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## **Influence of environmental factors on the frost resistance of concrete : a contribution to the BRITE/EURAM project BREU-CT92-0591 "The Residual Service Life of Concrete Structures"**

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Division of Building Materials

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**INFLUENCE OF ENVIRONMENTAL FACTORS ON THE  
FROST RESISTANCE OF CONCRETE**

A contribution to the BRITE/EURAM project  
BREU-CT92-0591  
"The Residual Service Life of Concrete Structures"

Göran Fagerlund

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# Preface

This report is produced within the BRITE/EURAM project BREU-CT92-0591 "The Residual Service Life of Concrete Structures".

Six partners are involved in the project:

- 1: British Cement Association, UK (The coordinator)
- 2: Instituto Eduardo Torroja, Spain
- 3: Geocisa, Spain
- 4: The Swedish Cement and Concrete Research Institute, Sweden
- 5: Cementa AB, Sweden
- 6: Division of Building Materials, Lund Institute of Technology, Sweden

Three deterioration mechanisms are treated in the project:

- 1: Corrosion of reinforcement
- 2: Freeze-thaw effects
- 3: Alkali-silica reaction

This report refers to Task 1 of the work, "Definition of the aggressivity of the environment", Sub-task 1.2 "Freeze-thaw".

Lund, March 20, 1994

Göran Fagerlund



# 1. Introduction and summary

The ability of a concrete to withstand frost attack depends not only of the concrete itself but also on the internal and external climatic factors. Most important *internal* factors are:

- 1: The moisture content expressed in terms of the degree of saturation of the cement paste and aggregate grains.
- 2: The minimum freezing temperature.
- 3: The concentration of salt in the pore water.
- 4: The gradient in salt concentration of the pore water.

The most important *external* factors are:

- 1: The "wetness" by which is meant the duration of very moist conditions and the possibility of the concrete to dry.
- 2: The rate of temperature lowering of outdoor air or water surrounding the concrete structure.
- 3: The minimum temperature of outdoor air or water surrounding the concrete structure.
- 4: "The freeze/thaw spectrum"; i.e. the number of freeze/thaw cycles of different type as regards freezing rate and minimum temperature.
- 5: The duration of freezing temperatures; especially the duration of the minimum temperature.
- 6: The salt concentration of water staying in contact with the concrete surface.

The external factors determine the values of the internal factors.

In the report all those internal and external factors and their interaction are discussed. The discussion is supported by numerical examples showing the effect of different environmental factors on the performance and on the service life of the concrete. Much is known but we still lack knowledge of such an important factor as the mechanism behind salt scaling. Therefore, we are rather uncertain of the exact values of the pessima of the outer and inner salt concentrations for concrete of different water/cement ratios exposed to different types of de-icing agents. So far, we have to use information that has been obtained by experiments on rather traditional OPC-concretes exposed to NaCl-solutions.

## 2. Types of frost damage

There are two types of frost damage:

- 1: *Internal damage* caused by freezing of water inside the concrete. The damage is almost always confined to such parts of the concrete where the degree of water saturation exceeds the critical value; cf paragraph 5.
2. *Surface scaling* caused by freezing of the concrete surface when it stays in contact with saline solutions of weak concentration.

Freezing of very moist concrete (also concrete containing salt water in its pores) but with no external salt water or pure water in contact with the surface seldom leads to surface scaling but more often to internal damage.

Freezing of concrete in presence of an external salt solution at the surface seldom leads to internal damage, but often to surface scaling.

The two types of destruction are visualized in Fig 1.

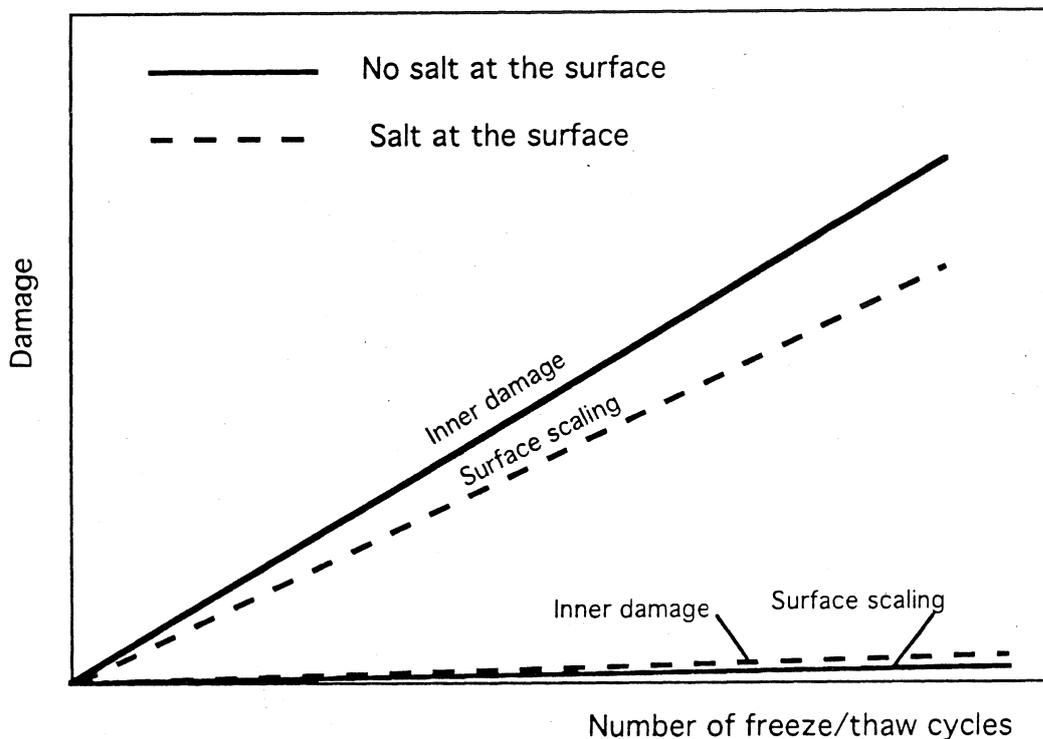


Fig 1: The principal difference between salt scaling and internal frost damage.

### 3. The destruction mechanism

#### 3.1 Main mechanisms

For a more detailed description of the destruction mechanisms, refer to /1/.

There are two major destruction mechanisms that will be shortly described below.

*The hydraulic pressure mechanism:* Water that is expelled from the pores due to the 9% increase in volume when water is transformed to ice causes a hydraulic pressure when it is forced through the gradually ice-filled pore system. The pressure will damage the cement paste (the concrete) when the pressure exceeds the tensile strength of the cement paste (the concrete). The pressure can be described:

$$P_h = 0.09 \cdot (dW_f/dt) \cdot (1/K) \cdot f(X) \quad (1)$$

Where

$P_h$	the hydraulic pressure (Pa)
$dW_f/dt$	the rate of ice formation [ $m^3/(m^3 \cdot s)$ ]
$K$	the permeability [ $m^2/(Pa \cdot s)$ ]
$f(X)$	a measure of the maximum distance of flow ( $m^2$ )

For the wall thickness,  $L$ , of a saturated cement paste shell surrounding a spherical air void, the following relation for  $f(X)$  is valid:

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

Where

$L$	the thickness of the shell wall (m)
$\alpha$	the specific area of the spherical void ( $m^{-1}$ )

$L$  is the same as the Powers' spacing factor; /2/.

The critical shell thickness (the critical Powers' spacing factor) is obtained by inserting eq (2) in (1) and putting the pressure equal to the tensile strength:

$$L_{CR}^2 \{L_{CR} \cdot \alpha / 9 + 1/2\} = f_t \cdot K / (0.09 \cdot dW_f/dt) \quad (3)$$

Where

$L_{CR}$	the critical (Powers') spacing factor (m)
$f_t$	the tensile strength (Pa)

This equation can be used for calculating the effect of the rate of freezing on the frost resistance. It is seen that the critical spacing factor is reduced when the freezing rate is increased. This will lower the frost resistance a bit as will be seen below in paragraph 8.1.

*Microscopic ice lens growth:* All free water in a concrete is not freezable at ordinary freezing temperatures and the ice formation occurs gradually. This depends on the very fine-porous structure of cement paste. A discussion of the freezable water in concrete is performed in /3/. This gradual freezing implies that the concrete contains at the same time ice bodies in the coarser pores and unfrozen water in the finest capillaries and gel pores. The lower the w/c-ratio the larger the fraction of unfrozen water. At any temperature below 0°C unfrozen water has a lower free energy than ice. The ice-bodies will therefore attract water. This freezes when it comes into contact with the ice. The microscopic ice-bodies will therefore grow and expose the pore walls to pressure. The free energy of ice increases with increased internal pressure whereby the free energy of unfrozen water decreases due to the drying effect caused by the water transfer. The growth of the ice bodies will therefore stop when the two free energies are equal. Before this happens, the concrete might be severely damaged.

If the non-freezable water is low enough, even a rather small water migration and ice growth will cause a drying effect that is sufficiently high to stop ice crystal growth before the concrete is damaged. Therefore, a concrete with low water cement ratio is more likely to be damaged by this mechanism than are concretes with normal and high w/c-ratio.

This mechanism is theoretically more pronounced the larger the amount of unfreezable water. Then, substantial water transfer can occur without the drying effect and thus the effect on the free energy of unfrozen water being too big. The mechanism is also more pronounced the longer the freezing period and the lower the temperature. In the first case, the process, which is based on diffusion of water, has more time to develop. In the latter case, the energy differential between ice and water becomes larger; it is proportional to the freezing temperature.

Like the hydraulic pressure mechanism the crystal growth mechanism predicts the existence of a critical spacing factor between air pores. Air pores always receive some expelled water from the initial freezing of the cement paste. Therefore, the air pores also contain ice bodies. They will attract unfrozen water from the cement paste by the same mechanism as that described above for ice in capillaries. Unlike ice in saturated capillaries ice in air pores can grow without restriction. Therefore, unfrozen water preferentially moves towards the air pores. The shorter the distance between the air pores the larger the portion of water that is transferred towards the air pore ice. If the spacing is small enough the water transfer to the ice in capillary pores is so marginal that no damage occurs. It is not possible for the time being to derive an equation for the critical spacing factor like it was done for hydraulic pressure.

### 3.2 Salt scaling versus ordinary frost attack

As said above, the presence of salt influences the frost attack. By what mechanism is not well understood. Some possible qualitative explanations will be given. There are four cases to consider; see Fig 2:

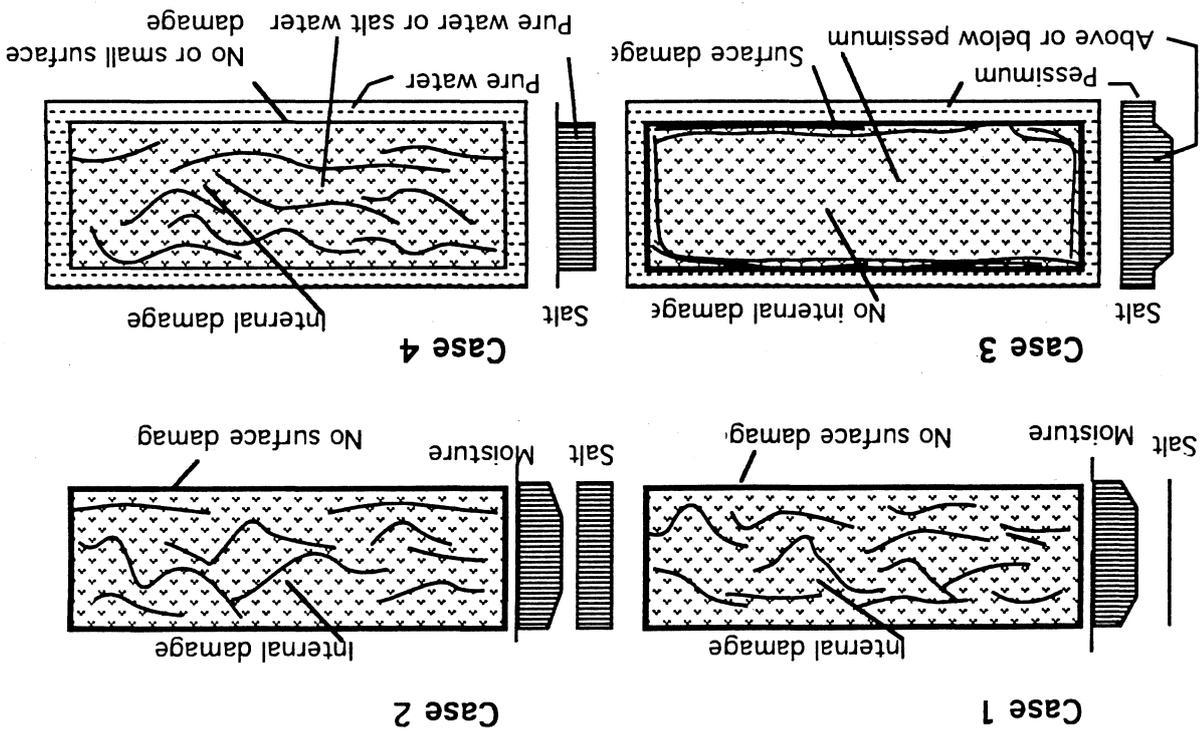


Fig 2: Four main cases of frost damage.

