 10^{6}$
1	0.68	0.32	$2.16 \cdot 10^5$
10	0.95	0.87	$1.55 \cdot 10^4$

Table A1.1: Relation between bubble size and pore size.

#### Note

The mechanism described explains the following experimental observations:

- That all capillary pores become directly water-filled at a capillary absorption experiment; c.f. Figure 19 which shows that the breaking-point in an absorption experiment almost exactly corresponds to the complete filling of all pores except the air-pores. Capillary pores have a maximum radius smaller than 0.05 µm.
- 2. That air-pores actually serve as such (although some pores can become activated by slow water absorption as described below); viz. air-pores are bigger than about 10 μm.
- That no air-pores smaller than about 5 to 10 μm can be observed on polished samples used for the linear traverse method. Smaller pores were simply compressed in the fresh cement paste.

## A: "Immediate" dissolution of small bubbles in surrounding pore water

The increased air pressure increases the solubility of air in water. If the bubble is small the water volume directly surrounding the bubble will be big enough to dissolve all air and the bubble will vanish rapidly; Figure A1.13. The required water volume ( $V_{w,req}$ , m<sup>3</sup>) and the corresponding thickness of the completely saturated cement paste ( $t_{req}$ , m) can be calculated. In (28) the following equation is derived:

$$V_{w,req} = (\rho_0/s_0)(1+10^5/\Delta P) (4\pi/3) r^3$$
(A1.34)

Where  $s_0$  is the solubility of air in water at the atmospheric pressure  $(3 \cdot 10^{-2} \text{ kg/m}^3 \text{ at } +10^{\circ}\text{C})$ .  $\rho_0$  is the density of air at 1 atmosphere (1.25 kg/m<sup>3</sup> at +10°C).  $\Delta P$  is given by equation (A1.28).

The radius r can be neglected compared with the shell thickness (see the examples below). Therefore, the required shell thickness becomes:

$$t_{req} \approx \{ [3/(4\pi)] \cdot [V_{w,req}/P_{tot}] \}^{1/3}$$
(A1.35)

Where  $P_{tot}$  is the total porosity in the cement paste (m<sup>3</sup>/m<sup>3</sup>). A normal value is 0.5 (50%).



Figure A1.13: Air-bubble surrounded by a saturated cement paste shell big enough to dissolve all air.

#### Example A1.9

An air-pore with radius 10  $\mu m$  corresponding to a bubble radius 9.5  $\mu m.$  Equations (A1.34) and (A1.35) give:

 $V_{w,req} = (1.25/3 \cdot 10^{-2})(1+10^{5} \cdot 9.5 \cdot 10^{-6}/2 \cdot 0.074)(4\pi/3)(9.5 \cdot 10^{-6})^{3} = 1.11 \cdot 10^{-12} \text{ m}^{3}$ 

 $t_{reg} = \{ [3/(4\pi)] \cdot [1.11 \cdot 10^{-12}/0.5] \}^{1/3} = 8.2 \cdot 10^{-5} \text{ m} = 82 \ \mu\text{m}$ 

#### Example A1.10

An air-pore with radius 50  $\mu$ m corresponding to a bubble radius 49  $\mu$ m.

 $V_{w,reg} = (1.25/3 \cdot 10^{-2})(1+10^{5} \cdot 49 \cdot 10^{-6}/2 \cdot 0.074)(4\pi/3)(49 \cdot 10^{-6})^{3} = 7.0 \cdot 10^{-10} \text{ m}^{3}$ 

 $t_{red} = \{ [3/(4\pi)] \cdot [7.0 \cdot 10^{-10}/0.5] \}^{1/3} = 7.0 \cdot 10^{-4} \text{ m} = 700 \text{ }\mu\text{m}$ 

The average spacing between air bubbles vary from bubble to bubble. A reasonable mean value for an air-entrained concrete might be about  $150\mu m$ , corresponding to a thickness of each shell surrounding an air bubble of about  $75\mu m$ . Therefore, Example A1.9 shows that *all bubbles smaller than about 10 \mu m will be rapidly dissolved already in the water surrounding them. No diffusion over longer distances, or to an adjacent bubble, is needed.* 

Example A1.10 shows that pores as big as 50µm are too big for air to be dissolved in the surrounding pore water. It is dissolved but only by a slow dissolution-diffusion process to adjacent air-pores, and finally to the material surface. This process is treated below and in paragraph A1.3.5.

# B: Slow dissolution of small bubbles by diffusion to bigger air-bubbles

The air-pressure is higher in a smaller bubble. Therefore, the concentration of dissolved air is higher around a smaller bubble than around a bigger; c.f. equation (A1.28). Consequently air is gradually transferred to the big bubble. The process is illustrated by Figure 14 (see also Figure A1.17).

The time process is very difficult to calculate for the following reasons:

- 1. The exact concentration gradient of dissolved air is not known since the size of the adjacent air-bubble is unknown. Moreover, the driving gradient gradually increases as the small bubble becomes gradually smaller, and its pressure therefore increases.
- 2. The effective cross-section of air flow is unknown. It depends on the sizes of the two air-bubbles between which air is exchanged. It also changes gradually because of the size reduction of the smallest bubble while the size of the big bubble is often practically constant.
- 3. The diffusivity of dissolved air in pore water in hardened cement paste is unknown. For diffusion of air in bulk water the diffusivity is about  $2 \cdot 10^{-9}$  m<sup>2</sup>/s when the concentration is expressed in kg dissolved air per m<sup>3</sup>.
- 4. The flow distance is unknown. It is equal to the spacing between the two pores, but this is different for different pares of pores.
- 5. In a real material the inter-pore diffusion does not take place in the simplified manner shown in Figure 14. Diffusion occurs simultaneously in a web of numerous pores.

In order to be able to make a rough calculation the following simplifications are made; see Figure A1.14:

- 1. The big recipient pore is assumed to be very much bigger than the smaller from which air is leaving. Its radius is supposed to be infinite. This means that the concentration of dissolved air around the recipient pore is equal to the air concentration in bulk water under atmospheric pressure.
- 2. Diffusion is supposed to be symmetrical within a material sphere with thickness L surrounding the small bubble. This is equivalent to assuming that the small bubble is surrounded by a number of big pores with infinite radii.
- 3. The effective area for air diffusion is supposed to be determined by the surface of a sphere in which the radius in square is replaced by the product of the radius of the small bubble and the outer radius of the shell;  $A_{eff}=4\pi r(L+r)$ .



Figure A1.14: Simplified model for calculation of air flow from a small bubble with radius r through a water-saturated shell with thickness L to a large number of surrounding very big pores with radius  $R \approx \infty$ .

Then, the diffusion equation for the flux of air q from the small bubble with radius r is:

$$q = \delta(dc/dx)A_{eff} \approx \delta(\Delta P \cdot s'/L)[4\pi r(L+r)] = \delta[(2\sigma)/r] \cdot s'/L)[4\pi r(L+r)]$$
(A1.36)

Where q is the air flux (kg/s),  $\delta$  is the diffusivity of dissolved air (m<sup>2</sup>/s),  $\Delta P$  is the overpressure in the small bubble (Pa), s' is the solubility of air in water (kg/(m<sup>3</sup>Pa)), L is the interpore distance; i.e. the thickness of the shell through which diffusion takes place (m), r is the radius of the small bubble (m). The solubility at +20°C is s'=2.5 \cdot 10<sup>-7</sup> kg/m<sup>3</sup>·Pa.

For facilitating the calculations it is assumed that the inter-pore spacing is proportional to the pore size;  $L=k\cdot r$  where k is a proportionality coefficient. Thus, the bigger the small pore, the longer is the distance to the nearest coarse pore. Then, equation (A1.36) is transformed to:

$$q \approx \delta \cdot \sigma \cdot s'(1+1/k) 8\pi \tag{A1.37}$$

Where  $\sigma$  is the surface tension between air and water (N/m).

It is interesting to note that the radius r of the small bubble vanishes. This means that the air flow rate is the same irrespectively of the pore size. Inserting values for  $\sigma$  and s' gives:

$$q = \delta \cdot 4.6 \cdot 10^{-7} (1 + 1/k) \text{ (kg/s)}$$
 (A1.37')

The inter-pore spacing expressed by the coefficient k is uncertain. A value k=5 might be reasonable. For example, it means that the spacing between bubbles with radius 100  $\mu$ m is 500  $\mu$ m. Equation (A1.37') is then changed to:

$$q=\delta \cdot 5.6 \cdot 10^{-7} (kg/s)$$
 (A1.37'')

In order to calculate the time needed to completely fill an air-bubble of given size, the weight of air must be transformed into volume of air,  $V(m^3)$ :

$$V=Q/\rho \tag{A1.38}$$

Where  $\rho$  is the initial density of air in the bubble (kg/m<sup>3</sup>), and Q the weight of air (kg). The density is increased due to the internal pressure which depends on the bubble size. It can be calculated by Boyle's law.

$$\rho/\rho_0 = 1 + (\Delta P/P_0) = 1 + (2\sigma/P_0)(V_0/V_1)^{1/3}/R ~(\approx 1; \text{ see the examples below})$$
 (A1.39)

Where  $\rho_0$  is the density of air at atmospheric pressure ( $\approx 1.2 \text{ kg/m}^3$ ).

Examples R=10 $\mu$ m: Equation (A1.31) gives: V<sub>0</sub>/V<sub>1</sub>=1.15. Equation (A1.39) gives  $\rho/\rho_0$ =1.16 R=20 $\mu$ m: V<sub>0</sub>/V<sub>1</sub>= 1.08.  $\rho/\rho_0$ =1.08 R=50 $\mu$ m: V<sub>0</sub>/V<sub>1</sub>= 1.03.  $\rho/\rho_0$ =1.03

These examples show that the real density  $\rho$  can be replaced by  $\rho_0$ . It is only for very small bubbles that the error is of importance.

Then, the time to completely fill an air-in a pore with radius R is:

$$t = (4\pi/3)r^3 \rho_0 / (\delta \cdot 5.6 \cdot 10^{-7}) = 9.0 \cdot 10^6 \cdot r^3 / \delta \qquad (seconds) \tag{A1.40}$$

Examples of the time required are given in Table A1.2.

*Table A1.2:Required time to completely water-fill an air pore with radius R.* 

R (µm)	Required time		
	$\delta = 10^{-11} \text{ m}^2/\text{s}$	$\delta = 10^{-12} \text{ m}^2/\text{s}$	
	$t=9.0\cdot10^{17}r^3$	$t=9.0\cdot10^{18}r^3$	
10	15 minutes	2.5 hours	
20	2 hours	20 hours	
50	31 h	129 days	
200	83 days	2.3 years	
500	3.5 years	35 years	

The Table shows that *small air pores are rapidly filled by water while it takes very long time to fill big pores.* Sooner or later, however, all air-pores in concrete will become water-filled when the concrete is stored in water.

A big problem using the theory -apart from all simplifications made- is that the diffusivity of dissolved air is almost totally unknown; see paragraph A1.6.3.

# A1.3.2 Relation between absorption time and actual degree of saturation

After a certain water absorption time  $t_w$  all pores smaller than  $r_w$  have become water-filled. The time required is given by equation (A1.40) with r exchanged for  $r_w$ . At that time the residual air-pore volume is  $a_a$  given by equation (A1.4). Relations between  $r_w$  and  $a_a$  for two types of air-pore systems are shown in Figure A1.4.

The actual degree of saturation at time  $t_w$  is calculated by equation (A1.41). This is equivalent to equation (A1.10) with  $S_{CR}$  replaced by the general degree of saturation  $S_{ACT}$ , and the critical air content  $a_{CR}$  replaced by the general air content  $a_a$ .

The principles are illustrated by Figure A1.15.





The calculation process is shown by some examples. The same concretes as in examples A1.1-A1.4 in paragraph A1.2.2 are treated. In all examples, it is assumed that the diffusivity  $\delta = 10^{-12} \text{m}^2/\text{s}$ .

#### Example A1.11 (The same as Example A1.1)

Exponential air-pore distribution.  $\alpha_0=30 \text{ mm}^{-1}$ . Total air content 4.5%. S<sub>CR</sub>=0.86.

According the previous calculation of Example A1.1 the critical pore radius when  $S_{CR}$  is reached is  $r_w=124\mu m$ .

According to equation (A1.40) this gives a service life:

 $t_{life}=9.0\cdot10^{6}\cdot(124\cdot10^{-6})^{3}/10^{-12} = 1.72\cdot10^{7}$  seconds=199 days

This means that the concrete can stand more than six months of water absorption before it becomes damaged by frost.

#### Example A1.12 (The same as Example A1.2)

Power type of air-pore distribution.  $\alpha_0$ =30 mm<sup>-1</sup>. Total air content 4.5%. S<sub>CR</sub>=0.74.

According the previous calculation of Example A1.2 the critical pore radius when  $S_{CR}$  is reached is  $r_w=74\mu m$ .