Case 1: Frost attack caused by pure water in the pores and no salts or pure water at the surface is well described by the two mechanisms above. If the inner pressure caused by one or both of the mechanisms is higher than the tensile strength, internal damage will occur. It will be shown below, in paragraph 5, that the internal pressure increases with increasing water content in the pores. The major factor describing the destructive forces and the frost resistance therefore is the water content inside the concrete. At the surface, a certain drying will normally occur and excess water caused by ice formed in the surface part can be expelled from the specimen without causing damage. Therefore, the forces at the surface is normally smaller than at the interior. Therefore, inner damage but no surface damage occurs.

Case 2: Frost attack caused by *saline pore water inside the concrete but no salt water or pure water at the surface* can also be described by the mechanisms above. The larger the salt concentration the lower the freezable water. Therefore, the rate of freezing and therefore the hydraulic pressure is reduced with increased inner salt concentration. The pressure due to microscopic ice crystal growth, on the other hand, is increased. When ice is formed in the coarser pores, only a portion of the water in the pore is freezing. The remaining unfrozen part of the salt water inside the pore obtains a much higher concentration than water in finer pores that contain no ice. Salt migrates much slower than water in the fine gel pore system. Therefore, the ordinary pressure difference between ice in coarse pores and unfrozen water in small pores described above in connection with the ice growth mechanism, is increased by osmotic pressure caused by this concentration difference.

On the other hand, when the salt concentration before freezing is very high the amount of unfreezable water is so high and the number of ice bodies is so low that the total pressure is just as low, or lower, than in the case of pure pore water. Therefore, one might expect a salt concentration pressure mechanism of the type shown in Fig 3. The total internal pressure is the sum of the two pressures. It might very well be that the maximum pressure is obtained at a certain pessimum inner salt concentration. This is not so well mapped out but it often seems to be of the order of size 2,5 %; see Fig 22-24. Also in this case, the pressure and thus the damage is mostly depending on *the total amount of water inside the concrete*. The maximum stresses appear in the internal part of the concrete. Therefore, due to the same reasons as were discussed for case 1, *inner damage occur but no surface damage*.

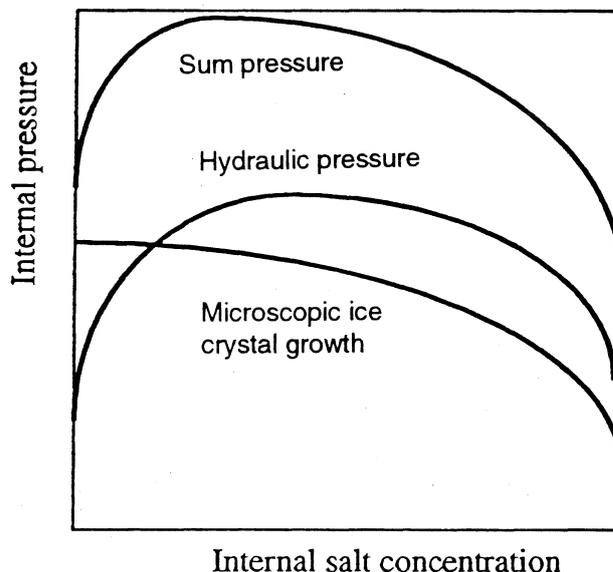


Fig 3: Hypothetical effect of the inner salt concentration on the pressures caused by the two main damage mechanisms. Single effects and the sum effect.

Case 3: Frost attack caused by *salt solution of a dangerous (pessimum) concentration in contact with the surface and pure water or salt water inside the concrete* is not so easy to explain in terms of the two main mechanisms described above only. It seems as if water transfer over a certain distance inside the concrete to the surface part does also play a rôle. The pessimum outer salt concentration seems to be about the same as in case 2; i.e. about 3%. This is seen in Fig 27-30.

When *the inner concentration is lower than the outer* one might imagine that the salt concentration between the surface and the inner part of the concrete causes a moisture migration towards the surface in order to equalize the concentration; viz. the diffusivity of water is much higher than the diffusivity of chloride. Then, the moisture content will be the highest in the surface part while the inner part is dryer. This means that the maximum water contents and therefore the maximum pressures occur at the surface part. Consequently one gets *surface scaling but no or very little inner damage*.

When *the inner salt concentration is higher than the outer*, the moisture transfer should instead be directed inwards from the surface. However, water that migrates from the surface will immediately be replaced by water from the solution.

Therefore, the concentration gradient between the inner and outer part of the concrete will probably be maintained for quite a long time. This means that the surface part has a salt concentration that is pessimum according to case 2 above while the inner part has a higher concentration that is above the pessimum. Then, as is shown in the discussion of case 2, it is natural to assume that the water contents and thus the stresses are the highest at the surface. Therefore, *only surface damage but no or little inner damage* occurs.

When *the inner concentration is the same as the outer and both are pessimum* one might imagine that both inner and surface damage should occur, perhaps with inner damage being the most severe as in case 2 which this case resembles, except for the fact that the surface is not allowed to dry in Case 3. Even in this case, however, it seems as if mostly surface damage occur; see Fig 28-30. This is not so easy to understand. One possibility is that a certain moisture transfer occurs towards the surface due to the temperature gradient causing ice to be first formed at the surface. Therefore, during a short period, the salt concentration is a bit higher at the surface than in the interior. This also happens in case 2 but then the surface part is normally a bit drier than the interior since it can dry outwards. This is not possible in case 3 where the specimen is covered with a salt solution. The time available for moisture flow is however very short and it is not quite clear whether any substantial flow has time to occur. On the other hand, also a very small increase or decrease in the moisture content can make the concrete considerably more frost sensitive or frost insensitive. If this mechanism is correct, it should create the biggest stresses in the surface thereby causing *surface damage but less internal damage*.

Case 4: Frost attack caused by *pure water at the concrete surface and pure water or salt water in the interior* can fairly well be described by the two main mechanisms above. In this case, the stresses are higher in the interior than at the surface as long as the inner salt concentration is not far above the pessimum. The most severe inner damage ought to occur at an inner concentration of about 2,5%; see Fig 22-24. At the surface there will a certain moisture inflow in the concrete and a diffusion of chloride outwards. Both processes reduce the salt concentration to a lower value than the initial, thus reducing the stresses. On the other hand, the concrete can not dry at the surface which means that the risk of surface damage is a bit higher than in Case 1 and Case 2. However, the stresses across the section of the concrete are such that one can expect *inner damage but no or smaller surface damage*.

The discussion of the four cases above are based on the following three reasonable assumptions:

- 1: When the salt concentration is constant, the most severe damage occurs in that part of the concrete that has the highest moisture content. There exist critical water contents above which the concrete is severely damaged by frost and below which is not harmed. The critical water content is further discussed below in paragraph 5.
- 2: There exists a pessimum salt concentration of pore water; at equal moisture content, the frost damage is lower both at higher and lower salt concentrations. Thus, the critical moisture content is a function of the salt concentration.
- 3: There is water flow inside the concrete and between the concrete and the surrounding salt solution. The flow goes from a lower salt concentration towards a higher. Therefore, the local degree of saturation might change before and during the freezing process. This might, as discussed above, explain the phenomenon of a pessimum outer salt concentration that seems to be more or less independent of the inner salt concentration; see Fig 28-30.

## 4. The critical spacing factor

Both destruction mechanisms described in paragraph 2 predict that a critical spacing factor between air-filled pores exists. The size of this spacing factor is discussed in /1/. One must distinguish between a fictitious spacing factor,  $L_f$  and a true spacing factor,  $L$ . The former is based on the assumption that no air-pores are waterfilled in practise or in a freeze/thaw test. It is not a true material constant but depends also on the size distribution of the airpores. The true spacing factor is the material constant which was discussed and derived above in paragraph 3.

The critical fictitious spacing factor is fairly well-known; see /1/. For normal concrete with normal water/cement ratio the following range of  $L_{f,CR}$  seem to be valid:

Freezing in pure water:

$$L_{f,CR} \approx 0,22-0,25 \text{ mm}$$

Freezing with salt water of pessimum concentration at the surface

$$L_{f,CR} \approx 0,16-0,20 \text{ mm}$$

The critical true spacing factor,  $L$ , is less well-defined. An analysis performed in /1/ based on direct measurements of the fragments created by freezing of completely saturated cement pastes or by an analysis based on the critical degree of saturation (see below in paragraph 5.3) and the airpore distribution gives the following very approximative range of  $L_{CR}$ :

Freezing in pure water:

$$L_{CR} \approx 0,35-0,40 \text{ mm}$$

Freezing with salt solution of a pessimum concentration in the pore water and around the specimen:

$$L_{CR} \approx 0,5 \text{ mm}$$

The last value is very uncertain. It is based on one single observation. It does not seem reasonable to assume that the critical spacing factor is higher in salt solution than in pure water considering the fact that the worst expansions during a test of cement mortars freezing without moisture exchange with the surroundings occurred at the concentration 2,5%; see Fig 22-24.

It is not probable that the critical spacing factor should be completely independent of the water/cement ratio. In /3/ a theoretical derivation is made on the effect of the w/c-ratio on the critical spacing factor. The derivation is based on the hydraulic pressure mechanism and on the assumption that the permeability at all freezing temperatures is proportional to the amount of water that is not frozen at the actual temperature. Examples of the theoretically calculated critical thickness are shown in Fig 4. The value is supposed to be 100% at w/c=0,40. The w/c-ratio of outdoor concrete produced during the last decades normally varies between 0,45 and 0,60. This gives a theoretical variation in the critical thickness of about 25%. The lower the w/c-ratio the bigger the critical spacing factor.