According to equation (A1.40) this gives a service life:

 $t_{\text{life}} = 9.0 \cdot 10^6 \cdot (74 \cdot 10^{-6})^3 / 10^{-12} = 3.65 \cdot 10^6 \text{ seconds} = 42 \text{ days}$ 

Despite the fact that the air content and the specific surface are the same as in Example A1.11 the service life is reduced to 20% of that in example 1. *This example shows the very big drawback of using pore characteristics of the empty air-pore system at estimation of frost resistance, as is the case when the Powers spacing factor concept is used in the traditional way. Consideration must be taken to water absorption in air-pores.* 

#### Example A1.13 (The same as Example A1.3)

Power type of air-pore distribution.  $\alpha_0=30 \text{ mm}^{-1}$ . Total air content 10.2%. S<sub>CR</sub>=0.56.

According the previous calculation of Example A1.3 the critical pore radius when  $S_{CR}$  is reached is  $r_w=124\mu m$ .

Since the assumption behind Example A1.3 is that the same size of  $r_w$  should be used as in Example A1.1, the service life is also the same.

tlife=199 days

*Thus, in order to obtain the same service life as in Example A1.11 the air content must be raised from 4.5% to 10.2%!* 

#### Example A1.14 (The same as Example A1.4)

Exponential air-pore distribution.  $\alpha_0$ =50 mm<sup>-1</sup>. Total air content 4.5%. S<sub>CR</sub>=0.92

According the previous calculation of Example A1.4 the critical pore radius when  $S_{CR}$  is reached is  $r_w=110\mu m$ .

According to equation (A1.40) this gives a service life:

 $t_{\text{life}} = 9.0 \cdot 10^{6} \cdot (110 \cdot 10^{-6})^{3} / 10^{-12} = 1.20 \cdot 10^{7} \text{ seconds} = 139 \text{ days}$ 

The increased fineness in comparison to Example A1.11 causes a decrease in the service life. The reason is that the  $S_{CR}$ -value now corresponds to a smaller size of the biggest water-filled air-pore. The example illustrates the fact that *it is not necessarily favourable to have a very fine air-pore system*. This fact is further discussed in paragraph A1.5.

The longer the duration of water uptake is, the bigger is the size of the biggest water-filled pore -equation (A1.40)- and the higher is the degree of saturation. The water absorption process can be calculated according to the procedure described in A1.3.1 and A1.3.5.

An example of the calculated increase in degree of saturation is shown by the following example.  $S_{CAP}$  is calculated by:

$$S_{CAP} = 1 - a_a / P_{tot} \tag{A1.41}$$

Where  $P_{tot}$  is the total porosity (%) and  $a_a$  the air-filled porosity (%).

#### Example A1.15

Exponential pore-size distribution.  $\alpha_0=30$  mm<sup>-1</sup>.  $\delta=10^{-12}$  m<sup>2</sup>/s. Total porosity exclusive of air pores 12%

The water-filled pore volume is obtained from Figure A1.4. The calculated results are shown in Table A1.3.

Water absorption time	r <sub>w</sub>	$a_a/a_0$	a <sub>0</sub> =3%		a <sub>0</sub> =7%	
	(µm)		P <sub>tot</sub> =15%		P <sub>tot</sub> =19%	
			a <sub>a</sub> (%)	<b>S</b> <sub>CAP</sub>	a <sub>a</sub> (%)	S <sub>CAP</sub>
At the breaking-point	0	1	3	0.800	7	0.632
24 hours	21	0.99	2.97	0.802	6.93	0.635
1 week (168 hours)	41	0.95	2.85	0.810	6.65	0.650
1 month (720 hours)	67	0.86	2.58	0.828	6.02	0.683
6 months (4 320 hours)	121	0.55	1.65	0.890	3.85	0.797
2 years (17 520 hours)	193	0.20	0.60	0.960	1.40	0.926
5 years (43 800 hours)	262	0.05	0.15	0.990	0.35	0.982

*Table A1.3: Effect of absorption time on capillary degree of saturation* 

In paragraph 4.4 it was said that the time evolution of  $S_{CAP}$  might be described by equation (21):

 $S_{CAP} = S_b + e \cdot t^d$ 

(21)

Where  $S_b=1-a_0$ 

Application of this equation to the data in Table A1.3 give the following results:

When the diffusivity is increased by a factor 10 to  $\delta = 10^{-11} \text{ m}^2/\text{s}$  the following relations are obtained:

3% air:  $S_{CAP}=0.800+25.7\cdot10^{-4}\cdot t^{0.54}$  r<sup>2</sup>=0.99 (t in hours) 7% air:  $S_{CAP}=0.632+45.8\cdot10^{-4}\cdot t^{0.54}$  r<sup>2</sup>=0.99

Some very interesting observations are made:

- 1. The theoretical analysis of the long-term water absorption process made above actually, with high precision, predicts an absorption-time curve that can be described by equation (21). Such absorption curves have also been observed in experiments of water absorption lasting for 2 weeks to 2 months, and in some experiments up to <sup>1</sup>/<sub>2</sub> year. This strengthens the possibility of using data from a fairly short absorption experiment for an extrapolation of the long-term absorption, as it is described in paragraph 5.3 and 5.4, for calculation of a *potential service life*.
- 2. The exponent d is independent of the air content and of the diffusivity. This strengthens the hypothesis put forward in paragraph 4.2 that d is mainly dependent on the shape of the airpore distribution. The distribution was not changed in the example.
- 3. The coefficient e is increased with increased diffusivity which is reasonable. A 10-fold increase in diffusivity causes an increase in e by a factor 3.5 for both air contents.

4. The calculation shows that the rate of increase in  $S_{CAP}$  increases with increasing air content. The reason is that the rate determining coefficient e in equation (21) is increased in almost direct proportion to the air content. This happens despite the fact that the diffusivity is assumed to be independent of the air content.

The increased rate of increase in  $S_{CAP}$  has also been observed at experiments. Examples are shown in Figure 13. For these experiments the following equations are valid (based on only 1 month of absorption):

Thus, also the experimental results indicate an almost direct proportionality between air content and coefficient e.

# **Note** The reason why the exponent d is much lower than the calculated value in Example A1.15 is probably due to the fact that the real air-pore size distribution was very much different from that assumed in Example A1.15.

Also the coefficient e differs from the calculated example based on the diffusivity  $10^{-12}$  m<sup>2</sup>/s. The agreement between the example and the experiments is good if the diffusivity in the example is raised to about  $5 \cdot 10^{-11}$  m<sup>2</sup>/s, which is not an unrealistic value considering the fact that diffusion of air in bulk water is determined by a diffusivity which is about  $2 \cdot 10^{-9}$  m<sup>2</sup>/s.

# A1.3.3 Effect of air content on the actual degree of saturation

If, for a given pore size distribution, the air content is increased, the degree of saturation at a given water absorption time will be reduced. This is obvious since the size of the biggest air-filled pore is constant for each absorption time irrespectively of the amount of air. The fact is best illustrated by an example; see Figure A1.16.



Figure A1.16: Effect of a doubling of the air content on the amount of water-filled air-pores



It was shown previously in paragraph A1.2.2 that the critical degree of saturation is decreased when the air content is increased; see Examples A1.2 and A1.3. Now it was shown that also the actual degree of saturation is reduced with increased air content. The reduction in  $S_{ACT}$  is bigger however, which decreases the risk of frost damage; see the examples A1.17 and A1.18 below.

The effect of air content on  $S_{ACT}$  can be calculated analytically if the air-pore size distribution is known. For the two distributions in Figure A1.3, Figure A1.4 can be used for assessment of the effect of air on  $S_{ACT}$ . This will be shown by two examples.



This example shows that increased air content reduces the values of both  $S_{CR}$  and  $S_{ACT}$  but that the reduction in  $S_{ACT}$  is dominant so that the net effect becomes positive. This will be further discussed in paragraph A1.5.

Example A1.18. Power type of air-pore distribution. Long absorption time (1 year) Power type of air-pore distribution. α<sub>0</sub>=40 mm<sup>-1</sup>. Porosity excluding air-pores is 12%. Cement paste volume excluding air pores is 27%. δ=10<sup>-12</sup> m<sup>2</sup>/s
Absorption time is 1 *year*. Equation (A1.24) shows that his corresponds to r<sub>w</sub>=155µm.
According to Figure A1.4 the water-filled part of the air-pore system for this size of water-filled pore is 32%. Thus, the air-filled part is 100-32=68%.
(a) *Air content 2%*. Total porosity 12+2=14% The residual air content is 0.68·2=1.36% S<sub>ACT</sub>=(14-1.36)/14=0.90
(b) *Air content 4*%. Total porosity 12+4=16% The residual air content is 0.68·4=2.72% S<sub>ACT</sub>=(16-2.72)/16=0.83

Example A1.18, continued
(c) Air content 6%. Total porosity 12+6=18% The residual air content is $0.68.6=4.08\%$ $S_{ACT}=(18-4.08)/18=0.77$
(d) Air content 12%. Total porosity 12+12=24% The residual air content is $0.68 \cdot 12=8.2\%$ S <sub>ACT</sub> =(24-8.2)/24= <b>0.66</b>
<ul> <li><i>Note: The critical degree of saturation</i> for the same three air contents can be calculated by the method described in paragraph A2.2. The critical flow distance (the critical spacing factor) is assumed to be 0.40 mm.</li> <li>Figure A1.4 and A1.5 and using equation (A1.7) gives the following values:</li> <li>(a) <i>Air content 2%:</i> r<sub>w,CR</sub>=45 µm. a<sub>a,CR</sub>=1.8%. S<sub>CR</sub>=(14-1.8)/14=0.87 (S<sub>CR</sub><s<sub>ACT. Risk of frost damage)</s<sub></li> </ul>
(b) Air content 4%: $r_{w;CR}$ =70 µm. $a_{a,CR}$ =3.4%. $S_{CR}$ =(16-3.4)/16=0.79 ( $S_{CR}$ <s<sub>ACT. Risk of frost damage)</s<sub>
(c) Air content 6%: $r_{w,CR}$ =100 µm. $a_{a,CR}$ =4.7%. S <sub>CR</sub> =(18-4.7)/18=0.74 (S <sub>CR</sub> <s<sub>ACT. Risk of frost damage)</s<sub>
(d) Air content 10%: $r_{w,CR}$ =170 µm. $a_{a,CR}$ =8.0%. $S_{CR}$ =(24-8)/24=0.67 ( $S_{CR}$ <s<sub>ACT. Low risk of frost damage)</s<sub>

A comparison of Example A1.18 with Example A1.17 shows that the power type of pore system can stand more than1 year of absorption without obtaining higher degrees of saturation than the exponential type of pore system reaches already after 1 month.

On the other hand, also the critical degree of saturation is lower for the power type of pore system. The net effect is that there is big risk of frost damage unless the air content is extraordinarily high. In this case about 12%. This result is in accordance with Example A1.3.

# A1.3.4 Comments on the precision in calculation of S<sub>ACT</sub>

The calculations of  $S_{ACT}$  made above were *deterministic* as it was assumed that the air diffusion could be described by a simple equation (A1.36) and (A.1.37). In reality the theoretical background to these equations is not verified. It is based on simplified reasoning that can be questioned:

- 1. The assumption behind equation (A1.36) that the recipient air bubble is of infinite size is only valid for pores close to the surface of the material.
- 2. The effective cross-section of diffusion,  $A_{eff}$ , is more complex than the formula suggested in equation (A1.36).
- 3. The diffusion path is probably not directly proportional to the pore size as was suggested in equation (A1.37).
- 4. The transport of dissolved air does not have the well-defined constant value suggested in equations (A1.37) and (A1.40). Moreover, the diffusivity of dissolved air is uncertain.
- 5. The assumption that a small pore is always completely water-filled before a coarser pore is reasonable, but not proven.

Despite these uncertainties, the theory is in fair agreement with observations, as was described in connection with example A1.15 above. The theoretical time function of water uptake agrees perfectly with observed water absorption; equation (21). Also the absolute time needed for certain absorption based on reasonable values of diffusivity of air in water agrees well with the observed time. This strengthens the hypothesis that the mechanism behind long-term water absorption is dissolution of air in air-pores and migration of this air to coarser airbubbles causing a volume reduction that leads to water absorption from outside.

Another deterministic feature of the treatment is that the air-pore size distribution was assumed to have a well-defined shape. In reality the exact air-pore distribution has a certain variation from unit cell to unit cell. This affects the  $S_{ACT}$ -value as described in the examples in paragraph A1.3.2 above.

A calculation of the order of size of variations in S<sub>ACT</sub> is made in the following example.