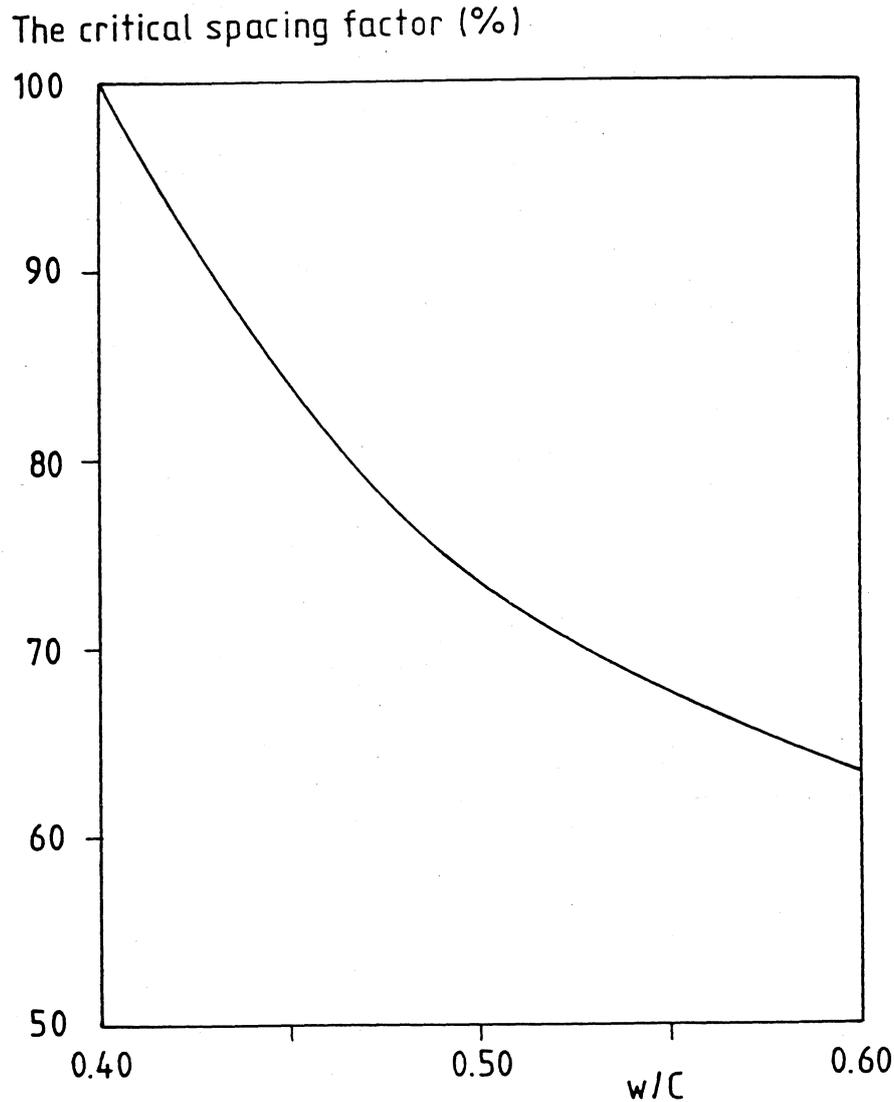


Fig 4: Theoretical relation between the water/cement ratio and the critical spacing factor. The calculation is based on the hydraulic pressure mechanism /3/.

## 5. Effect of the inner water content

### 5.1 General

The water content in the concrete is by far the most important factor determining the frost resistance. If the water content is above a critical value, frost damage will occur at one single freezing. The critical water content is expressed in terms of a critical degree of saturation of the concrete as a whole or in terms of a critical water-filling of the air pore system. It will be shown that the critical degree of saturation is a consequence of the existence of a critical spacing factor. It will also be shown how the critical degree of saturation can be calculated when the critical spacing factor and the airpore distribution curve are known.

## 5.2 Concrete without air pores -entrapped or entrained

Pores smaller than 0,1  $\mu\text{m}$  can always be assumed to be water-filled during normal outdoor conditions. This is proven theoretically in /4/. This means that a concrete which has no air pores and which has a freezable water content above 5 to 10 litres per  $\text{m}^3$  will be severely harmed by frost; see /1/. A certain drying of the capillary pores is needed if a concrete without air pores shall be frost resistant. The drying must proceed until an air-filled volume of about 9% of the amount of freezable water is obtained. Then, the average distance between air-filled capillaries are far below the critical spacing at the same time as the 9% expansion of water that freezes can be accommodated without causing harm to the concrete. This drying means that the *effective* degree of saturation must be below 0,917 which is easily shown:

$$S_{\text{eff,CR}} = W_f / (W_f + a) = W_f / (W_f + 0,09 \cdot W_f) = 0,917 \quad (4)$$

Where

$S_{\text{eff}}$	the effective degree of saturation
$W_f$	the amount of freezable water ( $\text{m}^3/\text{m}^3$ )
$a$	the amount of air-filled pores ( $\text{m}^3/\text{m}^3$ )

This criterion for frost resistance can also be expressed in terms of the "total" degree of saturation when all evaporable water -freezable and non-freezable- is regarded.

$$S_{\text{CR}} = W_e / P = S_{\text{eff,CR}}(1 - k_\theta) + k_\theta = 0,917(1 - k_\theta) + k_\theta \quad (5)$$

Where

$S$	the (total) degree of saturation
$W_e$	the amount of evaporable water ( $\text{m}^3/\text{m}^3$ )
$P$	the total porosity ( $\text{m}^3/\text{m}^3$ )
$k_q$	the relation between the non-freezable water and the porosity:

$$k_\theta = (W_e - W_f) / P \quad (6)$$

*Example 1:*

The non-freezable water contents for different concretes are given in /3/.

1: A concrete with the w/c-ratio 0,60 has a non-freezable water content corresponding to  $k_\theta \approx 0,40$  at  $-20^\circ\text{C}$ . Thus, the critical degree of saturation is:

$$S_{\text{CR}} = 0,917(1 - 0,4) + 0,4 = 0,950$$

This drying corresponds to the emptying of about 7,5 % of the capillary pores.

2: A concrete with the w/c-ratio 0,40 has a non-freezable water content corresponding to  $k_0=0,70$  at  $-20^\circ\text{C}$ . Thus, the critical degree of saturation is:

$$S_{CR}=0,917 (1-0,7)+0,7=0,975$$

This corresponds to the drying of about 6% of the capillary pore volume.

This means that a rather small drying of a concrete containing no air pores will make it frost resistant. On the other hand, a short exposure to water will cause complete saturation of all capillary pores and the concrete will therefore be damaged by frost.

### 5.3 Concrete with air pores -entrapped or entrained

When the concrete contains air pores of sufficiently high volume, the capillary pores and some of the air pores can be allowed to be completely water-filled and the concrete is still frost resistant. The water-filling of the air pore system can proceed until the residual spacing between pores, that are still air-filled, is equal to the critical spacing. If this level is transgressed, frost damage will occur. This means that there exists a critical degree of water-filling of the air-pore system and also a critical degree of saturation of the concrete as a whole.

The mechanism behind the water absorption in the air-pore system is described in /4/. Water absorption can be assumed to proceed in consecutive order of size of the air-pores; the smallest pores being filled at first and then gradually coarser and coarser air pores.

The spacing between air pores can be described by the Powers' spacing factor,  $L$ . This is defined according to Fig 5. All air filled pores are supposed to be of equal size. This is determined by the condition that the specific area of each pore shall be the same as the specific area of the entire air-filled pore system. This leads to the following relation between the residual spacing between pores that are still air-filled,  $L_r$ , and the residual specific area,  $\alpha_r$ , and the residual volume of these pores,  $a_r$ :

$$L_r=(3/\alpha_r)\cdot\{1,4(V_p/a_r+1)^{1/3}-1\} \quad (7)$$

Where

$L_r$	the residual spacing between air-filled pores (m)
$\alpha_r$	the residual specific area of air-filled pores ( $\text{m}^{-1}$ )
$a_r$	the residual volume of air-filled pores ( $\text{m}^3/\text{m}^3$ of concrete)
$V_p$	the volume of cement paste exclusive of air-filled pores but including water-filled air pores ( $\text{m}^3/\text{m}^3$ of concrete)

Eq (7) is based on a pore geometry that is not very realistic. There are other models for calculating the residual spacing factor that are based on more realistic models in which can also be considered the real pore size distribution; see /5/.

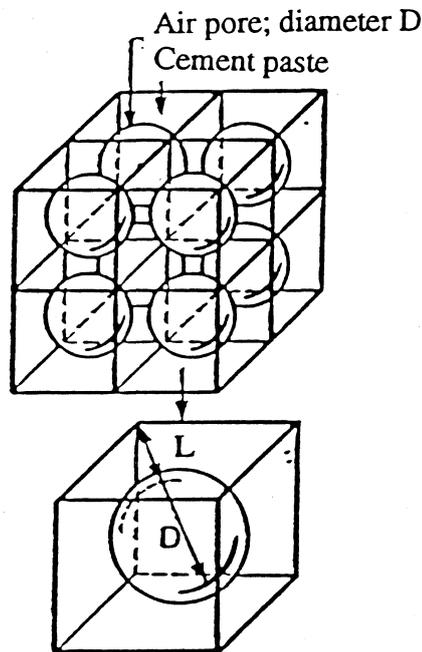


Fig 5: Model defining the Powers' spacing factor; /2/.

It is, as said above, assumed that a smaller airpore is always water-filled before a coarser. Then, the residual air volume is:

$$a_r = \int_{r_{\min}}^{r_{\max}} f(r) \cdot \left(\frac{4\pi}{3}\right) \cdot r^3 \cdot dr \quad (8)$$

Where

- $f(r)$  the frequency function of the air pore system (number of pores per  $m^3$  of concrete)
- $r_{\max}$  the radius of the coarsest airpore (m)
- $r_{\min}$  the radius of the coarsest water-filled airpore (m)

The residual total pore area is:

$$A_r = \int_{r_{\min}}^{r_{\max}} f(r) \cdot 4\pi \cdot r^2 \cdot dr \quad (9)$$

Where

- $A_r$  the residual pore area ( $m^2/m^3$  of concrete)

The residual specific area is:

$$\alpha_r = A_r / a_r \quad (10)$$

The change in the residual spacing due to the gradual water absorption in the airpore system can be calculated by eq (7) by inserting the different values of  $\alpha_r$  and  $a_r$ . Two hypothetical examples of the changes in the specific area  $\alpha_r$  and the air-filled volume  $a_r$  are shown in Fig 6.

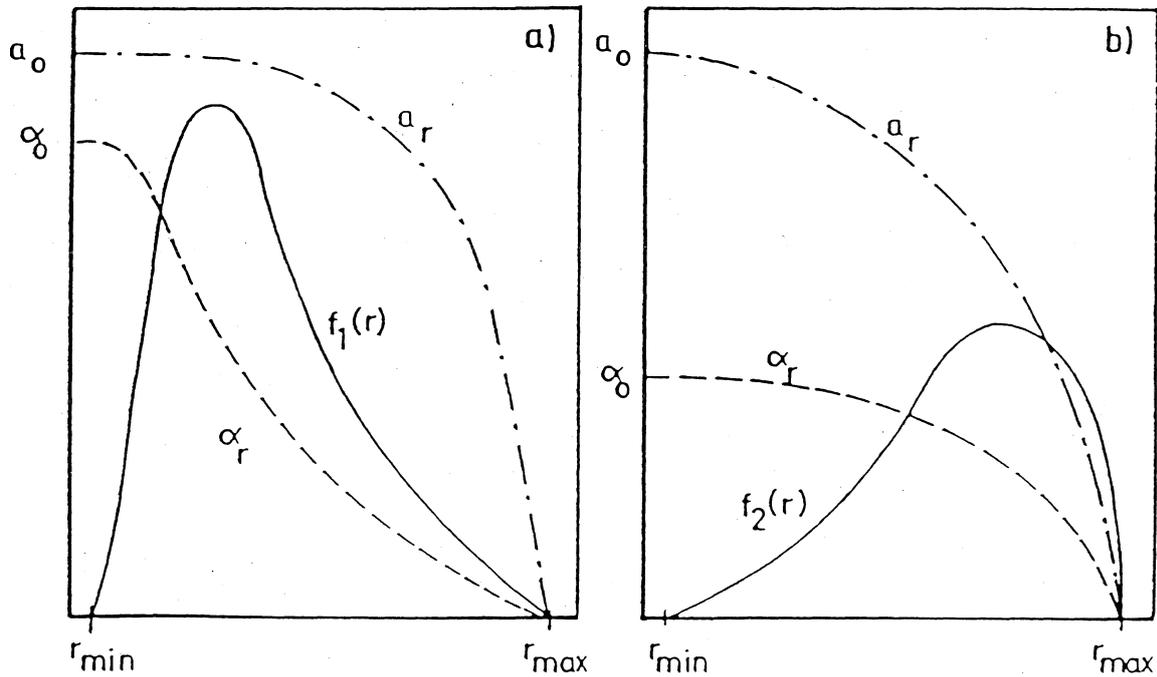


Fig 6: Hypothetical airpore distributions and the influence of a gradual water-absorption on the residual airpore volume,  $a_r$ , and the specific area of air-filled pores,  $\alpha_r$ .