# Example A1.19 In order to get an idea of the magnitude of variations in SACT a calculation is made for a concrete with the following variations (The same as was used for calculation of the variations in $S_{CR}$ , see Example A1.5.) The air-pore structure is described by the exponential frequency function, equation (A1.10). The specific surface $\alpha_0$ varies between 30mm<sup>-1</sup> and 40 mm<sup>-1</sup>. The air diffusivity varies between $5 \cdot 10^{-12} \text{m}^2/\text{s}$ and $10^{-12} \text{m}^2/\text{s}$ . The air content $a_0$ varies between 5% and 5.5%. The porosity exclusive of air pores varies between 12.1% and 12.8%. S<sub>ACT</sub> is calculated for an absorption time of 1 month. The maximum value of SACT is reached for the following combination of data: $\alpha_0 = 40 \text{ mm}^{-1}$ , $a_0 = 5\%$ , diffusivity $5 \cdot 10^{-12} \text{m}^2/\text{s}$ , $P_{\text{gel+capillaries}} = 12.8\%$ , $P_{\text{tot}} = 12.8 + 5 = 17.8\%$ . The minimum value of $S_{ACT}$ is reached for the following combination of data: $\alpha_0 = 30 \text{ mm}^{-1}$ , $a_0 = 5.5\%$ , diffusivity $10^{-12} \text{m}^2/\text{s}$ , $P_{\text{gel+capillaries}} = 12.1\%$ , $P_{\text{tot}} = 12.1+5.5=17.6\%$ . Calculation of maximum S<sub>ACT</sub>: Equation (A1.40): 1 month of water absorption corresponds to $r_w=114 \mu m$ . Figure A1.4: The residual air content $a_a=33\%$ of the total air content, i.e. 0.33.5=1.7%SACT=(17.8-1.7)/17.8=0.904 Calculation of minimum S<sub>ACT</sub>: Equation (A1.40): 1 month of water absorption corresponds to $r_w=67 \mu m$ . Figure A1.4: The residual air content a<sub>a</sub>=88% of the total air content, i.e. 0.88.5.5=4.8 % S<sub>ACT</sub>=(17.6-4.8)/17.6=0.727

According to this example the uncertainty in  $S_{ACT}$  might be about ±0.09. According to Example A1.5, this is a bigger uncertainty than for  $S_{CR}$ . If the limiting values are supposed to correspond to the 5% fractiles the standard deviation in  $S_{ACT}$  is 0.055.

# A1.3.5 Inter-pore exchange of air and water uptake caused by this

## A1.3.5.1 Introduction

In the previous paragraphs the kinetics of water filling of individual air-bubbles due to air diffusion has been described. It was not described, however, how this air diffusion can lead to water uptake, or how this water uptake proceeds in the concrete.

In connection with Figure 14 in the main report it is postulated that the inter-pore diffusion causes a net air volume reduction, and that this is the explanation for the observed water absorption in a capillary absorption test. It was also postulated that the water uptake does not proceed as a moving boundary process but that the water taken up is distributed more or less evenly over a bigger material volume. These postulates will now be commented upon.

## A1.3.5.2 Volume changes caused by inter-pore diffusion-principles

Consider the 2-pore model in Figure A1.17. In each of the pores there is an air-bubble that was enclosed already at "time zero". The pressure is higher in the small bubble and therefore transport of air will occur from the small to the big bubble, as was described in paragraph A1.3.1. The air transport process can be divided in two stages:

- *Stage 1:* A gradual reduction of air content in the small bubble (inside pore 1) and a gradual increase of air content in the big bubble (inside pore 2). Water is therefore displaced from the big pore to the small pore. During this stage there is not any water uptake from outside as will be shown below.
- *Stage 2:* All initial water in the big pore has been displaced. Air continues to flow from the small pore to the big, but this flow will not cause displacement of water. Instead it will cause an increased air pressure in the big pore. This pressure is counter-balanced by the appearance of curved menisci in narrow water-filled pores ending at the periphery of the big pore. Air transport ceases when the air pressure in the two pores is equally high, or if the small pore has become completely water-filled. Water needed to fill the small pore must come from outside.



Figure A1.17: Inter-pore air diffusion and water transport during two stages.

### A1.3.5.3 Inter-pore air diffusion. Stage 1

The initial mass of air in pores 1 and 2 are  $m_1$  and  $m_2$ :

$$m_1/m_2 = (R_1/R_2)^3$$
 (A1.42)

After time t the air mass  $\gamma \cdot m_1$  is lost from pore 1 and transferred to pore 2.

Boyles law for constant temperature is:

$$P \cdot V/m = constant$$
 (A1.43)

Application to the 2-pore model gives:

Pore 1: 
$$(10^5 + 2\sigma/r_{1,0})(4\pi/3)r_{1,0}^{3/m_1} = (10^5 + 2\sigma/r_{1,t})(4\pi/3)r_{1,t}^{3/m_1}(1-\gamma)$$
 (A1.44)  
or

$$10^{5} + 2\sigma/r_{1,0} = (10^{5} + 2\sigma/r_{1,t})(r_{1,t}/r_{1,0})^{3}/(1-\gamma)$$
or
(A1.44')
or

$$P_{1,0} = P_{1,t}(r_{1,t}/r_{1,0})^3 / (1-\gamma)$$
(A1.44'')

Pore 2:  $(10^5 + 2\sigma/r_{2,0})(4\pi/3)r_{2,0}^3/m_2 = (10^5 + 2\sigma/r_{2,1})(4\pi/3)r_{2,1}^3/(m_2 + \gamma \cdot m_1)$  (A1.45) Inserting equation (A1.42) gives:  $10^5 + 2\sigma/r_{2,0} = (10^5 + 2\sigma/r_{2,1})(r_{2,1}/r_{2,0})^3/[1 + \gamma \cdot (R_1/R_2)^3]$  (A1.45') or  $P_{1,2} = P_2 (r_2 / r_{2,2})^3/[1 + \gamma \cdot (R_2/R_2)^3]$  (A1.45')

$$P_{2,0} = P_{2,t}(r_{2,t}/r_{2,0})^{3} / [1 + \gamma \cdot (R_{1}/R_{2})^{3}]$$
(A1.45'')

Where  $r_{1,0}$  and  $r_{2,0}$  are the initial bubble radii, and  $r_{1,t}$  and  $r_{2,t}$  are the radii at time t.  $P_{1,0}$  and  $P_{2,0}$  is the initial air pressure in pores 1 and 2.

 $P_{1,t} \, \text{and} \, P_{2,t} \, \text{is the air pressure in pores 1 and 2 at time t.}$ 

The initial bubble radii are given by equation (A1.32):

Pore 1: 
$$R_1 = [r_{1,0}^2(r_{1,0} + 2\sigma/10^5)]^{1/3}$$
 (A1.46)  
Pore 2:  $R_2 = [r_{2,0}^2(r_{2,0} + 2\sigma/10^5)]^{1/3}$  (A1.47)

Equations (A1.44') and (A1.45') give the following relations between the bubble radius at time t and the air mass lost or gained:

Pore 1:

$$10^{5} \cdot r_{1,t}^{3} + 2\sigma \cdot r_{1,t}^{2} = r_{1,0}^{3} (10^{5} + 2\sigma/r_{1,0})(1-\gamma)$$
(A1.48)
Pore 2:

$$10^{5} \cdot \mathbf{r}_{2,t}^{3} + 2\sigma \cdot \mathbf{r}_{2,t}^{2} = \mathbf{r}_{2,0}^{3} (10^{5} + 2\sigma/\mathbf{r}_{2,0}) \left[1 + \gamma \cdot (\mathbf{R}_{1}/\mathbf{R}_{2})^{3}\right]$$
(A1.49)

The pressure in the two bubbles is given by equations (A1.44'') and (A1.45''):

Pore 1:

Pore 2:

$$P_{1,t} = (10^{5} + 2\sigma/r_{1,0})(r_{1,0}/r_{1,t})^{3}(1-\gamma)$$
(A1.50)

$$P_{2,t} = (10^{5} + 2\sigma/r_{2,0})(r_{2,0}/r_{2,t})^{3} [1 + \gamma \cdot (R_{1}/R_{2})^{3}]$$
(A1.51)

The evolution of pressure in pore 1 will depend on the pore size and the amount of air that has left. The pressure can be calculated by equation (A1.50) using equation (A1.48) for calculation of the relation between amount of air transported away expressed in terms of  $\gamma$ , and the bubble radius,  $r_{1,t}$ . An example of the evolution of pressure in a pore is shown in Example A1.20.

#### Example A1.20

Pore radius R<sub>1</sub>=100 µm.

According to equation (A1.46):  $r_{1,0}=98.6 \mu m$ .

Inserting actual data in equation (A1.50) gives:  $P_{1,t}=(10^5+2.0.074/98.6\cdot10^{-6})(98.6\cdot10^{-6}/r_{1,t})^3(1-\gamma)$ 

The relation between  $\gamma$  and  $r_{1t}$  is shown in the table. The data are plotted in the figure.



reduction of the bubble radius. When about 50% of the air mass has left, pressure starts to diminish. The reason is that the effect of reduction of mass is bigger than the effect of reduction of bubble size. When about 70% of air has left pressure starts to increase again.

During stage 1 the bubble radius in pore 1 will gradually decrease, and the radius in pore 2 gradually increase. Therefore, the air pressure in bubble 1 will always be higher than in bubble 2. This means that bubble 1 can vanish completely and be replaced by water forced out of pore 2; provided all air in pore 1 can be taken care of in pore 2 without emptying this.

Air flow will cause air volume changes in the bubbles; see Figure A.18:

Pore 1: $\Delta V_1 = -(r_{1,0}^3 - r_{1,t}^3) 4\pi/3$	Volume reduction	(A1.52)
Pore 2: $\Delta V_2 = +(r_{2,t}^3 - r_{2,0}^3)4\pi/3$	Volume increase	(A1.53)

The net volume change of air is:

$$\Delta V = \Delta V_1 + \Delta V_2 \tag{A1.54}$$

If the net volume change is negative there is room for water to be taken up in pore 1 from outside.



Figure A.18: Volume changes caused by inter-pore air diffusion.

During stage 1 there will be a net air volume *increase* since the initial air pressure in pore 1 is reduced when air is arriving to the bigger pore 2. Thus, stage 1 will not lead to any water uptake from outside, but rather to loss of water. This is shown by three examples.



#### **Example A1.21. Continued**

 $r_{2,t}$  is by definition equal to the pore radius:

 $r_{2,t} = R_2 = 20 \mu m$ 

According to equations (A1.52) and (A1.53) the volume changes are:  $\Delta V_1 = -(9.42^3 - 4.44^3)(10^{-6})^3 \cdot 4\pi/3 = -3.133 \cdot 10^{-15} \text{ m}^3$   $\Delta V_2 = +(20^3 - 19.30^3)(10^{-6})^3 \cdot 4\pi/3 = +3.395 \cdot 10^{-15} \text{ m}^3$ Thus, the net volume change is still positive. No water uptake occurs.

# Example A1.22: Large pores with small size ratio $R_1$ =100µm. $R_2$ =200µm

Equations (A1.46) and (A1.47) give:  $r_{1,0}=98.6\mu m$  $r_{2,0}=197.8\mu m$ 

According to equation (A1.55) Stage 1 will last until  $\gamma = \gamma_{\text{limit}} = 0.27$ . At this stage pore 2 becomes empty.

**γ=**γ<sub>*imit*</sub>=0.27: Equation (A1.48) gives: r<sub>1,t</sub>=88.8μm

 $r_{2,t}$  is by definition equal to the pore radius:  $r_{2,t}=R_2=200\mu m$ 

According to equations (A1.52) and (A1.53) the volume changes are:  $\Delta V_1 = -(98.6^3 - 88.8^3)(10^{-6})^3 \cdot 4\pi/3 = -1.082 \cdot 10^{-12} \text{ m}^3$   $\Delta V_2 = +(200^3 - 197.8^3)(10^{-6})^3 \cdot 4\pi/3 = +1.093 \cdot 10^{-12} \text{ m}^3$ 

Thus, the net volume change is somewhat positive. No water uptake occurs.

# Example A1.23: Large pores with large size ratio $R_1$ =100 $\mu$ m. $R_2$ =400 $\mu$ m

Equations (A1.46) and (A1.47) give:  $r_{1,0}=98.6\mu m$  $r_{2,0}=396.3\mu m$ 

According to equation (A1.55) Stage 1 will last until  $\gamma = \gamma_{\text{limit}} = 1.8 > 1$ . This means that *all air can be displaced from pore 1 before pore 2 is emptied*.  $\gamma$  cannot be bigger than 1.

 $\begin{array}{l} \gamma = \gamma_{imit} = 1: \\ \text{Then all air has left pore 1. Therefore, according to equation (A1.48):} \\ r_{1,t} = 0 \\ r_{2,t} \text{ is calculated by equation (A1.49):} \\ r_{2,t} = 398.4 \ \mu\text{m} \end{array}$ According to equations (A1.52) and (A1.53) the volume changes are:  $\Delta V_1 = -(98.6 \cdot 10^{-6})^3 \cdot 4\pi/3 \qquad = -4.01 \cdot 10^{-12} \text{ m}^3$   $\Delta V_2 = +(398.4^3 \cdot 396.3^3)(10^{-6})^3 \cdot 4\pi/3 = +4.16 \cdot 10^{-12} \text{ m}^3$ 

Thus, the net volume change is positive. No water uptake occurs.