The residual spacing factor,  $L_r$ , is calculated by eq (7) or by a relation which gives a more accurate representation of the real air pore distribution. The critical airpore absorption is obtained when the residual spacing factor is equal to the critical spacing factor. Then the parameters  $a_r$ ,  $\alpha_r$  and  $L_r$  adopt the values  $a_{CR}$ ,  $\alpha_{CR}$  and  $L_{CR}$ . The critical airpore absorption is defined:

$$S_{a,CR} = 1 - a_{CR}/a_0 \quad (11)$$

Where

$S_a$  the degree of saturation of the air pore system ( $m^3/m^3$ );  $S_a$  is zero when no air pores are water filled ( $a_r = a_0$ )

$a_0$  the total volume of the empty airpore system ( $m^3/m^3$ )

There is a relation between the critical degree of saturation of the airpore system and the critical degree of saturation of the concrete as a whole:

$$S_{CR} = 1 - a_{CR}/P = 1 - \{a_0(1 - S_{a,CR})\}/P \quad (12)$$

Where

$P$  the total porosity ( $m^3/m^3$ )

It is quite clear that the critical airpore filling and the critical degree of saturation are functions of the critical spacing factor and the airpore distribution. This will be shown by the following example.

Example 2:

The air pore distribution is described by the following frequency function:

$$f(r) = a \cdot \ln b / b^r \quad (13)$$

Where

$a$  a constant which is determined by the condition that the total airpore volume calculated by eq (8) shall be equal to the real airpore volume.

$b$  a coefficient determining the shape of the airpore distribution.

There is a relation between  $b$  and the specific area,  $\alpha_0$ , of the total airpore system:

$$\alpha_0 = \ln(b) \quad (14)$$

Where

$\alpha_0$  the specific area of the empty airpore system ( $m^{-1}$ )

The value of  $b$  depends on the unit used for specific area. In the calculations it is convenient to use  $\mu m^{-1}$  for the specific area. Then,  $b$  obtains values close to 1. Example:  $\alpha_0 = 0,030 \mu m^{-1}$  ( $30 \text{ mm}^{-1}$ ) corresponds to  $b = 1,03$ .

The following two airpore systems are considered:

Concrete 1:  $\alpha_0 = 0,020 \mu m^{-1}$  or  $20 \text{ mm}^{-1}$  (rather coarse airpore system):  $b = 1,020$

Concrete 2:  $\alpha_0 = 0,030 \mu m^{-1}$  or  $30 \text{ mm}^{-1}$  (rather fine airpore system):  $b = 1,031$

The air content is supposed to be 4 % in both concretes.

The cement paste content is 30% in both concretes.

The total porosity is 16% in both concretes.

The critical spacing factor is 0,40 mm in both concretes.

The relations between the coarsest air-filled airpore and the residual parameters  $a_r$ ,  $\alpha_r$  and  $L_r$  are shown in Fig 7(a) and (b).

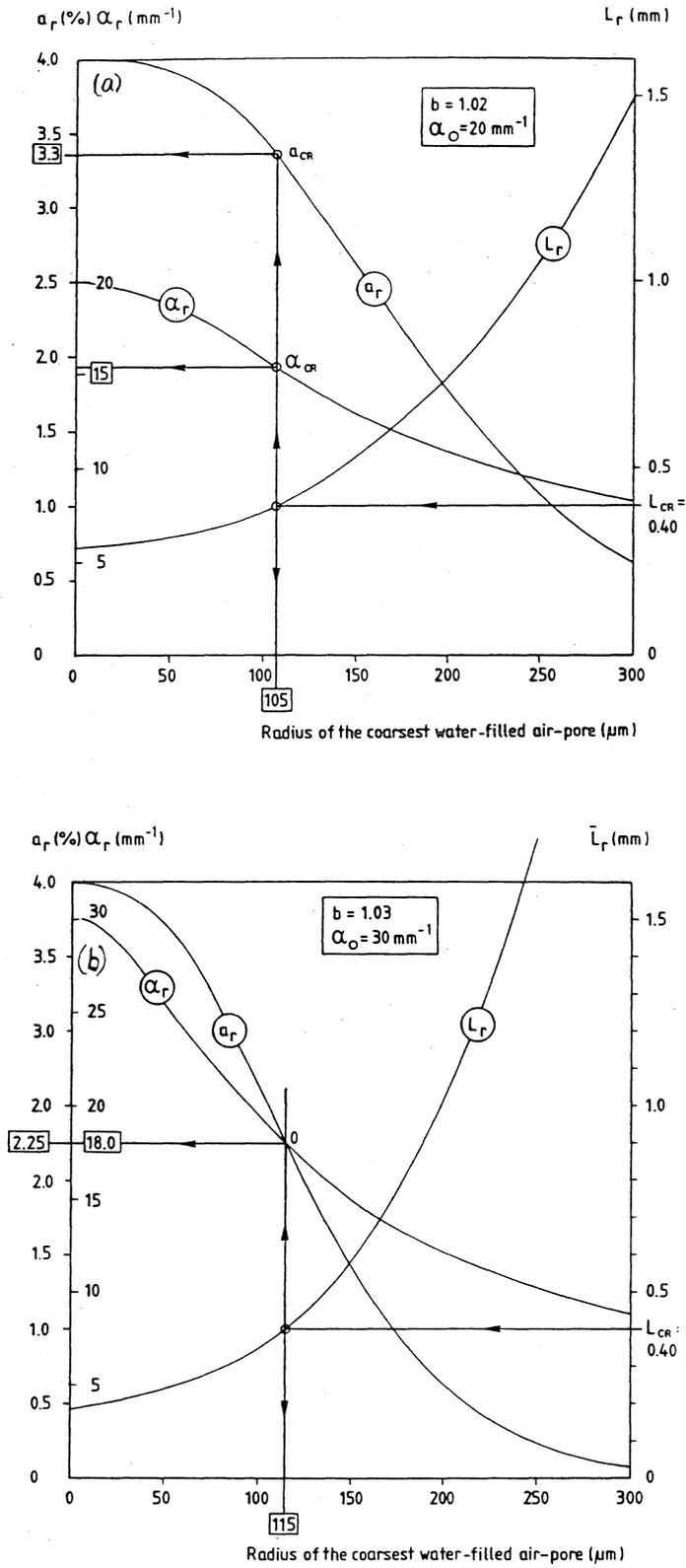


Fig 7: Example of the calculation of the critical degree of saturation of the air-pore system; Example 2. (a) Coarse-porous air-pore system; (b) Fine-porous air-pore system.

The following values are valid for the two concretes:

Concrete 1: Coarse-porous ( $b=1,02$ ):

\*  $r_{CR}=105 \mu\text{m}$  (the radius of the biggest water-filled air pore at  $S_{CR}$ )

\*  $\alpha_{CR}=15 \text{ mm}^{-1}$

\*  $a_{CR}=3,3\%$

\*  $S_{a,CR}=1-3,3/4=0,175$  [eq (11)]

\*  $S_{CR}=1-\{4(1-0,175)\}/16=0,795$  [eq (12)]

Concrete 2: Fine-porous ( $b=1,03$ ):

\*  $r_{CR}=115 \mu\text{m}$

\*  $\alpha_{CR}=18 \text{ mm}^{-1}$

\*  $a_{CR}=2,25\%$

\*  $S_{a,CR}=1-2,25/4=0,438$

\*  $S_{CR}=1-\{4(1-0,438)\}/16=0,860$

In this example the radius of the biggest water-filled air pore is about the same when the critical saturation is reached. The more fine-porous concrete can however stand considerably more water in the air-pore system. No less than 44% of the airpore volume can be water-filled without danger of frost damage. In the coarse air pore system only 18% of the air pore volume can be allowed to be water-filled.

## 5.4 Water in the aggregate

Pores in aggregate grains will absorb water if they are small enough to have a suction (a capillary under-pressure) that is greater than the suction in the capillary pores of the cement paste. This means that the pore size should be smaller than about  $0,1 \mu\text{m}$ . Also bigger pores in the aggregate take up water due to the same mechanism as airpores in the cement paste; i.e. by a "dissolution-of-air, replacement-by-water" process.

Small aggregate particles will not harm the concrete even when they are completely saturated. The volume of freezable water is so low that the expelled water from the aggregate can be taken care of within the air pores of the cement paste.

Coarse aggregate particles can cause severe damage to the concrete if their porosity is high and their degree of saturation is above 0,917. In /6/ the following relation is derived for the tensile stress in the cement mortar as function of the amount of freezable water, the amount of aggregate and the degree of saturation of the aggregate:

$$\sigma_t = \frac{W_{f,a} [0,09 - (1 - S_{\text{eff},a}) / S_{\text{eff},a}] \cdot E_m}{3[(1 - v_m) - v_m \cdot 2(1 - g_a) / (2 \cdot g_a + 1)]} \quad (15)$$

Where

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

This equation shows that no stresses occur when the effective degree of saturation is below 0,917. Already a small water content above the threshold value 0,917 will however cause large stresses.

Example 3:

A concrete with the following characteristics of the aggregate is considered:

$$W_{f,a} = 0,03; E_m = 30 \text{ GPa}; v_m = 0,20; g_a = 0,35.$$

The stresses in the cement mortar as function of the degree of saturation are plotted in Fig 8. The stresses are very high when the degree of saturation is above 0,917. Then, one should consider the fact that the porosity of the aggregate is only 3 %. A tensile strength of 4 MPa, but hardly more, is possible. This means that the maximum tolerable degree of saturation is 0,925.

The equation also shows that very little porosity in the coarse aggregate can be accepted if the aggregate is completely saturated.

Example 4:

A concrete with the following characteristics is considered:

$$E_m = 30 \text{ GPa}; v_m = 0,20; g_a = 0,35; S_{a,\text{eff}} = 1; \sigma_t = 4 \text{ MPa}.$$

The maximum tolerable amount of freezable water (the "porosity") is only  $0,003 \text{ m}^3/\text{m}^3$  or 0,3 volume-% when the aggregate is completely saturated.

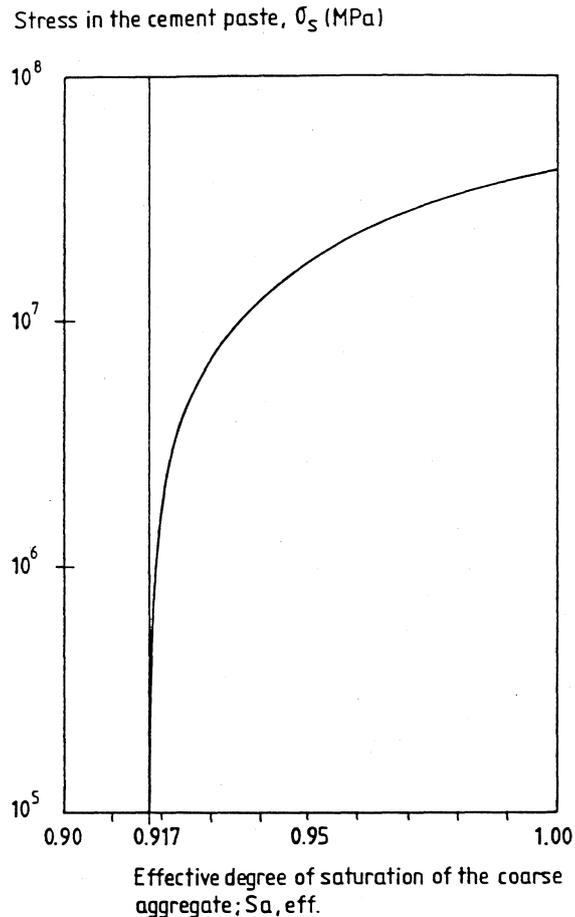


Fig 8: The tensile stress in the cement paste as function of the degree of saturation of the embedded aggregate grain; Example 3.