The first two examples show that the small pore cannot be completely filled before the big pore is emptied (i.e.  $\gamma_{\text{limit}} < 1$ ). Thus, also air transfer within stage 2 will occur. The third example shows that under certain pore-size conditions stage 2 of air flow will not occur.

All examples show that no water uptake will occur during stage 1.

#### A1.3.5.4 Inter-pore air diffusion. Stage 2

When all water has been displaced from pore 2 it can still take up air from pore 1 but at the expense of increased air-pressure. The air transfer  $\gamma_{\text{limit}}$  when this happens can be derived by solving equation (A1.49) for  $r_{2,t}=R_2$ :

$$\gamma_{\text{limit}} = (R_2/R_1)^3 \{-1 + [10^5 \cdot R_2^3 + 2\sigma \cdot R_2^2] / [r_{2,0}^3 (10^5 + 2\sigma/r_{2,0})]\}$$
(A1.55)

Pore 1: Equations (A1.44), (A1.48) and (A1.50) are valid.

*Pore 2:* Boyle's law, equation (A1.43), is changed since the bubble volume is constant during stage 2 and equal to the volume of pore 2 ( $r_{2,t}=R_2$ ):

$$P_{2,\text{limit}} \cdot V_2 / m_{2,\text{limit}} = P_{2,t} \cdot V_2 / m_{2,t}$$
(A1.56)

or

$$P_{2,limit}/m_{2,limit} = P_{2,t}/m_{2,t}$$
 (A1.56)

Where  $P_{2,\text{limit}}$  is the pressure just when  $\gamma = \gamma_{\text{limit}}$ .  $V_2$  is the volume of pore 2 ( $4\pi R_2^3/3$ ),  $m_{2,\text{limit}}$  is the air mass in pore 2 just when  $\gamma = \gamma_{\text{limit}}$ ,  $P_{2,t}$  is the air pressure in pore 2 at time t,  $m_{2,t}$  is the air mass in pore 2 at time t.

 $P_{2,limit}$  is given by equation (A1.51):

$$P_{2,\text{limit}} = (10^5 + 2\sigma/r_{2,0})(r_{2,0}/R_2)^3 [1 + \gamma_{\text{limit}} \cdot (R_1/R_2)^3]$$
(A1.57)

m<sub>2,limit</sub> is:

 $m_{2,\text{limit}} = m_2 + \gamma_{\text{limit}} \cdot m_1 \tag{A1.58}$ 

 $m_{2,t}$  is:

$$\mathbf{m}_{2,t} = \mathbf{m}_{2,\text{limit}} + (\gamma - \gamma_{\text{limit}}) \cdot \mathbf{m}_1 = \mathbf{m}_2 + \gamma \cdot \mathbf{m}_1 \tag{A1.59}$$

Inserting equations (A1.42) and equations (A1.57)-(A1.59) in (A1.56') gives the following expression for the pressure in pore 2 during stage 2:

$$P_{2,t} = (10^5 + 2\sigma/r_{2,0})(r_{2,0}/R_2)^3 / [1 + \gamma \cdot (R_1/R_2)^3]$$
(A1.60)

Air flow stops when the pressure in pore 2 becomes equal to the pressure in pore 1. The pressure in pore 1,  $P_{1,t}$  is given by equation (A1.50). The pressure in pore 2 is given by equation (A1.60). The following condition for stop of air flow is valid:

or

$$P_{1,t} = P_{2,t}$$
 (A1.61)

$$(10^{5}+2\sigma/r_{1,0})(r_{1,0}/r_{1,t})^{3}(1-\gamma_{max}) = (10^{5}+2\sigma/r_{2,0})(r_{2,0}/R_{2})^{3}/[1+\gamma_{max}\cdot(R_{1}/R_{2})^{3}]$$
(A1.61)

)

Where  $\gamma_{max}$  is the maximum possible air flow. The radius  $r_{1,t}$  is dependent on the mass transfer  $\gamma_{max}$ . The relation is given by equation (A1.48).

The air volume change in pore 1 is calculated by equation (A1.52). The air volume change in pore 2 is calculated by:

# $\Delta V_2 = + (R_2^3 - r_{2,0}^3) 4\pi/3$

The total volume change in the 2-pore system is calculated by equation (A1.54). The volume changes will depend on the size of the pores and of the size ratio between the two pores. Stage 2 will always lead to negative total volume change and water uptake from outside. This is shown by an example.

	The san F	Example A1 ne 2-pore system a R <sub>1</sub> =100μm. R <sub>2</sub> =200	.24 s Example A1.22 µm	
Equations (A1.46) and ( $r_{1,0}=98.6\mu m$ $r_{2,0}=197.8\mu m$	A1.47) give:			
Equation (A1.55): $\gamma_{\text{limit}} = (200/100)^3 \{-1+$ $(10^5+2 \cdot 0.074/(197.8 \cdot 1)^2)^2 = 0.27$	$[10^{5} \cdot (200 \cdot 10^{-6})]$	) <sup>3</sup> +2·0.074·(200·10 <sup>-1</sup>	<sup>5</sup> ) <sup>2</sup> ]/[(197.8·10 <sup>-6</sup> ) <sup>3</sup>	
(i.e. when 27% of air in	pore 1 has left	, pore 2 is empty of	water)	
Condition 2 is expressed	by equation (	A1.61).		
<i>Pressure in pore 1</i> is giv (A1.50)). Inserting actual data giv	ven by the left	hand side of equation	on (A1.61) (the sam	ne as equation
$P_{1,t} = (10^5 + 2 \cdot 0.074/98.0)$	6·10 <sup>-6</sup> )( 98.6·10	$(1-\gamma)^{-6}/r_{1,t}^{-6}$		(A1.50')
The relation between $r_{1,1}$ is calculated in Example	and $\gamma$ is given A1.20.	by equation (A1.48	3). Data for the actu	ual pore size
Calculated values are given in the table in Example A1.20 and are plotted in the figure below (the same as the figure in Example A1.20.)				
<b>Pressure in pore 2</b> is given the same as equation (A) Inserting actual data given $P_{2,t} = (10^5 + 2 \cdot 0.074/19)^2$	ven by the righ (1.60)). es: 7.8·10 <sup>-6</sup> )(197.8)	thand side of equation $(200)^3 [1+\gamma(100/200)^3]$	tion (A1.61′). ) <sup>3</sup> ]	(A1.61')
Calculated values are gi	ven in the table	e and are plotted in	the figure below.	
-	γ	$P_{2,t}(Pa)$		
	0.27	1.007.105		
	0.30	$1.011 \cdot 10^{5}$		
	0.40	$1.025^{\circ}10$ 1.036 $\cdot10^{5}$		
	0.60	1.048.105		
	0.70	$1.060 \cdot 10^5$		
	0.80	$1.072 \cdot 10^{5}$		
	0.90	1.084.10°		



# A1.3.5.5 Inter-pore air diffusion. Conclusions

- Stage 1 of air diffusion will always lead to an increase in the air volume. Therefore, this air transfer creates no room for water absorption from outside.
- Normally, a *stage 2* is following stage 1. Only when the size ratio between the small and big air bubble is big will stage 2 be missing due to the fact that all air in pore 1 can move to pore 2 without displacing all water in this.
- *Stage 2* will lead to a decrease in the air volume. Therefore, water can enter the concrete from an outside source to compensate for this volume decrease.
- The inter-pore air diffusion in air-pores involving a stage 2 explains experimental observations that concrete takes up water at long-term water storage.

## A1.3.5.6 Comments to the water uptake process

The process described above occurs simultaneously in numerous air-bubbles across the entire specimen volume. In 1 cm<sup>3</sup> of cement paste containing 18 volume-% of air with an average air-pore radius of 100  $\mu$ m (specific surface 30 mm<sup>-1</sup>) there are more than 40 000 air bubbles.

Therefore, there is an extremely complicated web of air diffusion paths inside the concrete. The air volume reductions described above, caused by inter-pore air diffusion, takes place over a big material volume. The water absorption observed in a *capillary absorption test* (see Figure 13) is therefore not only occurring in air-bubbles adjacent to the water surface, but the water taken up is distributed across a bigger volume. Thus, there is not a "moving boundary" absorption process going on but a more homogeneous "bulk absorption" in the concrete.

The height  $L_{limit}$  from the water surface below which homogeneous water absorption occurs depends on the rate of air transport between air-bubbles (determined by the diffusivity of dissolved air), and the rate of water transport upwards from the water surface (determined by the permeability to saturated water transport). The rate of water transport is inversely proportional to the transport length, L. On heights smaller than a given limiting value,  $L_{limit}$ , water absorption occurs homogeneously.

The specimen height in a long-term capillary absorption experiment must be smaller than  $L_{\text{limit}}$  if the water long-term absorption shall be used for calculating the long-term increase in degree of saturation,  $S_{\text{CAP}}$ , using an equation of type (21).

The complex net-work of inter pore diffusion is illustrated by Figure A1.19.



Figure A1.19: Inter-pore exchange of air in a specimen with thickness  $L < L_{limit}$  exposed to a long-term absorption experiment. Water absorption is distributed more or less homogeneously across the entire specimen volume.

An attempt will be made to evaluate the order of size of the thickness  $L_{limit}$ . The model in Figure A.20 is used. In every 2-pore model it is the smallest pore that absorbs water, while water is leaving the big pore; see Figure A1.17. Under certain conditions, as described previously in this paragraph, the net volume change is such that water absorption is dominating.



Figure A1.20: Model for calculating the limiting distance  $L_{limit}$  from the outer water source within which water absorption occurs homogeneously.

The small (absorbing) pore is connected to the water source by saturated cement paste. The distance between the pore and the water surface is L. The "flow channel" for liquid water transport has a width that is equal to the width of the absorbing pore.

The liquid water transport upwards to the pore is determined by Darcy's law:

$$q_{w} = B \cdot (\Delta P/L) (\pi R_{1}^{2})$$
(A1.62)

Where  $q_w$  is the water flux (kg water/s), B is the water permeability (s),  $\Delta P$  is the pressure difference between air in the pore and the air pressure acting on the outer water source (=the atmospheric pressure) (Pa), R<sub>1</sub> is the radius of the absorbing pore and flow channel (m).

The air diffusion is determined by equation (37''):

$$q_{air} = \delta \cdot 5.6 \cdot 10^{-7} \text{ (kg air/s)}$$
 (A1.37'')

From a volume point of view, 1 kg air corresponds to 1200 kg of water. Therefore, in order to be able to compare with equation (A1.62) equation (A1.37'') has to be changed to:

$$q_{air} = \delta \cdot 5.6 \cdot 10^{-7} \cdot 1200$$
 (litres air/s) (A1.65)

The rate of air transport from the pore is equal to the rate of water transport to the pore when the following condition is fulfilled:

$$q_{air} = q_w \tag{A1.66}$$

$$\delta \cdot 5.6 \cdot 10^{-7} \cdot 1200 = B \cdot (\Delta P/L) \cdot (\pi R_1^2)$$
(A1.66')

Redistribution of the terms in this equation gives the following expression for the maximum flow distance  $L_{limit}$ :

$$L_{\text{limit}} = \mathbf{B} \cdot \Delta \mathbf{P}(\pi \mathbf{R}_1^{\ 2}) / (\delta \cdot 5.6 \cdot 10^{-7} \cdot 1200)$$
(A1.67)

The pressure difference  $\Delta P$  is uncertain. If no water is taken up in the pore, a "suction" will appear in this. The suction, which is equal to  $\Delta P$ , depends on the radius of the air bubble. When this is equal to the final, equilibrium, radius  $r_{1,t}$ , the suction is zero. When the radius is equal to the initial value,  $r_{1,0}$  the suction is maximum. Boyle's law gives:

$$\Delta P = P_0 (1 - (r_1 / r_{1,0})^3)$$
(A1.68)

Where  $P_0$  is the atmospheric pressure (10<sup>5</sup> Pa) and  $r_1$  is the actual bubble radius.

The maximum pressure difference is

$$\Delta P_{\text{max}} = P_0 [1 - (r_{1,t}/r_{1,0})^3]$$
(A1.69)

Inserting this equation in (A1.67) gives the maximum value of L<sub>limit</sub>:

$$L_{\text{limit,max}} = \mathbf{B} \cdot \mathbf{P}_0 [1 - (\mathbf{r}_{1,t}/\mathbf{r}_{1,0})^3] (\pi \mathbf{R}_1^2) / (\delta \cdot 5.6 \cdot 10^{-7} \cdot 1200)$$
(A1.70)

If the pressure difference is smaller the value of L<sub>limit</sub> will be proportionally smaller.

Example A1.25				
The 2-pore system in example A1.24. $R_1$ =100 µm. $R_2$ =200 µm.				
Example A1.24 gives: $r_{1,0}$ =98.7 µm. $r_{1,t}$ =85.4 µm.				
The maximum pressure difference is: $10^{5}[1-(85.4/98.7)^{3}]=3.5\cdot10^{4}$ Pa				
The permeability of cement paste with w/c-ratio 0.6 is of the order B= $100 \cdot 10^{-15}$ s <sup>6</sup> .				
Inserting data in equation (A1.70) give:				
$L_{\text{limit,max}} = 100 \cdot 10^{-15} \cdot 10^{5} [1 - (85.4/98.7)^{3}] \pi (100 \cdot 10^{-6})^{2} / (\delta \cdot 5.6 \cdot 10^{-7} \cdot 1200) = 1.6 \cdot 10^{-13} / \delta$				
$\begin{array}{lll} \delta = 10^{-12} \text{ m}^2/\text{s:} & L_{\text{limit,max}} = 0.160 \text{ m (16 cm)} \\ \delta = 5 \cdot 10^{-12} \text{ m}^2/\text{s:} & L_{\text{limit,max}} = 0.032 \text{ m (3.2 cm)} \\ \delta = 10^{-11} \text{ m}^2/\text{s:} & L_{\text{limit,max}} = 0.016 \text{ m (1.6 cm)} \end{array}$				

or

<sup>&</sup>lt;sup>6</sup>) Powers, T.C, Hayes, L.E., Mann, H.M.: *Permeability of Portland cement paste*. ACI Journal. Proceedings 51 (1954):3.

#### Example A1.26

The 2-pore system in example A1.21.  $R_1=10 \ \mu m$ .  $R_2=20 \ \mu m$ .

Example A1.24 gives:  $r_{1,0}=9.42 \mu m$ .  $r_{1,t}\approx 4 \mu m$ .

The maximum pressure difference is:  $10^{5}[1-(4/9.4)^{3}]=9.2 \cdot 10^{4}$  Pa

Inserting data in equation (A1.70) give:

 $L_{\text{limit,max}} = 100 \cdot 10^{-15} \cdot 10^{5} [1 - (4/9.4)^{3}] \pi (100 \cdot 10^{-6})^{2} / (\delta \cdot 5.6 \cdot 10^{-7} \cdot 1200) = 4.3 \cdot 10^{-13} / \delta$ 

 $\begin{array}{lll} \delta = 10^{-12} \text{ m}^2 \text{/s:} & L_{\text{limit,max}} = 0.430 \text{ m} (43 \text{ cm}) \\ \delta = 5 \cdot 10^{-12} \text{ m}^2 \text{/s:} & L_{\text{limit,max}} = 0.086 \text{ m} (8.6 \text{ cm}) \\ \delta = 10^{-11} \text{ m}^2 \text{/s:} & L_{\text{limit,max}} = 0.043 \text{ m} (4.3 \text{ cm}) \end{array}$ 

#### Example A1.27

The same as examples A1.25 and A1.26 but lower water permeability.

The permeability is  $10 \cdot 10^{-15}$  s corresponding to a w/c-ratio of about 0.40 (see footnote 6).

*Example A1.25:* Inserting data in equation (A1.70) give:

L<sub>limit,max</sub>=1.6·10<sup>-14</sup>/δ

 $\begin{array}{lll} \delta = 10^{-12} \text{ m}^2 / \text{s:} & L_{\text{limit,max}} = 0.016 \text{ m} & (1.6 \text{ cm}) \\ \delta = 5 \cdot 10^{-12} \text{ m}^2 / \text{s:} & L_{\text{limit,max}} = 0.0032 \text{ m} & (3.2 \text{ mm}) \\ \delta = 10^{-11} \text{ m}^2 / \text{s:} & L_{\text{limit,max}} = 0.0016 \text{ m} & (1.6 \text{ mm}) \end{array}$ 

Example A1.26: Inserting data in equation (A1.70) give:  $L_{limit,max}$ =4.3·10<sup>-14</sup>/8

The examples indicate that homogeneous water uptake during long-term water storage occurs on a considerable depth from the water surface. This means that specimens with a thickness of a few centimetres can normally be used for evaluation of the long-term absorption using equation (21).

# A1.4 Calculation of the frost damage risk

# A1.4.1 Deterministic calculation of frost damage risk

The  $S_{CR}$ -value calculated according the theory described in paragraph A1.2 can be compared with the  $S_{ACT}$ -value calculated according to the theory described in paragraph A1.3. The frost resistance F is defined:

$$\mathbf{F} = \mathbf{S}_{\mathbf{C}\mathbf{R}} - \mathbf{S}_{\mathbf{A}\mathbf{C}\mathbf{T}} \tag{A1.71}$$

- A positive value of F indicates that no frost damage can occur. The higher the positive value of F, the bigger is the probability that no frost damage will occur.
- A negative value of F indicates that frost damage will occur. The higher the negative value of F, the bigger is the probability that frost damage will occur, and the more extensive is frost damage.

As described in paragraph A1.2 the value of  $S_{CR}$  is practically independent of the moisture conditions. On the other hand, the value of  $S_{ACT}$  will depend on the "wetness" of the environment; the longer the water absorption time, the higher is the value of  $S_{ACT}$  and, therefore, the lower is the frost resistance as defined by equation (A1.71).

#### Example A1.28

The concrete in Example A1.1.  $S_{CR}$ =0.86 Assumptions. : (i) Air diffusivity  $10^{-12}$ m<sup>2</sup>/s, (ii) absorption time 6 months. This gives:  $r_w$ =120 $\mu$ m.  $a_a$ =0.51·4.5=2.3%. Thus,  $S_{ACT}$ =(16.5-2.3)/16.5=0.86

 $F=0.86-0.86=\pm0$  (Risk of frost damage)

## Example A1.29

The concrete in Example A1.4.  $S_{CR}$ =0.92 Assumptions. : (i) Air diffusivity  $10^{-12}m^2/s$ , (ii) absorption time 6 months. This gives:  $r_w$ =120 $\mu$ m.  $a_a$ =0.3·4.5=1.35%. Thus,  $S_{ACT}$ =(16.5-1.35)/16.5=0.92

 $F=0.92-0.92=\pm0$  (Risk of frost damage)

A comparison of the two examples shows that both  $S_{CR}$  and  $S_{ACT}$  are increased with increased fineness of the air pore system ( $\alpha_0$ =30mm<sup>-1</sup> in Example A1.28, and 50mm<sup>-1</sup> in Example A1.29). This is one more example of the fact that it is not necessarily favourable to have airpore systems with high fineness. The observation is further treated and explained in paragraph A1.5.

# A1.4.2 Probabilistic calculation of frost damage risk

Uncertainties in material parameters determining the values of  $S_{CR}$  and  $S_{ACT}$  make the calculated values uncertain.

Material parameters determining S<sub>CR</sub> are:

- The critical flow distance
- The size distribution of the air-pore system (determines also the specific surface)
- The total air content
- The total porosity

Material properties determining S<sub>ACT</sub> are:

- The diffusivity of dissolved air
- The size distribution of the air-pore system (determines also the specific surface)
- The total air content
- The total porosity

S<sub>ACT</sub> is also determined by the *wetness of the environment*. This can suitably be expressed in terms of an equivalent capillary absorption time; c.f. paragraph 4.5.

If the variations in material properties are known, the variation in calculated  $S_{CR}$  and  $S_{ACT}$  can be estimated; see Examples A1.5 and A1.19.

Due to variations in material properties, the uncertainty in the calculation of  $S_{CR}$  and  $S_{ACT}$  can be quite big. Therefore, a deterministic calculation of frost resistance using equation (A1.71) is not very precise. An example of this is given in Example A1.30 below.

A better alternative is to perform a *probabilistic* calculation of the risk of frost damage using equation (23):

$$P\{\text{frost damage}\} = P\{S_{ACT} > S_{CR}\} = \int F(S_{CR}) \cdot f(S_{ACT}) \cdot dS$$

$$0$$
(23)

This is equivalent to:

$$P\{\text{frost resistance}\}=1-P\{\text{frost damage}\}=P\{S_{CR}>S_{ACT}\}=\int_{0}^{\infty}F(S_{ACT})\cdot f(S_{CR})\cdot dS \quad (23')$$

An application of a probabilistic calculation of frost damage risk is made in the following example.

#### Example A1.30

Results from Example A1.5 for variations in  $S_{CR}$ , and Example A1.19 for variations in  $S_{ACT}$  are used below.

#### A: Deterministic calculation of frost resistance based on equation (A1.71):

Calculated values of  $S_{CR}$  and  $S_{ACT}$  from the two examples give the following calculated frost resistance, F:

1. The minimum frost resistance is obtained for S<sub>CR,min</sub> and S<sub>ACT,max</sub>:

 $F_{min}=S_{CR,min}-S_{ACT,max}=0.830-0.0904=-0.074$  Big frost damage risk.

2. The maximum frost resistance is obtained for S<sub>CR,max</sub> and S<sub>ACT,min</sub>:

 $F_{max}=S_{CR,max}-S_{ACT,min}=0.910-0.727=+0.183$  Low frost damage risk.

3. The mean frost resistance is obtained for  $S_{CR,mean}$  and  $S_{ACT,mean}$ .

 $F_{mean} = S_{CR,mean} - S_{ACT,mean} = 0.870 - 0.816 = +0.054$  Low frost damage risk.

This example shows that a *deterministic* assessment is very uncertain. Any result can be obtained depending on which values are used.

#### B: Probabilistic calculation of frost resistance based on equation (23):

The analysis made in Examples A1.5 and A1.19 indicates that the standard variation in calculated  $S_{CR}$  and  $S_{ACT}$  are of the order 0.02 and 0.055.

Calculated mean values and estimated standard deviations of  $S_{CR}$  and  $S_{ACT}$ , for the two examples are used for calculating the frost damage risk using equation (23):

- S<sub>CR</sub> is assumed to be normal distributed with mean value 0.870 and standard deviation 0.02; see Example A1.5.
- $S_{ACT}$  is assumed to be normal distributed with mean value 0.816 and standard deviation 0.055; see Example A1.19.

Equation (23) gives the following probability of frost damage:

P{frost damage}=17%

# A1.5 Calculation of the required air content for required service life

# A1.5.1 Introduction. The Powers spacing factor versus the true spacing factor

## The Powers spacing factor

In a famous paper from 1949 T.C. Powers derived the so-called *Critical Spacing Factor* concept. The background was the assumption that hydraulic pressure was the dominating destruction mechanism; (11). The spacing factor is a sort of idealised flow distance between air-pores; for definition of "flow distance", see Figure 2. The definition of spacing factor is shown in Figure A1.21.



Figure A1.21: Definition of the Powers spacing factor; (11).

Powers proved theoretically, based on the assumption of hydraulic pressure being the destruction mechanism, that the spacing factor L must not exceed a certain critical value  $L_{CR}$  if the concrete should be frost resistant. He made some calculations indicating that  $L_{CR}$  ought to be of the order 0.25 mm. The concept critical Powers spacing factor is now often used for any type of frost damage, also for salt-frost scaling, irrespectively of the real destruction mechanism. The following values of  $L_{CR}$  based on the definition of L according to Powers are often stated:

Internal frost damage:	L <sub>Powers,CR</sub> ≈0.23 à 0.27 mn
Salt-frost scaling:	L <sub>Powers,CR</sub> ≈0.16 à 0.20 mn

Almost all values of  $L_{CR}$  stated in literature have been determined on the basis of *open* freezethaw tests during which the specimens have had different possibilities to absorb water or loose water. Therefore, different researchers often state different values.

The basic idea behind the critical spacing factor, as defined by Powers, is that all air pores are assumed to stay air-filled at all time. This means that a concrete with a given spacing factor will have the same frost resistance in all types of environment, might it be fairly dry or fairly moist.
In deriving an expression for the spacing factor all air pores are assumed to be of equal size and placed in a loose-packed array; Figure A1.21. The mean pore size is calculated by:

 $r_{\text{mean}} = 3/\alpha_0 \tag{A1.72}$ 

Where  $\alpha_0$  is the specific surface of the air pore system (m<sup>-1</sup>).

 $\alpha_0 = s_0 / a_0 \tag{A1.73}$ 

Where  $s_0$  is the total envelope surface of the entire air-pore system (m<sup>2</sup>), and  $a_0$  is the total air content (m<sup>3</sup>).

The Powers spacing factor is calculated by equation (A1.7') with  $\alpha$  exchanged for  $\alpha_0$  and a exchanged for  $a_0$  (the flow distance D defined by the spacing factor L):

$$D_{Powers} = L_{Powers} = (3/\alpha_0) \cdot \{1.4(V_p/a_0)^{1/3} - 1\}$$
(A1.7'')

#### The true spacing factor

As was shown in paragraph A1.3 the air-pore system will take up water. This means that the real, or true, spacing between air-pores that are still air-filled,  $L_{real}$ , will always be bigger than the Powers spacing factor. It is calculated by equation (A1.7')

$$D_{true} = D_a = L_{true} = (3/\alpha_a) \cdot \{1.4(V_p/a_a)^{1/3} - 1\}$$
(A1.7')

Values of  $L_{true,CR}$  can be calculated from measurements of the critical degree of saturation by knowledge of the air-pore size distribution. The method is described in paragraph A1.2.4, Example A1.8.