## 6. Effect of the outer moisture conditions

The outer moisture conditions influence the inner moisture content; the more moist the environment the higher the moisture content inside the concrete. The effect of a varying RH of the outdoor air and of short rains is calculated by a method presented and exemplified in /7/. The effect of a continuous water storage on the airpore water absorption is described theoretically in /4/. This is the most dangerous situation causing the highest moisture levels. The discontinuous water absorption caused by rain and drying cycles give lower degrees of saturation.

The continuous water absorption process is a function of the airpore distribution. In /4/ it is shown that the time process can be described by a function of the following type assuming water absorption goes on simultaneously in airpores of all size:

$$S_a(t)' = A \cdot \alpha_0^B \cdot t^C \quad (16)$$

Where

$S_a(t)'$  the degree of saturation of the air pore system after the water absorption time  $t$ . All air pore water is included in  $S_a'$ ; i.e. also water in pores that are not completely filled.

A; B; C coefficients

$\alpha_0$  the specific area of the empty airpore system ( $\text{mm}^{-1}$ ; NOTE!)

$t$  the exposure time to liquid water (s)

For a pore size distribution described by eq (13) the following relation is valid:

$$S_a(t)' = 7,9 \cdot 10^{-8} \cdot \alpha_0^{2,27} \cdot t^{0,587} \quad \text{for } \delta = 10^{-11} \text{ m}^2/\text{s} \quad (17a)$$

$$S_a(t)' = 2,0 \cdot 10^{-8} \cdot \alpha_0^{2,27} \cdot t^{0,587} \quad \text{for } \delta = 10^{-12} \text{ m}^2/\text{s} \quad (17b)$$

Where

$\delta$  the diffusivity of dissolved air in pore water ( $\text{m}^2/\text{s}$ )

The real degree of saturation  $S_a(t)$  as it is defined in eq (11) where only completely water-filled air pores are considered is related to  $S_a(t)'$  through the following relation which is valid for an airpore distribution of type eq (13).

$$S_a(t) = 0,918 \cdot S_a(t)'^{1,45} \quad (18)$$

Inserting eq (18) in (17) gives the following relation for the degree of saturation of the airpore system:

$$S_a(t) = 4,62 \cdot 10^{-11} \cdot \alpha_0^{3,3} \cdot t^{0,85} \quad \text{for } \delta = 10^{-11} \text{ m}^2/\text{s} \quad (19a)$$

$$S_a(t) = 6,30 \cdot 10^{-12} \cdot \alpha_0^{3,3} \cdot t^{0,85} \quad \text{for } \delta = 10^{-12} \text{ m}^2/\text{s} \quad (19b)$$

By comparing the actual degree of saturation of the airpore system with the critical value one can calculate a sort of potential service life. This is shown by an example.

Example5:

The same as example 2 above.

In example 2 the following critical water absorptions were calculated:

Concrete 1: Coarse-porous:  $S_{a,CR} = 0,175$

Concrete 2: Fine-porous:  $S_{a,CR} = 0,438$

The time process of the increase in the degree of saturation of the airpore system is calculated by eq (19). The equation is depending on the pore size distribution expressed in terms of the specific area  $\alpha_o$ . The following equations are valid for the two airpore systems:

$$\begin{aligned} \text{Concrete 1: Coarse-porous } (\alpha_o=20 \text{ mm}^{-1}): S_a &= 9,1 \cdot 10^{-7} \cdot t^{0,85} & \text{for } \delta=10^{-11} \text{ m}^2/\text{s} \\ S_a &= 1,24 \cdot 10^{-7} \cdot t^{0,85} & \text{for } \delta=10^{-12} \text{ m}^2/\text{s} \end{aligned}$$

$$\begin{aligned} \text{Concrete 2: Fine-porous } (\alpha_o=30 \text{ mm}^{-1}): S_a &= 3,46 \cdot 10^{-6} \cdot t^{0,85} & \text{for } \delta=10^{-11} \text{ m}^2/\text{s} \\ S_a &= 4,72 \cdot 10^{-7} \cdot t^{0,85} & \text{for } \delta=10^{-12} \text{ m}^2/\text{s} \end{aligned}$$

The critical degrees of saturation are obtained after the following suction times (potential service lives),  $t_f$ :

$$\begin{aligned} \text{Concrete 1: Coarse-porous: } t_f &= 1,6 \cdot 10^6 \text{ sec} = 457 \text{ hours} = 19 \text{ days} & \text{for } \delta=10^{-11} \text{ m}^2/\text{s} \\ t_f &= 1,7 \cdot 10^7 \text{ sec} = 4770 \text{ hours} = 199 \text{ days} & \text{for } \delta=10^{-12} \text{ m}^2/\text{s} \end{aligned}$$

$$\begin{aligned} \text{Concrete 2: Fine-porous: } t_f &= 1,0 \cdot 10^6 \text{ sec} = 280 \text{ hours} = 12 \text{ days} & \text{for } \delta=10^{-11} \text{ m}^2/\text{s} \\ t_f &= 1,1 \cdot 10^7 \text{ sec} = 2930 \text{ hours} = 122 \text{ days} & \text{for } \delta=10^{-12} \text{ m}^2/\text{s} \end{aligned}$$

This calculation shows that a coarse-porous airpore system might have a longer service life than a fine-porous when the air content is the same. Then it must be observed that the fine-porous system can stand more water before it is frost damaged. *The more rapid absorption of a fine-porous system evidently outweighs its higher critical degree of saturation.* The calculation also shows that the service life is inversely proportional to the diffusivity of dissolved air.

By a similar calculation the effect of an increase in the air content can be found.

Example 6:

The same as example 2 above but the air content is increased from 4 % to 5 %.

Then, the  $L_r$ -curves in Fig 7a and 7b are moved to the right see eq (7). The critical spacing factor 0,40 mm therefore corresponds to a higher allowable airpore saturation. The new critical degrees of saturation are:

$$\text{Concrete 1: Coarse-porous: } S_{a,CR} = 0,237$$

$$\text{Concrete 2: Fine-porous: } S_{a,CR} = 0,510$$

The maximum allowable water absorption increases somewhat. Inserting the new  $S_{a,CR}$ -values in eq(19) above gives the new service lives:

$$\begin{aligned} \text{Concrete 1: Coarse-porous: } t_f &= 2,35 \cdot 10^6 \text{ sec} = 653 \text{ hours} = 27 \text{ days} & \text{for } \delta=10^{-11} \text{ m}^2/\text{s} \\ t_f &= 2,46 \cdot 10^7 \text{ sec} = 6830 \text{ hours} = 285 \text{ days} & \text{for } \delta=10^{-12} \text{ m}^2/\text{s} \end{aligned}$$

Concrete 2: Fine-porous:  $t_f=1,2 \cdot 10^6 \text{ sec}=330 \text{ hours}=14 \text{ days}$  for  $\delta=10^{-11} \text{ m}^2/\text{s}$   
 $t_f=1,25 \cdot 10^7 \text{ sec}=3470 \text{ hours}=145 \text{ days}$  for  $\delta=10^{-12} \text{ m}^2/\text{s}$

The potential service life is increased by about 40% for the coarse-porous system and by about 15% for the fine-porous system when the air content is increased by 1 %.

## 7. Effect of the number of freeze/thaw cycles; fatigue

### 7.1 Moisture isolated freeze/thaw

The number of freeze thaw cycles seems to have a very small effect as long as the water content inside the concrete is constant, i.e. as long as it is isolated from the environment by some sort of tight membrane. This is seen in Fig 9 and 10 where two studies of the effect of the number of the freeze/thaw cycles on the critical degree of saturation are shown.

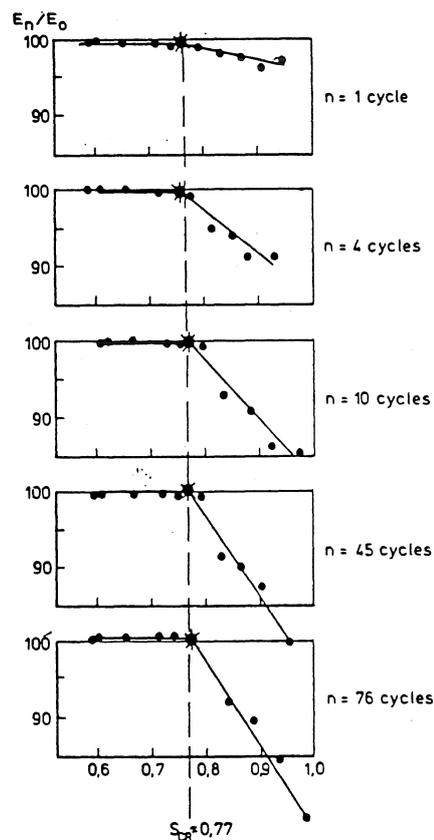


Fig 9: Effect of the number of freeze/thaw cycles on the dynamic E-modulus of cement mortar specimens with the water/cement ratio 0,40; /8/.

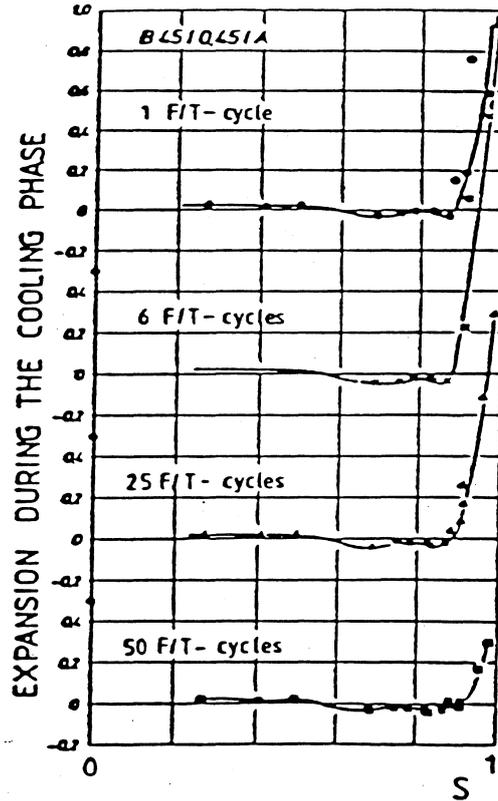


Fig 10: Effect of the degree of saturation and the number of freeze/thaw cycles on the expansion of a concrete during freezing; /9/.

An increased number of freeze/thaw cycles only increases the damage of such concretes that are more than saturated but does not seem to lower the value of the critical degree of saturation. The damage above  $S_{CR}$  is fairly linear with increasing value of  $S$ . Thus, an expression of the following type might describe the damage as function of the number of freeze thaw cycles:

$$\text{Damage}=D=0 \quad \text{for } S \leq S_{CR} \quad (20a)$$

$$\text{Damage}=D=K_N(S-S_{CR}) \quad \text{for } S > S_{CR} \quad (20b)$$

Where

$D$             the extent of damage  
 $K_N$           a coefficient that describes the extent of damage

The coefficient  $K_N$  is a function of the number of freeze/thaw cycles,  $N$ . The first cycles give the most severe damage. It is also reasonable to assume that there is a sort of fatigue limit  $N_e$  for the number of cycles above which there is no further damage. An equation of the following type could perhaps be used:

$$K_N = A \cdot N / (B + N) \quad (21)$$

Where

A            the damage limit for  $N = \infty$   
 B            coefficient

Example 7:

*Cement mortar:*

Fig 9 is used as an example. The damage is linear as described by eq (20). Damage is defined by:

$$\text{Damage} = D = (E_0 - E_N) / E_0 \quad (22)$$

Where

$E_0$             the E-modulus before freeze/thaw (Pa)  
 $E_N$             the E-modulus after N freeze/thaw cycles (Pa)

The coefficient  $K_N$  has the following value for different number of cycles.

N	$K_N$
1	0,23
4	0,62
10	0,77
45	1,08
78	1,08

Little additional damage obviously occur after about 45 cycles. The following approximative relation can be used for the coefficient  $K_N$ :

$$K_N = 1,18 \cdot N / (4,1 + N) \quad (23)$$

This means that the value of  $K_N$  cannot exceed 1,18 even when  $N = \infty$ . A comparison of the experimental data and eq (23) is shown in Fig 11.

A certain damage D occurs after a certain number of cycles,  $N_D$ . This number of cycles is different for different degrees of saturation:

$$N_D = B \cdot D / \{A(S - S_{CR}) - D\} \quad (24)$$

In the actual example and for 15% damage ( $E_N = 0,85 \cdot E_0$ ) the following relation is valid:

$$N_{15\%} = 4,1 \cdot 0,15 / \{1,18(S - 0,77) - 0,15\} \quad (25)$$

The following number of cycles are needed for 15% damage:

$S = S_{CR} = 0,77$ :	$N_{15\%} = \infty$
$S = 0,85$ :	$N_{15\%} = \infty$ (because 15% damage cannot be reached at $S = 0,85$ )
$S = 0,90$ :	$N_{15\%} = 180$ cycles
$S = 0,95$ :	$N_{15\%} = 10$ cycles
$S = 1$ :	$N_{15\%} = 5$ cycles

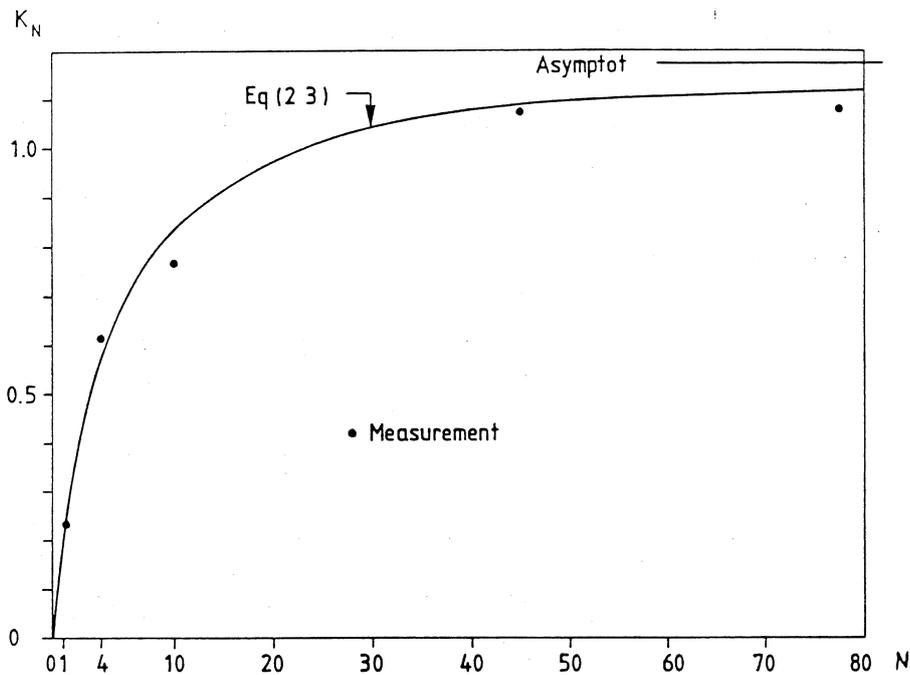


Fig 11: The coefficient  $K_N$  determining the degree of damage as function of the number of freeze/thaw cycles. Comparison between experimental data and eq (23).

The cement mortar evidently has a rather ductile behaviour; also rather large transgressions of the critical moisture content give fairly small damage. One reason might be that the freeze/thaw cycle was rather mild. Another reason could be that the sand grains lock the further crack extension. Concrete is normally considerably more brittle. Two examples are shown in Fig 12; /10/. The effect of the more brittle behaviour is that rather few cycles are needed for severe damage.

Example 8:

*Concrete:*

The concretes in Fig 12 are used as examples. The damage is expressed in the same manner as above. The number of freeze/thaw cycles is 6.

The coefficient  $K_N$  has the following value for 6 cycles:

Concrete type I:  $K_6=7$

Concrete type II:  $K_6=8$

These values are about 15 times as high as for the cement mortar in example 7.

The fatigue limit is not known. The shape of the  $K_N$ -curve is supposed to be the same as for the cement mortar in example 7. Then, the coefficient  $B$  is the same ( $B=4,1$ ). The coefficient  $A$  is obtained from the damage after 6 cycles. For concrete type II the following equation for  $K_N$  is valid:

$$K_N = 13,5 \cdot N / (4,1 + N)$$

(26)

The number of cycles,  $N_D$ , for a certain damage,  $D$ , is:

$$N_D = 4,1 \cdot D / \{13,5(S - 0,80) - D\}$$

The following number of cycles are needed for 50% damage:

$S = S_{CR} = 0,80$ :	$N_{50\%} = \infty$
$S = 0,85$ :	$N_{50\%} = 12$
$S = 0,90$ :	$N_{50\%} = 3$ cycles
$S = 0,95$ :	$N_{50\%} = 2$ cycles
$S = 1$ :	$N_{50\%} = 1$ cycle

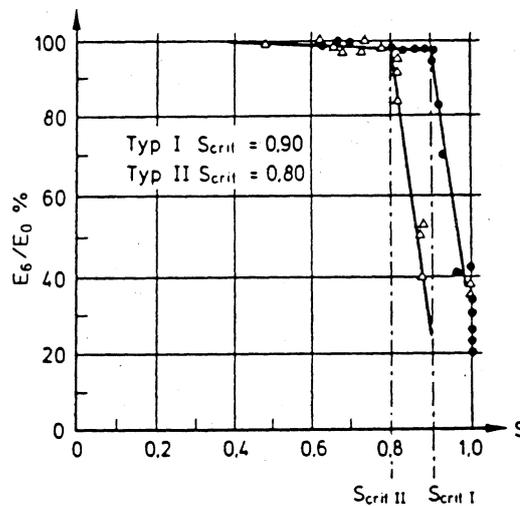


Fig 12: Effect of the degree of saturation on the change in the dynamic E-modulus of two concretes. 6 freeze/thaw cycles; /10/.

## 7.2 Unisolated freeze/thaw

### 7.2.1 General

If the concrete is frozen and/or thawed in water it can either take up water or lose water. The latter case is trivial since the concrete will be subjected to gradually lower stresses with increasing number of freeze/thaw cycles. If it is not damaged during the first cycle it will not be damaged due to the following cycles either.

The first case, with increasing moisture content, is important. In this case, the concrete will sooner or later become critically saturated. Three examples of this is seen in Fig 13 where the E-modulus of three cement mortars is plotted versus

the number of unisolated freeze/thaw cycles; /11/. The mortars of type C and D are more than saturated already from the beginning. Each new cycle gives about the same damage. The mortar of type Q on the other hand is not damaged until it has been exposed to 400 cycles. After that each new cycle gives about the same amount of damage. It seems reasonable to assume that the concrete took up water during each cycle. After 400 cycles the mortar was critically saturated.

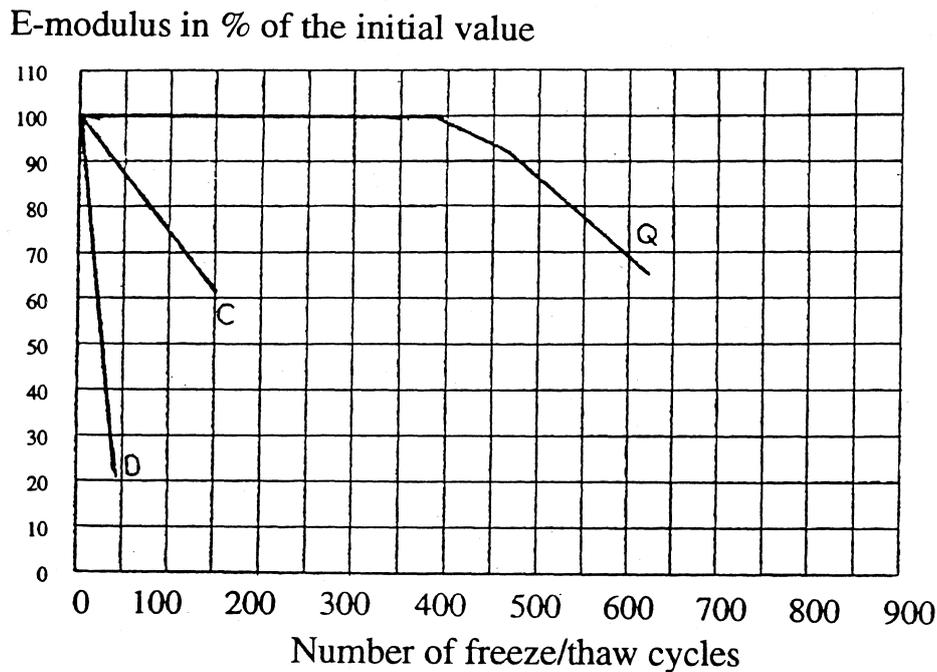


Fig 13: The damage as function of the number of freeze/thaw cycles at unisolated freeze/thaw testing of three cement mortars; /11/.

The following conditions seem to be valid for uninsulated freeze/thaw:

$$N \leq N_{CR}: \quad S \leq S_{CR} \quad \text{Damage}=0 \quad (26a)$$

$$N > N_{CR}: \quad S > S_{CR} \quad \text{Damage}=K \cdot N \quad (26b)$$

Where

$N_{CR}$  the number of freeze/thaw cycles that are needed in order that the concrete shall become critically saturated

$K$  a constant describing the additional damage for each new cycle

The fact that the coefficient  $K$  is constant while the coefficient  $K_N$  (paragraph 7.1) decreases with increasing number of isolated freeze/thaw cycles reflects the fact that the moisture content is not constant during the freeze/thaw but that it increases during each new cycle.

### 7.2.2 Water absorption before the critical saturation is reached

The rate of water absorption during ongoing freeze/thaw compared with the water absorption during isothermal water uptake is not well known. It is reasonable to assume that the rate is about the same as long as the concrete is unharmed. Then, the number of cycles until the concrete becomes critically saturated can be calculated by the theory in /4/ provided the time of wetness during each cycle is known.

Example 9:

The same concrete as the coarse-porous in example 2 and 5 with the diffusivity  $10^{-12} \text{ m}^2/\text{s}$ :

The critical degree of saturation of the airpore system is 0,175 (see Example 2).

The degree of saturation of the airpore system when the freeze/thaw test starts is 0,050. According to Example 5 this corresponds to the following water absorption time  $t_0$  before start of freeze/thaw:

$$t_0 = \{0,050 / 1,24 \cdot 10^{-7}\}^{1/0,85} = 46 \text{ days}$$

The total water storage time in order to reach the critical saturation is 199 days (see example 5). Let us assume that each freeze/thaw cycle consists of 12 hours with the concrete in contact with water and 12 hours in the frozen state. This means that every cycle corresponds to half a day in liquid water.