Examples of calculated values using this method are shown in Figure A1.11. For OPC the following mean value seems to be valid:

An alternative is to calculate  $L_{true,CR}$  from measurements of the critical thickness using equation (A1.16). Examples are given in paragraph A1.2.4. The value is less well defined and depends on the air-pore size distribution; see Example A1.6 from which the following values are taken:

*Comparison between the Powers critical spacing factor and the true critical spacing factor* As said, by using the Powers spacing factor concept no consideration is taken to the wetness of the environment. The concrete is either frost resistant or not, irrespectively of the outer conditions.

By using the true spacing factor consideration is taken to the actual moisture conditions. The frost resistance will be highly dependent on the environment in which the concrete is used.

The difference between the two different ways of defining spacing factor (or flow distance) is best described by an example.

<b>Example A1.31</b> A concrete with cement paste volume excluding air-pores of 28%.	
(A) Calculation based on the Powers critical spacing factor: $L_{Powers,CR}=0.25$ mm. The specific surface $\alpha_0=20$ mm <sup>-1</sup> . The required air content is calculated by equation (A1.7'') reformulated as: $a_{0,required}=V_p/\{0.364(L_{Powers,CR}\cdot\alpha_0/3+1)^3\}$	(A1.74)
Inserted values give: $a_{0,required} = (28 + a_{0,required}) / \{0.364(0.25 \cdot 20/3 + 1)^3\} = 4.7\%$	
<ul> <li>(B) Calculation based on the true critical spacing factor</li> <li>L<sub>true,CR</sub>=0.38 mm (Note: Higher than the critical Powers spacing factor). The specific surface α<sub>0</sub>=20 mm<sup>-1</sup>.</li> <li>Additional information is now needed:</li> <li>(i) The required air content will depend on the amount of water taken up. Therefore, the diffusivity of dissolved air must be known. The value 5·10<sup>-12</sup>m<sup>2</sup>/s is assumed.</li> <li>(ii) The relation between water-filled pore size, and residual air content, and residual spec surface is used in the calculation. Therefore, the shape of the pore size distribution must known. Exponential distribution is assumed.</li> </ul>	ce ific be
$\label{eq:result} \begin{array}{l} \textit{I week absorption} \\ \text{The time corresponds to } r_w = 70 \mu m; \text{ equation (A1.40)}. \\ \text{Figure A1.4 gives: } a_a a_o = 0.95 \\ \text{Figure A1.5 gives: } \alpha_a = 18 mm^{-1} \\ \text{The required residual air content is obtained by equation (A1.7') reformulated as:} \\ a_{a,required} = V_p / \{ 0.364 (L_{true,CR} \cdot \alpha_a / 3 + 1)^3 \} \end{array} \tag{A}$	1.75)
With inserted values: $a_{a,required} = (28 + a_{a,required})/(0.364(0.38 \cdot 18/3 + 1)^3) = 2.4\%$	
The total required air is: $a_{0,required}=2.4/0.95=2.5\%$	
1 month absorption The time corresponds to $r_w=113\mu m$ . Figure A1.4 gives: $a_a/a_o=0.90$ Figure A1.5 gives: $\alpha_a=15 mm^{-1}$ The required residual air content is: $a_{a,required}=(28+a_{a,required})/\{0.364(0.38\cdot15/3+1)^3\}=3.6\%$	
The total required air is: $a_{0,required}=3.6/0.90=4.3\%$	
6 months absorption The time corresponds to $r_w=206\mu m$ . Figure A1.4 gives: $a_a/a_o=0.80$ Figure A1.5 gives: $\alpha_a=11.5 mm^{-1}$ The required residual air content is: $a_{a,required}=(28+a_{a,required})/\{0.364(0.38\cdot11.5/3+1)^3\}=6.4\%$ The total required air is: $a_{0,required}=6.4/0.80=8.0\%$	



The results of the calculations are shown in Figure A1.22.



Figure A1.22: Results of Example A1.31.

The Powers spacing factor concept overestimates the need of air for short water absorption times and underestimates it for long absorption times. For an absorption time of about  $1\frac{1}{2}$  month the two different ways of calculating the required air content give the same required air.

The example shows that the required air content increases with increased wetness of the environment. According to the Powers spacing concept the air content is constant irrespectively of how moist the concrete is. This is the main reason why it has been so difficult to find well-defined values for the critical Powers spacing factor based on open freeze-thaw experiments. The moisture level in the specimen will be quite different depending on the design of the critical Powers spacing factor, and vice versa. The true critical spacing factor is however constant and not depending on how the freeze-thaw test is designed.

#### A1.5.2 The required air content

The analysis made in this APPENDIX shows that the air content required for a given concrete in a given environment can be calculated provided the following information is at hand:

- The true critical flow distance (might be expressed in terms of a spacing factor)
- The shape of the air-pore size distribution
- The diffusivity of dissolved air in pore water
- The wetness of the environment expressed in terms of an equivalent uninterrupted capillary suction

An example of such a calculation was shown in Example A1.31 above; see Figure A1.22.

The results of such calculations are shown in Figure A1.23, taken from reference (3) where also a number of calculated numerical values are given. Only one type of pore size distribution is treated; the exponential type described by equation (A1.10). The diagram is valid for any diffusivity by re-scaling the time axis in direct proportion to the diffusivity. The time scale shown is valid for the diffusivities  $10^{-11}$  m<sup>2</sup>/s and  $10^{-12}$  m<sup>2</sup>/s. The diagram is valid for the true critical spacing factor 0.35 mm.

In the figure, the required air content is expressed in terms of the *cement paste excluding air*. The required *air-filled pore volume* in the cement paste is calculated by a modified equation (A1.7) taking care of the fact that only the cement paste is considered and that air is not included in definition of "cement paste":

$$a_{a,required,paste} = 1/\{0.364(L_{true,CR} \cdot \alpha_{CR}/3 + 1)^3 - 1\}$$
(A1.76)

The required *total* air content shown in Figure A1.23 is calculated from the relation between air-filled pore volume and total air volume,  $a_a/a_0=\delta$ 

$$a_{0,required,paste} = a_{a,required,paste} / \delta$$
 (A1.77)

The required air content in the *concrete* is calculated by:

$$a_{0,required,concrete} = V'_{p} \cdot a_{figureA1.23}$$
(A1.78)

Where  $a_{figureA1.23}$  is the air content given by Figure A1.23 (%) and V'<sub>p</sub> is the volume fraction of *air-free* cement paste (in this definition of cement paste, air is *not* included).

#### Example

 $a_{figureA1.23} = 20\%. \\ Cement content 300 kg/m^3. w/c=0.50 \\ V'_p = V_{cement} + V_{water} = 300/3.1 + 300 \cdot 0.50 = 0.25 m^3/m^3.$  (3.1 is the density of cement (kg/litre) This gives  $a_{0,required \ concrete} = 0.25 \cdot 20 = 5\%$ 

(V<sub>p</sub>=30+5=35%)



Figure A1.23: The required air content in the cement paste (not including air-pores) as function of the fineness of the air-pore system and the water absorption time.
 Assumed air diffusivity 10<sup>12</sup>m<sup>2</sup>/s and 10<sup>11</sup>m<sup>2</sup>/s. Exponential pore size distribution; (3).

The construction of Figure A1.23 is shown by some examples. The diffusivity is  $10^{-12}$  m<sup>2</sup>/s in all examples

Example A1.32. Fine pore system, short absorption timeSpecific surface  $\alpha_0 = 30 mm^{-1}$ . Absorption time 1.2 months.Equation (A1.40): $r_w = 70 \mu m$ Figure A1.4: $a_a/a_0 = 0.84$ Figure A1.5: $\alpha_{CR} = 23 mm^{-1}$  $a_{a,required,paste} = 1/{0.364(0.35 \cdot 23/3 + 1)^3 - 1} = 0.058 = 5.8\%$  $a_{0,required,paste} = 5.8/0.84 = 6.9\%$ 

#### Example A1.33. Fine pore system, long absorption time

Specific surface  $\alpha_0 = 30 \text{ mm}^{-1}$ . Absorption time 12 months.

#### Example A1.34. Coarse pore system, short absorption

Specific surface  $\alpha_0 = 20 \text{ mm}^{-1}$ . Absorption time 1.2 months.

#### Example A1.35. Coarse pore system, long absorption

Specific surface  $\alpha_0 = 20 \text{ mm}^{-1}$ . Absorption time 12 months.

The results of these examples are included in Figure A1.23. They are also plotted in Figure A1.24.



Figure A1.24: Results from Examples A1.32-A1.35.

The analysis shows that it is favourable to have a fine air-pore structure when the water absorption time is short (moderately moist conditions), while it is favourable to have a coarse air-pore system when the environment is very moist. The analysis also shows -as was shown in the previous paragraph- that more air is needed in all concretes when the water absorption time increases.

#### A1.5.3 The required air content. Probabilistic calculation

Consideration can be taken to uncertainties in material and environmental parameters used for the analysis. Examples of how to consider variations in parameters determining the critical moisture content  $S_{CR}$  are given in paragraph A1.2.3. Similarly, in paragraph A1.3.5 variations in the water content reached in the structure  $S_{ACT}$  are discussed. The standard deviations were found to be of the order 0.02 à 0.03 for  $S_{CR}$  and 0.05 à 0.06 for  $S_{ACT}$ .

In the analysis made on variations in  $S_{ACT}$  water absorption time was assumed to be constant. In reality the translation of the real environment to an equivalent absorption time is very unsafe. This will increase the uncertainty in calculated required air content.

An analysis of the order of size of the spread in required air content and the reasons for this spread is shown by the following example.

Example A1.36				
Variation in diffusivity: Variation in equivalent absorption time: Variation in specific surface: Variation in critical true spacing factor:	5·10 <sup>-12</sup> to 10 <sup>-12</sup> m <sup>2</sup> /s 1 month to 2 months 20 mm <sup>-1</sup> to 30 mm <sup>-1</sup> 0.35 mm to 0.40 mm			
The investigation of the effects of variation in parameters is made as a sort of sensitivity analysis keeping all variables constant except one.				
(A) Variation in specific surface Constants: (i) time, 1 month, (ii) spacing factor, 0 (a) Specific surface 20 mm <sup>-1</sup> : Equation(A1.40): $r_w=67\mu m$ FigureA1.4: $a_a/a_0=0.95$ Figure A1.5: $\alpha_{CR}=17.5 mm^{-1}$ $a_{a,required,paste}=1/{0.364(0.40\cdot17.5/3+1)^3-1}=0.03$ $a_{0,required,paste}=8.0/0.95=8.4\%$	40 mm, (iii) diffusivity, 10 <sup>-12</sup> m <sup>2</sup> /s			
(b) Specific surface 30 mm <sup>-1</sup> : Equation(A1.40): $r_w=67\mu m$ Figure A1.4: $a_a/a_0=0.84$ Figure A1.5: $\alpha_{CR}=23mm^{-1}$ $a_{a,required,paste}=1/\{0.364(0.40\cdot23/3+1)^3-1\}=0.043$ $a_{0,required,paste}=4.3/0.84=5.1\%$	=4.3%			
(B) Variation in diffusivity Constants: (i) time, 1 month, (ii) spacing factor, 0.40 mm, (iii) specific surface, 20 mm <sup>-1</sup> (a) Diffusivity $5 \cdot 10^{-12} m^2/s$ : Equation(A1.40): $r_w = 115 \mu m$ Figure A1.4: $a_a/a_0 = 0.82$ Figure A1.5: $\alpha_{CR} = 15 mm^{-1}$ $a_{a,required,paste} = 1/{0.364(0.40 \cdot 15/3 + 1)^3 - 1} = 0.113 = 11.3\%$ $a_{0,required,paste} = 11.3/0.82 = 13.8\%$				
(b) Diffusivity $10^{-12}m^2/s$ : The same as case (A)(a) above; i.e.: $a_{0,required,paste}$ =8.4%				



The calculated air contents are plotted in Figure A1.25. The diffusivity of dissolved air has the biggest effect. It is remarkable that the water uptake time has lower effect on the required air than variations in the other parameters.



Figure A1.25: Calculated air contents from Example A1.36. (Air is not included in definition of "cement paste").

The mean air content and the standard deviation in air content for the variations made are:

Mean value:	9.2%
Standard deviation:	2.5%

The upper 5% fractile gives the following air requirement in the cement paste for the variations in Example A1.36.

#### 13.3%

If the cement paste volume with air not included is 26%, the air requirement in concrete based on the upper 5% fractile is about:

13.3.0.26=3.5%

## A1.6 Experimental determination of parameters determining service life

#### A1.6.1 Air-pore size distribution

The air-pore size distribution is needed for calculating  $S_{CR}$  and  $S_{ACT}$ , and is therefore also needed for calculating service life.

The traditional way of determining the size distribution is by use of the so-called "linear traverse method" described in ASTM C457. A carefully polished concrete surface is traversed under a microscope. The length of intersected air-pore chords, and the number of chords traversed are monitored, either by eye or automatically by a TV-camera. The chord size distribution is transformed to a pore radius distribution using a technique described in<sup>7</sup>. The precision of the linear traverse technique was analysed by Warris in<sup>8</sup>.