This means that the number of cycles needed to reach critical saturation is:

$$N_{CR} = (199 - 46) \cdot 2 = 306$$

### 7.2.3 Water absorption in the frost damaged concrete

When the critical saturation is transgressed, every new cycle will cause damage. It is probable that the absorption in a damaged specimen is a bit more rapid than before the critical saturation was reached. In a frost damaged concrete there will probably be cracks which open the concrete to in-flow of water in the airpores. This causes a more rapid water uptake in the airpore system than that described theoretically in /4/. The mechanism is visualized in Fig 14.

In Fig 15 are shown some examples of the water absorption in cement mortars during unisolated freeze/thaw; /12/. It seems as if the absorption is not linear but retarded. The reason is not quite clear but does not necessarily contradict the information in Fig 13 that every new freeze/thaw cycle causes the same damage.

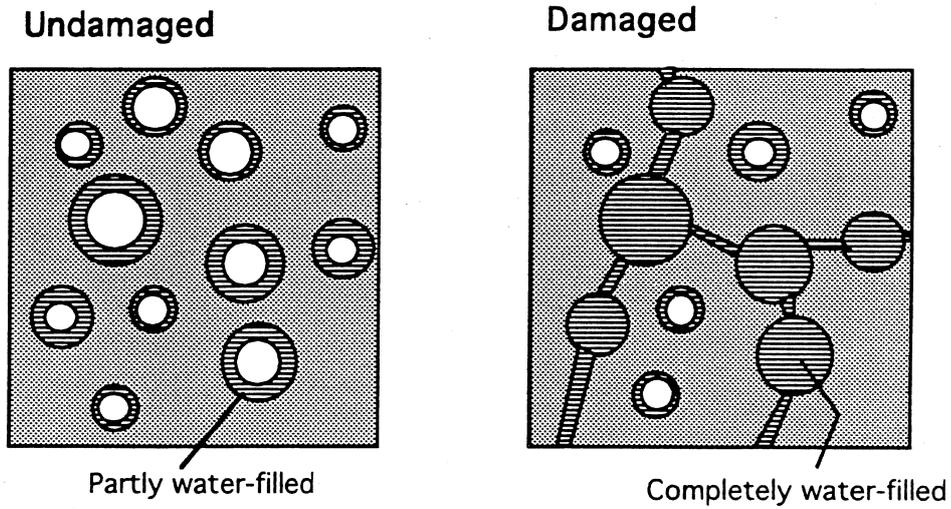


Fig 14: Water absorption in the airpore system of undamaged and frost damaged concrete; principles.

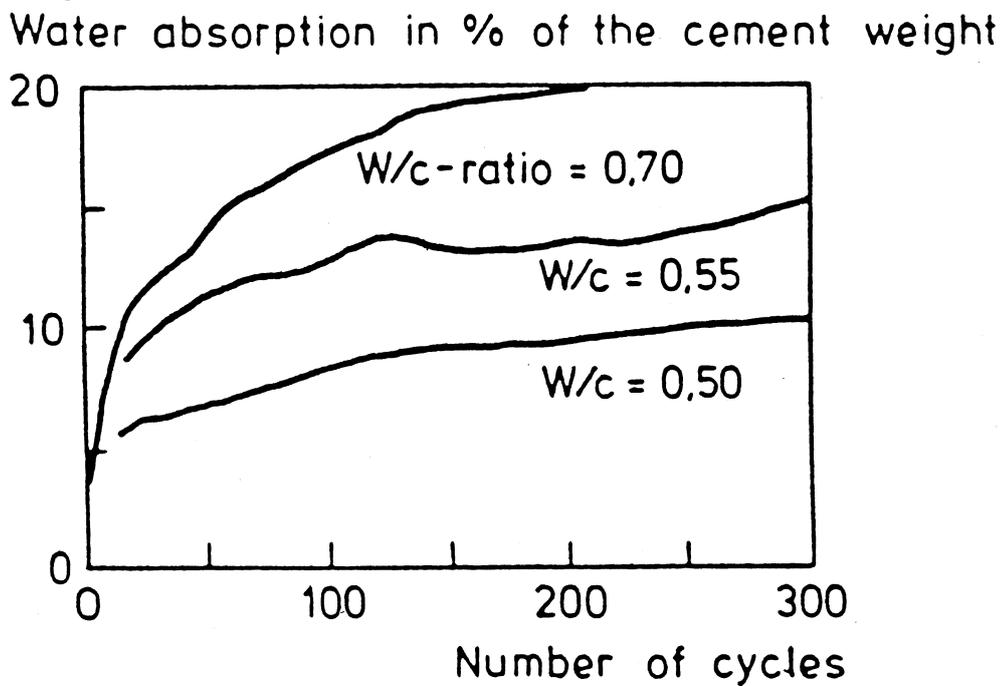


Fig 15: Water absorption in three concretes during unisolated freeze/thaw; /12/.

## 8. The effect of the rate of freezing

### 8.1 Moisture isolated freeze/thaw

The freezing rate in nature might vary by a factor less than 5. Normal variations are much smaller.

Increasing the rate of the temperature lowering of the outdoor air increases the rate of temperature lowering and the rate of ice formation in the concrete; see /13/. The rate of ice formation can be formulated:

$$dW_f/dt = dW_f/d\theta \cdot d\theta/dt \quad (28)$$

Where

- $dW_f/dt$  the rate of ice formation [ $m^3/(m^3 \cdot sec)$ ]
- $dW_f/d\theta$  the increase in freezable water for 1 °C decrease in temperature [ $m^3/(m^3 \cdot degree)$ ]
- $d\theta/dt$  the rate of temperature lowering of the concrete (degree/sec)

The function  $dW_f/d\theta$  is a material characteristic. It is independent of the rate of freezing.  $d\theta/dt$  is independent of the concrete and is only dependent of the outer temperature conditions.

Examples of the curves  $W_f=f(\theta)$  for some concretes are shown in Fig 16; /14/. The curves are depending on the pre-treatment of the concrete. If this has been pre-dried and re-saturated the amount of water frozen at each temperature is very much increased. A further discussion of the freezable water is given in /3/.

Eq (28) implies that the rate of ice formation is directly proportional to the rate of temperature lowering of the concrete.

The effect on the frost resistance can be estimated through its effect on the critical spacing factor. The hydraulic pressure mechanism is assumed. The effect on the critical spacing factor can be estimated by eq (3). It is assumed that the specific area is constant. This is not altogether correct since a change in  $L_{CR}$  changes the critical degree of saturation and hence the specific area of the air-filled part of the airpore system. The error is however small and can in a first approximation be neglected.

An increase in the rate of freezing will decrease the value of  $L_{CR}$ . This causes a decrease in the critical airpore absorption and consequently a shorter service life.

Example 9:

The same concrete as in Example 2 and 5. The fine-porous concrete. The diffusivity is  $10^{-12} \text{ m}^2/\text{s}$ .

*"Slow freezing"; freezing rate 100%*

The critical spacing factor is assumed to be 0,40.

This gives according to Example 2:

Critical specific area :  $\alpha_{\text{CR}}=18 \text{ mm}^{-1}$

Critical airpore saturation:  $S_{\text{a,CR}}=0,438$

Critical degree of saturation:  $S_{\text{CR}}=0,860$

Potential service life:  $t_1=122 \text{ days}$

*"Rapid freezing"; freezing rate 200%*

According to eq (3) the new critical spacing factor and specific area are:

$L_{\text{CR}}=0,30 \text{ mm}$  (reduction by 25%)

$\alpha_{\text{CR}}=21 \text{ mm}^{-1}$

The new critical degree of airpore absorption is:

$S_{\text{a,CR}}=0,250$

The new critical degree of saturation is:

$S_{\text{CR}}=0,813$

The new potential service life is:

$t_1=63 \text{ days}$

The effect of an increase in the freezing rate on the critical absorption is not so important as one might assume. On the other hand, the reduction in the service life is of the same order of size as the increase in the rate of freezing. The effect will also depend on the airpore distribution curve. It might very well be that another distribution curve gives another response to a change of the freezing rate. The response can be both bigger and smaller than that calculated in Example 9.

An unintended study of the effect of the freezing rate on the critical degree of saturation was made in a cooperative study of the so-called critical degree of saturation method; /10/. The freezing rate varied between  $1,9 \text{ }^\circ\text{C/h}$  to  $7,1 \text{ }^\circ\text{C/h}$ ; i.e. by a factor 3,7. The result is shown in Fig 17. There is a clear tendency that the critical degree of saturation diminishes when the freezing rate increases. The effect is however not so big as one might expect which can be explained by the type of calculation presented in Example 9.

The effect of the freezing rate on the moisture isolated freezing with salt in the pore water has not been investigated. In this case there are osmotic effects involved and internal migration of moisture to ice-bodies. These processes take time. Therefore, it might be that a slower freezing is more dangerous than a rapid. It also might be that the duration of the freezing temperatures is of greater importance than the rate of freezing; a longer period of low temperatures being more harmful than a shorter period. The time it takes to arrive at the minimum temperature might be of less importance.

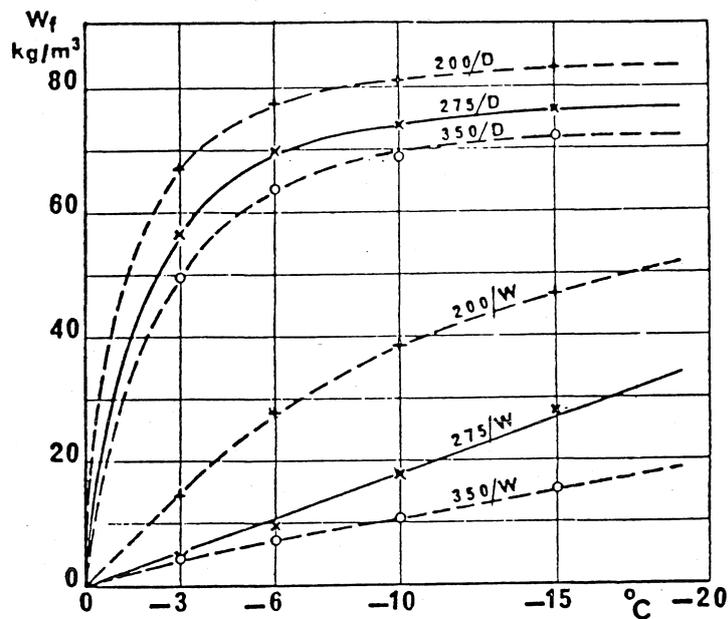


Fig 16: Effect of the freezing temperature on the freezable water of three types of concrete. Never-dried specimens (W) and pre-dried and re-saturated specimens (D); /14/. (The cement content within the paranthesis)

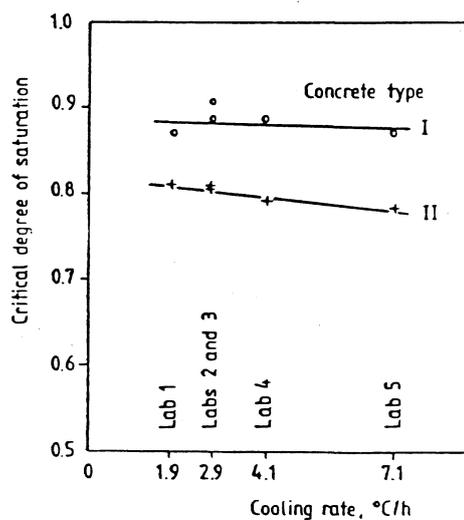


Fig 17: Effect of the freezing rate on the critical degree of saturation of two types of concrete; /13/.

## 8.2 Unisolated freeze/thaw

If the concrete is unprotected from drying or moisture uptake during freeze/thaw, the effect of an increased freezing rate can be both positive and negative. Which effect is valid depends on the shape of the freeze/thaw cycle. If the cycle is "moist", meaning that the concrete has the possibility of taking up water, a slower freezing might be very negative simply because the water absorption is bigger. On the other hand, if the concrete's possibility to take up water during the cycle is reduced, an increased freezing rate is positive.