Another possibility is to make an image analysis of a number of polished surface whereby the observed calotte size distribution can be transformed to a pore radius distribution. Technique for this transformation has been described in<sup>9</sup>.

#### A1.6.2 Critical spacing factor

The true critical spacing factor is determined by the method described in Example A1.18.

The critical degree of saturation and the size distribution of air pores are determined. By assuming that water at the determination of  $S_{CR}$  is located in the finest part of the pore system the value of  $L_{true,CR}$  can be calculated.

Note: Any other location of water can be assumed. This will lead to another and smaller critical distance.

#### A1.6.3 Diffusivity of dissolved air

The diffusivity of dissolved air has big influence on the required air content as shown by Example A1.36. Some tests of diffusion of oxygen through cement paste have been performed by Tuutti<sup>10</sup>. The test procedure is shown in Figure A1.26. The specimen is located between two streams of gas with equal pressure. The gas stream on the top surface consists of pure nitrogen. The gas stream at the bottom surface is a mixture of nitrogen and oxygen. Due to the partial pressure difference oxygen diffuses through the specimen. The steady state flow is

<sup>&</sup>lt;sup>7</sup>) Lord, S.W & Willis, TF: Calculation of air bubble size distribution from results of a Rosiwal traverse of aerated concrete. ASTM Bulletin 177, Oct. 1951.

<sup>&</sup>lt;sup>8</sup>) Warris, B: *The influence of air-entrainment on the frost-resistance of concrete. Part A: Void distribution.* Swedish Cement and Concrete Research Institute. Proceedings, Nr 35, 1963.

<sup>&</sup>lt;sup>9</sup>) Reid, W.P.: *Distribution of sizes of spheres in a solid from study of slices of the solid*. J. of Mathematics and Physics, Cambridge, Mass. No 35, 1955.

<sup>&</sup>lt;sup>10</sup>) Tuutti, K.: *Corrosion of steel in concrete*. Swedish Cement and Concrete Research Institute. Research Fo 4.82, 1982

monitored by an oxygen analyzer measuring the oxygen concentration in the upper gas stream.



*Figure A1.26: Tuutti's method for determination of diffusivity of dissolved oxygen through cement paste.* 

Results of Tuutti's measurements are shown in Figure A1.27. For the saturated specimens (100%RH) the diffusivity is about  $10^{-10}$  m<sup>2</sup>/s. This is a remarkably high value. Additional investigations are needed.



Figure A1.27: Results of determination of diffusivity of oxygen using the method in Figure A1.26.

#### A1.6.4 Time of water absorption

The time of water absorption can be obtained by use of the concept "equivalent capillary absorption time" described in paragraph 4.6 using field observations of the type described in paragraph 4.7.

## **APPENDIX 2**

# Assessment of the residual service life of frost damaged concrete

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#### A2.1 Introduction

This is a condensed version of the theory developed in reference (9).

A representative unit cell is considered. The cell has been frost damaged which means that its critical moisture content has been transgressed,  $S_{ACT}>S_{CR}$ . Thus, according to Chapter 3.5 *"Effect of repeated freeze-thaw – fatigue"*, the damage-moisture relation is "located" on a sloping damage-moisture line of the type shown in Figure 7, (see also APPENDIX 3). Since the structure is supposed to have been exposed to frost for some years, one might assume that the damage is determined by the line describing the "fatigue limit"; i.e. no further damage will occur provided the moisture content is not increased. On the other hand, if moisture increases in the future, the cell will become more damaged. The principles and the fatigue limit are shown in Figure A2.1.



*Figure A2.1: Relation between amount of damage (D), degree of saturation (S) and number of freeze/thaw (F/T) cycles (N). (See also Figure 7, and equations (2b) and (3b)).* 

The future damage of the cell will evidently depend on the future moisture conditions. There are three possibilities; see Figure A2.2:

Case 1; "Moderately moist".

The moisture level will not increase in the future. Therefore, damage will not increase.

Case 2: "Moist"

There will be a periods of drying alternating with periods of water absorption. The conditions are such, however, that certain slow increase in moisture level will occur in the future. Damage will increase "slowly".

Case 3: "Very moist"

The concrete is all the time in contact with water causing a never ceasing water uptake. Damage will increase "rapidly".



*Figure A2.2: Three possibilities for development of future damage.* (*"Damage" can be loss of strength, loss of bond, loss of stiffness).* 

The three cases are discussed below.

#### A2.2 Case 1; "Moderately moist"

The unit cell is only temporarily exposed to free water. Its inner moisture conditions expressed in terms of  $S_{ACT}$  will not increase in the future.

Since the concrete is supposed to have been exposed to many years of frost, the fatigue limit has been reached. No more damage will occur.

 $\mathbf{D}_{\mathsf{t}} = \mathbf{D}_{\mathsf{0}} \tag{A2.1}$ 

Where  $D_t$  is damage at exposure time t and  $D_0$  is damage at "time of inspection".

The residual service life is very long (provided the actual damage level D<sub>0</sub> is accepted).

$$\mathbf{t}_{\text{residual}} = \boldsymbol{\infty} \tag{A2.2}$$

#### A2.3 Case 2; "Moist"

The concrete is only temporarily exposed to free water; wetting periods alternate with drying periods. The moisture conditions are such, however, that the moisture level increases before each new freezing cycle. Water absorption is supposed to be proportional to the square-root of time; see equation (21) with exponent d=0.5. Since moisture steadily increases each new cycle gives a certain increase in damage. This increases the diffusivity to dissolved air and moisture ingress, which further accelerates water uptake. The increase in diffusivity is assumed to be proportional to the square-root of the number of freeze cycles. Thus  $S_{ACT}$  can be written:

$$S_{ACT} = S_{CR} + \alpha \cdot N^{1/2} \tag{A2.3}$$

Where  $\alpha$  is a coefficient that describes the gradual water uptake in air-pores and that also includes the increase in moisture diffusivity at each new freeze/thaw cycle.

The equation assumes that S<sub>CR</sub> was transgressed already at the first freeze/thaw cycle.

Using the damage equation (2b) and inserting equation (3b) for the coefficient of fatigue  $K_N$  the following equation is obtained for the development of damage (D<sub>t</sub>):

$$D_{t} = [A \cdot N/(B+N)] \cdot \alpha \cdot N^{1/2} = A \cdot \alpha \cdot N^{3/2}/(B+N)$$
(A2.4)

The number of freeze/thaw cycles is assumed to be the same each year. Thus N can be replaced by the exposure time t.

$$N \approx \beta \cdot t$$
 (A2.5)

Where  $\beta$  is the number of freeze/thaw cycles each year. Thus, the damage equation becomes:

$$D_{t} = A \cdot \alpha \cdot (\beta \cdot t)^{3/2} / (B + \beta \cdot t)$$
(A2.6)

For long exposure times the coefficient B can be neglected (Example: For the fatigue in Figure 7, B=4 which can be compared with the parameter  $\beta$ ·t>100). Then Equation (A2.4) is transformed to:

$$D_{t} = A \cdot \alpha \cdot (\beta \cdot t)^{1/2}$$
(A2.7)

This equation shows that future damage will be proportional to the square-root of time.

Damage at future time t can therefore be described by:

$$\mathbf{D}_{t} = \mathbf{D}_{0} \cdot (t/t_{0})^{1/2} \tag{A2.8}$$

It is assumed that the maximum accepted damage is  $D_{max}$ . Then Equation (A2.7) shows that the service life of the unit cell counted from the day the structure was new will be:

$$t_{\text{life}} = D_{\text{max}}^{2} / [(\mathbf{A} \cdot \boldsymbol{\alpha})^{2} \cdot \boldsymbol{\beta}]$$
(A2.9)

The residual service life is:

$$\mathbf{t}_{\text{residual}} = \mathbf{t}_{\text{life}} - \mathbf{t}_0 \tag{A2.10}$$

Where  $t_0$  is the concrete age at "time of inspection".

The coefficient  $\alpha$  can be evaluated from Equation (A2.7) using the amount of damage observed at time of inspection:

$$\alpha = D_0 / [A(\beta \cdot t_0)^{1/2}]$$
(A2.11)

Where  $D_0$  is damage at time of inspection. The coefficient A is obtained from a determination of  $S_{CR}$  of the actual concrete. Often a value of the order 15 can be used. For the data in Figure 7 the value of A is much lower however; A=1.2.

Note

The number  $\beta$  describing the number of freeze cycles each year does not influence the value of  $\alpha$  very much. A normal value  $\beta$  can be 50, i.e. each year 50 freeze cycles, forceful enough to harm the cell, are supposed to occur. *Example:* t<sub>0</sub> is 20 years, and A=17. This gives  $\alpha$ =1.9·10<sup>-3</sup>·D<sub>0</sub> for  $\beta$ =50 cycles/year, and  $\alpha$ =1.3·10<sup>-3</sup>·D<sub>0</sub> for  $\beta$ =100 cycles/year.

#### A2.4 Case 3; "Very moist"

The structure is constantly exposed to free water. Therefore, the inner moisture level will increase also between different freeze-thaw cycles.

The time process of water absorption can be described by Equation (21). The exponent b is supposed to be 0.5 which is on the safe side.

$$S_{ACT} = S_{CR} + e \cdot t^{1/2}$$
(21a)

Where t is the total exposure time from the structure was erected.

As for Case 2 moisture diffusivity in moisture range 3 is supposed to increase by the squareroot of the number of cycles. Thus equation (21a) can be written:

$$S_{ACT} = S_{CR} + e \cdot t^{1/2} \cdot \gamma \cdot N^{1/2} = S_{CR} + \epsilon \cdot (t \cdot N)^{1/2}$$
(A2.12)

Where  $\varepsilon = e \cdot \gamma$  is a coefficient that is different for each concrete.

 $S_{CR}$  is supposed to have been reached already at the first freezing. Therefore, the damage equation using Equations (2b) and (3b) can be written:

$$D_{t} = K_{N} \cdot \varepsilon \cdot (t \cdot N)^{1/2} = A \cdot \varepsilon \cdot t^{1/2} \cdot N^{3/2} / (B + N)$$
(A2.13)

Using Equation (A2.5) for the number of freeze/thaw cycles each year and neglecting the coefficient B, the equation is transformed to:

$$D_{t} = A \cdot \varepsilon \cdot \beta^{1/2} \cdot t \tag{A2.14}$$

This equation shows that future damage will be *directly proportional to time*.

Damage at future time t can therefore be described by:

$$\mathbf{D}_{\mathbf{t}} = \mathbf{D}_{\mathbf{0}} \cdot (\mathbf{t}/\mathbf{t}_{\mathbf{0}}) \tag{A2.15}$$

It is assumed that the maximum accepted damage is  $D_{max}$ . Then Equation (A2.14) shows that the service life of the unit cell counted from the day the structure was new will be:

$$\mathbf{t}_{\text{life}} = \mathbf{D}_{\text{max}} / [\mathbf{A} \cdot \boldsymbol{\varepsilon} \cdot \boldsymbol{\beta}^{1/2}]$$
(A2.16)

The residual service life is given by Equation (A2.9).

The coefficient  $\varepsilon$  can be evaluated from Equation (A2.13) using the amount of damage observed at time of inspection:

$$\varepsilon = D_0 / [A \cdot \beta^{1/2} \cdot t_0] \tag{A2.17}$$

#### A2.5 Residual service life of the unit cell

Extrapolation of damage in the unit cell will depend on which of the three cases is relevant. Equations for extrapolation are (A2.1), (A2.8) and (A2.15). These equations are shown in Figure A3.  $D_0$  is damage observed at time  $t_0$ . The extrapolation to  $D_t=D_{max}$  gives the residual service life.



Figure A2.3: Principles for extrapolation of inner frost damage.

#### A6. Residual service life of the structure

As described above, the structure is composed of a very big number of unit cells; see Figure 27. Each unit cell will have its own future destruction curve; more moist cells will be destroyed more rapidly than more dry cells. In order to evaluate the residual service life of the entire structure extrapolation of damage must be made for all such cells that have big influence on the structural behaviour of the structure.

## **APPENDIX 3**

### Comments on the possibility of using traditional freezethaw tests as a basis for service life prediction

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#### A3.1 Open freeze-thaw versus sealed freeze-thaw

#### **Open freeze-thaw tests**

A traditional multi-cycle freeze-thaw test is performed as an *open*, or unsealed, test at which the specimen is able to take up or loose water during the test. This means that each new cycle is performed with a moisture content in the specimen that is different from the moisture content during the previous cycle. Moreover, one can expect that the moisture content is not the same across the entire specimen volume. Often, parts of the specimen close to the surface have higher moister content than interior parts of the specimen.

The result of such a test will depend on how the test procedure is designed. If the test is very moist, meaning that the specimen has no possibility to dry between each cycle, but will gradually increase its moisture content, there is big possibility that damage occurs after a certain number of cycles in parts of the specimen that have the highest moisture content. The higher the moisture level, the smaller number of cycles needed for damage to commence.

The characteristics of an open freeze-thaw test is illustrated by Figure A3.1(a).

#### Sealed freeze-thaw test

In a sealed freeze-thaw test the initial moisture content is kept constant during the test, which only involves a few freeze-thaw cycles. If the actual moisture content in the specimen is below the critical moisture content, no damage occurs. If it is higher than critical, considerable damage occurs. The amount of damage depends on how much  $W_{CR}$  is transgressed; see equation (A3.1) below. The sealed freeze-thaw test is illustrated by Figure A3.1(b).





(b) Sealed freeze-thaw test. Damage only occurs in specimens for which the actual moisture content exceeds the critical value. Damage is directly proportional to transgression of  $W_{CR}$ .

#### A3.2 Interpretation of results of an open freeze-thaw test

#### A3.2.1 Interpretation - Principles

As described above, the open test involves a *combination* of the critical moisture content,  $W_{CR}$  (or  $S_{CR}$ ) and the actual moisture content,  $W_{ACT}$  (or  $S_{ACT}$ ). The critical moisture content is independent of how the test is designed. The actual moisture content, on the other hand, is totally dependent on the design of the test.

Typical results of open freeze-thaw tests are illustrated by Figure A3.2.



*Figure A3.2: Typical results of open freeze-thaw tests. 7 different materials (a-g) are tested.* Damage is initiated after a certain number of "incubation cycles".

Results of real tests of a big number of cement mortars are shown in Figure A3.3. In this case the y-axis shows damage in terms of loss of E-modulus.<sup>1</sup>



Figure A3.3: Residual E-modulus of cement mortar specimens repeatedly frozen in air at -15°C and thawed in water at +5°C. 2 cycles per day.

<sup>&</sup>lt;sup>1</sup>) Bergström, S.G.: *Freezing and thawing tests on cement mortar*. Swedish Cement and Concrete Research Institute, Bulletin Nr. 32 Stockholm, 1955 (In Swedish).

The test procedure in Figure A3.3 was designed in such a way that water was gradually absorbed. Sooner or later, damage started to develop. After this had happened the future development of damage was more or less constant; each new cycle creating the same amount of damage.

The results in Figure A3.2 and A3.3 can be interpreted in the following way  $^2$ ; see Figure A3.4.

- 1: When the test starts, the initial moisture content,  $S_0$ , is below the critical value <sup>3</sup>. Consequently no damage occurs during the first cycles; points 1, 2, 3, 4 in Figure A3.4.
- 2: Due to water uptake during the cycles the water content is gradually increasing; Figure A3.4(a). Finally, the critical moisture content is reached in the whole, or in parts, of the specimen; Point 5 in Figure A3.4. The number of cycles for this to happen,  $N_{CR}$ , depends on the water uptake during each cycle,  $\Delta S$ , and on the difference between the initial moisture content  $S_0$  and the critical moisture content,  $S_{CR}$ . Thus, a higher number of cycles are needed for materials which are highly frost resistant, than for materials with low degree of frost resistance. This explains why different cement mortars in Figure A3.3 starts to deteriorate after different number of cycles.
- 3: Already one cycle after the critical moisture content has been reached, N<sub>CR</sub>+1, the water content is so high that frost damage occurs; point 6 in Figure A3.4. The amount of frost damage is determined by the amount by which the critical water content is transgressed. It is given by the following equation; see also equation (3b):

$$D=K_{\Delta N=1}(S-S_{CR})=[A\cdot 1/(B+1)](S-S_{CR})$$
(A3.1)

Where D is "damage",  $K_{\Delta N=1}$  is a "coefficient of fatigue" valid for one cycle above N<sub>CR</sub>. A general expression for  $K_{\Delta N}$  valid for any number of  $\Delta N$  is; see equation (3b):

$$K_{\Delta N} = A \cdot \Delta N / (B + \Delta N) \tag{A3.2}$$

Where A and B are coefficients that are individual for each concrete.  $\Delta N$  is the number of cycles above  $N_{CR}$ .

- 4: Because of frost damage the water absorption during each cycle probably increases in comparison to the water absorption before the critical moisture level was reached. This is illustrated by the steeper water uptake line in Figure A3.4(a).
- 5: According to equation (A3.1) damage depends not only on the amount by which the critical moisture content is transgressed,  $\Delta S$ , but also by the number of cycles. For each number of cycles, damage will be determined by a given "damage line" described by equation (2b) and (3b). See the different damage lines in Figure A3.4(b); Point 7 is on the line for 10 cycles, point 8 on the line for 20 cycles, point 9 on the line for 50 cycles, etc.

 $<sup>^{2}</sup>$ ) The reasoning is taken from reference (24).

 <sup>&</sup>lt;sup>3</sup>) Water content is expressed in terms of degree of saturation S. This is defined by equation (1). The relation between water content W (kg/m<sup>3</sup>) and degree of saturation S (m<sup>3</sup>/m<sup>3</sup>) is: S=W/(1000·P)

Where P is the total porosity  $(m^3/m^3)$  and 1000 is the density of water  $(kg/m^3)$ . *Example:* W=120 kg/m<sup>3</sup>. P=0.16: S=120/1000·0.16= 0.75

This means that the gradual damage observed in open freeze-thaw tests is not a consequence of a normal type of fatigue but a consequence of a gradual increase in moisture content, once this has transgressed the critical value.



Figure A3.4: Water absorption and development of damage in an open freeze-thaw test.
(a) Increase in degree of saturation with increasing number of freeze-thaw cycles.
(b) Development of damage with increasing degree of saturation; see equation (3b).
(c) Development of damage with increasing number of freeze-thaw cycles; combination of Figure (a) and (b).

## A3.2.2 Theoretical analysis of the relation between number of freeze-thaw cycles and damage

A method for a theoretical calculation of the relation between the number of freeze-thaw cycles and the amount of frost damage will be presented.

1. *Before initiation of damage:* S<S<sub>CR</sub>. N<N<sub>CR</sub> The development of degree of saturation is:

$$S = S_0 + N \cdot \Delta S_1 \tag{A3.3}$$

Where  $\Delta S_1$  is the water absorption during each new freeze-thaw cycle before frost damage has occurred.

The total number of freeze-thaw cycles before frost damage occurs is:

$$N_{CR} = (S_{CR} - S_0) / \Delta S_1 \tag{A3.4}$$

This means that the total number of freeze-thaw cycles that a material can sustain increases with increased difference between the critical water content and the initial water content when the test starts. This explains the reason why higher air content gives higher frost resistance in an open freeze-thaw test. Higher air-content reduces the value of  $S_0$  since the air-pores will be more or less empty of water when the test starts. Certainly also the value of  $S_{CR}$  is reduced a bit with increased air content (see APPENDIX 1, Example A1.17), but not to the same extent as  $S_0$ .

2: After initiation of damage: S<sub>CR</sub><S. N>N<sub>CR</sub>

The development of degree of saturation is:

$$S = S_{CR} + \Delta N \cdot \Delta S_2 \tag{A3.5}$$

Equation (2b) gives:

$$\mathbf{D}=\mathbf{K}_{\Delta \mathbf{N}}(\mathbf{S}-\mathbf{S}_{\mathbf{C}\mathbf{R}}) \tag{A3.6}$$

Inserting equation (A3.):

$$\mathbf{D} = \mathbf{K}_{\Delta N} [(\mathbf{S}_{CR} + \Delta \mathbf{N} \cdot \Delta \mathbf{S}_2) - \mathbf{S}_{CR}] = \mathbf{K}_{\Delta N} \cdot \Delta \mathbf{N} \cdot \Delta \mathbf{S}_2$$
(A3.7)

Where  $\Delta S_2$  is the water absorption during each new freeze-thaw cycle after frost damage has occurred. It can assumed to be a bit bigger than  $\Delta S_1$ .

The coefficient of fatigue  $K_{\Delta N}$  can be expressed by equation (A3.2):

Inserting equation (A3.5) in (A3.2) gives:

$$\mathbf{D} = [\mathbf{A} \cdot \Delta \mathbf{N}^2 / (\mathbf{B} + \Delta \mathbf{N})] \cdot \Delta \mathbf{S}_2 \tag{A3.8}$$

In this equation it is assumed that the amount of water taken up is the same irrespectively of the extent of damage. An alternative is to let  $\Delta S_2$  increase with increased number of cycles. One possibility is to use the following equation:

$$\Delta S_2 = \Delta S_1 + C \cdot \Delta N$$

Where C is a coefficient.

Inserting this equation in (A3.8) gives:

$$D = [A \cdot \Delta N^2 / (B + \Delta N)] \cdot (\Delta S_1 + C \cdot \Delta N)$$
(A3.10)

(A3.9)

Equation (A3.8) or (A3.10) can be used for estimation of the development of damage during open freeze-thaw tests. They can also be used for interpretation of the result of such tests.

<b>Example A3.1</b> The following data are valid for a certain concrete exposed to a certain open fragment them tost				
meeze-maw test.	с.	0.60		
	S <sub>0</sub> :	0.00		
	S <sub>CR</sub> .	0.63		
	$\Delta S_1$ :	0.003		
	$\Delta S_2$ :	0.007		
	A:	1.5		
	B:	4		
	C:	0		
The selected values of the parameters A and B are valid when "damage" is expressed as relative reduction in E-modulus; $D=\Delta E/E_0$ where $E_0$ is E before the test. Other definitions of "damage" will give other values of A and B. The values selected are based on the experimental results shown in Figure 7.				
values $0.003$ and $0.007$ assumed correspond to a water uptake of about 0.5 and 1.1 litres/m <sup>3</sup> during each cycle (1.5 grams and 3.3 grams in a 3 litre specimen). Real water absorptions might very well be higher, especially for concrete with high w/c-ratio. In a more dry test the values are lower.				
Equation (A3.4): N <sub>CR</sub> =(0.85-0.60)/0.003= 83 cycles				
Equation (A3.8): D= $[1.5 \cdot \Delta N^2/(4 + \Delta N)] \cdot 0.007$				
Some examples of calculated damage are shown in the table below				
N		D	]	
<83	0	0	1	
83	0	0	1	
90	7	0.05 (5%)		
100	17	0.14 (14%)		
150	67	0.66 (66%)	1	
185	102	1.00 (100%)	1	
100	102	1.00 (10070)	J	

The results are plotted in Figure A3.5. The result resembles typical experimental results from open freeze-thaw tests; see Figure A3.3.

All data used in the calculation are reasonable; either based on direct experiments like A and B, or based on "reasonable assumptions" like  $\Delta S_1$  and  $\Delta S_2$ .



Figure A3.5: Calculated development of damage in an open freeze-thaw test; results from Example A3.1.

#### A3.3 Open freeze-thaw test as a basis for service life prediction

The time needed in the test to initiate damage can be regarded as a *test service life*,  $t_{life,test}$ . The duration of one freeze-thaw cycle is  $t_{cycle}$ . Then, the test service life becomes:

$$t_{life,test} = N_{CR} \cdot t_{cycle} \tag{A3.11}$$

The test service life is not the same, however, as the *real service life*. The test service life will be quite different for the same material depending on the design of the test. This is shown by the following examples based on Example A3.1. The cycle length is assumed to be 12 hours in all tests.

*A: Example A3:1:*  $\Delta S_1 = 0.003$  and  $\Delta S_2 = 0.007$ 

 $N_{CR}$ =87 cycles  $t_{life,test}$ =87.0.5=**44 days** (14% damage requires N=117 cycles or **59 days**)

*B*: *Drier test*:  $\Delta S_1 = 0.001$  and  $\Delta S_2 = 0.003$ 

 $N_{CR}=(0.85-0.60)/0.001=250$  cycles  $t_{life,test}=250.0.5=125$  days (14% damage requires N=290 cycles or 145 days)

*C: More moist test:*  $\Delta S_1 = 0.005$  and  $\Delta S_2 = 0.010$ 

 $N_{CR}=(0.85-0.60)/0.005=50$  cycles t<sub>life,test</sub>=50·0.5=**25 days** (14% damage requires N=62 cycles or **31 days**)

*D: Very dry test:*  $\Delta$ S<sub>1</sub> =-0.002

 $N_{CR}{=}\infty$  since the concrete will dry out during the test.Therefore,  $S_{CR}$  will never be reached.

 $t_{life,test} = \infty$ 

#### **Conclusions:**

These examples show that an open freeze-thaw test can never be used for a prediction of the service life of a real structure in the real environment. Small changes in the design of the test will have an immense effect on the test result and on the test service life. The translation of the observed test service life to the real service life requires detailed information of how the moisture time field in the test specimen relates to the moisture time field in the real structure. Such information cannot be reached.

Another difficulty, making it impossible to use open freeze-thaw tests for assessment of service life of a real structure, is that damage caused by an open freeze-thaw test will normally not be homogeneously distributed across the entire specimen volume but be located to the most moist part. Thus, the test service life calculated according to the principles above will only be valid for most moist parts of the specimen.