Some examples are shown in Fig 18 and 19. They are taken from a cooperative test that was performed in 1959 in order to see the effect of the four standardized ASTM-methods for freeze-testing concrete; /15/. The four methods were "slow air" and "rapid air" in which freezing took place in air but thawing in water and "slow water" and "rapid water" in which both freezing and thawing took place in water. Three types of concrete were tested; Types "HG", "LG" and "LP".

The result of the two "air-methods" are shown in Fig 18. Many laboratories were participating and both the mean values and the standard deviations are presented. The more rapid freezing (3,8 degrees per hour) caused more damage than the more slow freezing (14 degrees per hour). The concrete "HG" had a high frost resistance judged by all test methods. It was more resistant than the two other concrete types. In both test methods, the concrete "LG" had a good frost resistance according to the test method "Slow air" but average frost resistance according to "Rapid air". The concrete "LP" had inferior frost resistance in both methods.

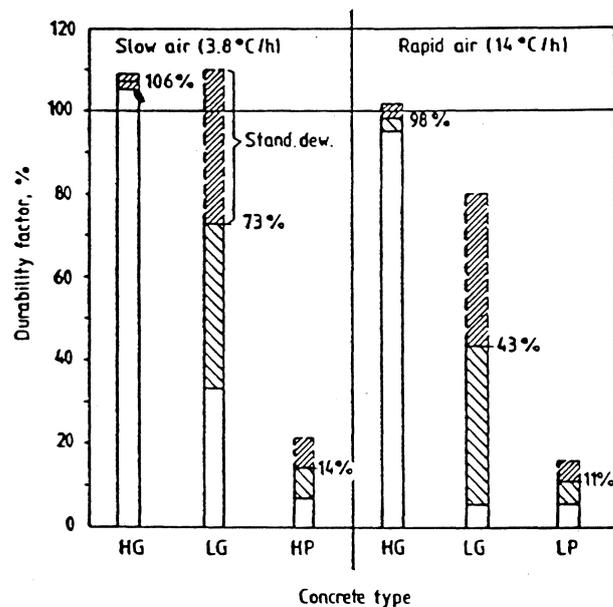


Fig 18: Results of a cooperative test of the effect of the freeze/thaw cycle on the durability of three types of concrete; /15/. Freezing in air and thawing in water.

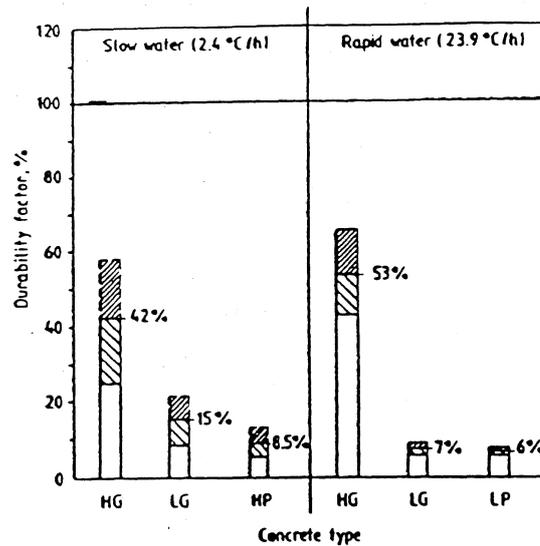


Fig 19: Results of a cooperative test of the effect of the freeze/thaw cycle on the durability of three types of concrete; /15/. Freezing and thawing in water.

The result of the two "water-methods" are shown in Fig 19. Tested by these methods all concretes were judged to be non-resistant. The rating of the concretes is however about the same as for the air-methods; type "HG" having the highest and type "LP" having the lowest frost resistance. In this case it seems as if the slow freezing and the rapid freezing are of about the same severeness. Then it must be observed that the rapid freezing is 10 times as rapid (23,9 versus 2,4 degrees per hour).

It is interesting to compare the severeness of the test with "the relative wetness" of the test expressed as the relation between the time in water and the time in air considering also the total time in water during each cycle. This comparison is made in Table 1. It is clearly seen that the more moist the test the more damage occurs. The reason is that the possibility of the concrete to absorb water during the test is higher and the possibility to dry smaller.

Table 1: Characteristics of the four freeze/thaw test cycles used for the concretes in Fig 18 and 19. Mean values for many participating laboratories.

method	time in air (h)	time in <sup>1)</sup> water (h)	$\frac{\text{time in air}}{\text{time in water}}$	relative <sup>2)</sup> wetness	mean durability factor
slow water	0	48	0	1	22
rapid water	0	3	0	2	22
rapid air	2	1	2	3	51
slow air	18	6	3	4	64

1) Including the time the specimen is frozen

2) 1 is the wettest, 4 is the driest

Another example of the effect of the freezing rate in an unisolated salt scaling test is seen in Fig 29-30. The rate of temperature lowering to  $-22^{\circ}\text{C}$  plays a big rôle on the amount of scaling. Other tests of the same type give similar or the reverse result. Nischer /16/ found that an increase in the freezing rate gave more scaling. Sellevold /17/ on the other hand found that a doubling of the rate of temperature lowering gave somewhat less scaling. Therefore, it is evident that small changes in an unisolated freeze/thaw test might have a great influence on the result. This most probably depend on the possibility the concrete has to take up or give away moisture and on the time possible for salt migration to take place.

A discussion of the effects of the freezing rate is also performed in /13/.

## 9. Effect of the minimum freezing temperature

The minimum freezing temperature has a great influence on the frost resistance. Some illustrative examples are given in Fig 27-29. These figures show the salt scaling as function of the outer and inner salt concentration. At the freezing temperatures  $-7^{\circ}\text{C}$  and  $-14^{\circ}\text{C}$  the scaling is small. At  $-22^{\circ}\text{C}$  on the other hand the scaling is bigger and it is very severe at the outer concentration 3% NaCl.

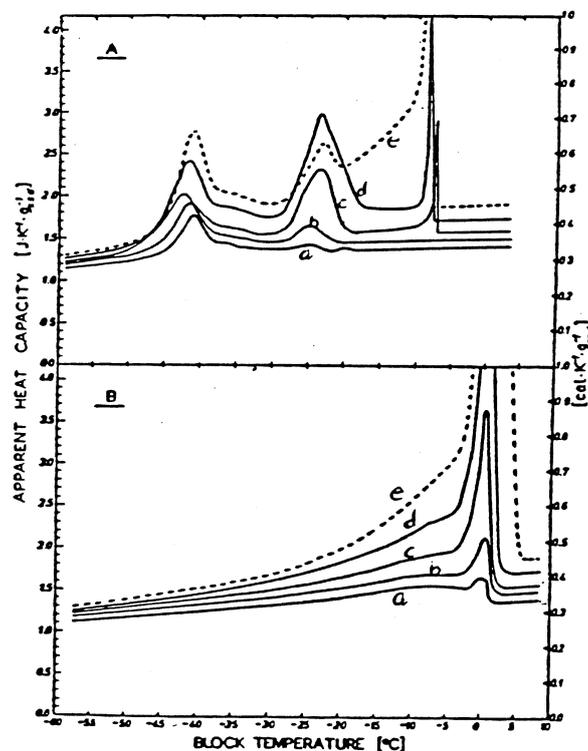


Fig 20: Calorimeter measurements of never-dried cement pastes with different water/cement ratio; /15/. A: Cooling phase. B: Thawing phase.  
(a. w/c=0,35; b. w/c=0,40; c. w/c=0,45; d. w/c=0,50; e. w/c=0,60).

The explanation closest at hand is that the amount of freezable water increases with decreasing temperature. Some examples of this are shown in Fig 20; /18/. At temperatures below about  $-15^{\circ}\text{C}$  rather large amounts of ice are formed in cement paste. It is however not obvious that a large amount of freezable water will give larger stresses in the concrete. The hydraulic pressure mechanism is promoted by rapid freezing and this is more likely to take place at higher temperatures than at lower. The ice crystal growth mechanism is more directly coupled to the amount of ice formed since every ice body causes a stress in the concrete. Also the hydraulic pressure mechanism can however be in accordance with the observed effect of low temperature if the influence of ice formation on the permeability is regarded. Principles for a calculation of this change in permeability will now be given.

The relation between the pressure and the flow through a cylindrical pore with constant radius is:

$$P_h = A \cdot L \cdot (dW/dt) / r^4 \quad (29)$$

Where

$P_h$	the hydraulic pressure (Pa)
$A$	a coefficient including the viscosity of the flow
$L$	the distance of the flow (m)
$dW/dt$	the rate of volume flow [ $\text{m}^3/(\text{m}^2 \cdot \text{s})$ ]
$r$	the pore radius (m)

In a real material there are many pores with different radius. Therefore the pressure is:

$$P_h = A \cdot L \cdot dW/dt \int_{r_{\min}}^{r_{\max}} g(r) \cdot \pi r^2 \cdot dr \quad (30)$$

Where

$g(r)$	the frequency function of pore radii
$r_{\max}$	the radius of the coarsest pore that is not filled with ice (m)
$r_{\min}$	the radius of the most narrow pore (m)

Thus, it is assumed that no pore containing ice will contribute to the flow of expelled water. This means that the pressure will be bigger and bigger with increasing amount of ice under condition that the total flow is not diminished.

The volume flow is a function of the rate of ice formation:

$$dW/dt = 0,09 \cdot dW_f/dt = 0,09 \cdot (dW_f/d\theta) \cdot (d\theta/dt) \quad (31)$$

Then, the pressure at a certain temperature  $\theta$  is obtained by:

$$P_h(\theta) = 0,09 \cdot (dW_f/d\theta)_\theta \cdot (d\theta/dt)_\theta \int_{r_{\min}}^{(r_{\max})_\theta} f(r) \cdot \pi r^2 \cdot dr \quad (32)$$

Where

$(dW_f/d\theta)_\theta$	the increase in freezable water per degree of temperature lowering at the temperature $\theta$ [ $m^3/(m^3 \cdot \text{degree})$ ]
$(d\theta/dt)_\theta$	the rate of temperature lowering at the temperature $\theta$ (degree/s)
$(r_{\max})_\theta$	the radius of the smallest ice-filled pore at the temperature $\theta$ (m)

The freezable water at a certain temperature can be obtained experimentally by a calorimeter experiment. The observed freezable water can then be used in eq (32) for calculating the hydraulic pressure. The problem is to find the relation between the temperature  $\theta$  and the corresponding pore radius  $(r_{\max})_\theta$ . As a first approximation, the theoretical relation according to the Kelvin equation between the freezing point and the pore radius can be used; /3/:

$$r_\theta = -2 \cdot \sigma_{sl} \cdot M / \{ \rho_1 \cdot \Delta H \cdot \ln[(T_0 - \Delta T) / T_0] \} + t_a \quad (33)$$

Where

$r_q$	the pore radius corresponding to the freezing point $\theta$
$\theta$	the temperature ( $^{\circ}\text{C}$ ). [ $\theta = -\Delta T$ ]
$\sigma_{sl}$	the surface tension water-air (N/m)
$M$	the molecular weight of water (kg/mole)
$\rho_1$	the density of bulk water ( $\text{kg}/m^3$ )
$T_0$	the freezing point of bulk water ( $^{\circ}\text{K}$ )
$\Delta T$	the freezing point depression ( $^{\circ}\text{K}$ )
$\Delta H$	the molar heat of fusion of water (J/mole)
$t_a$	the thickness of the adsorbed water layer (m)

If there are no super-cooling phenomenons the amount of freezable water at the temperature  $\theta$  can be calculated by:

$$(W_f)_\theta = \int_{(r_{\max})_\theta}^{r_{\max}} g(r) \cdot \pi r^2 \cdot dr \quad (34)$$

Where

$(W_f)_\theta$	the total freezable water at the temperature $\theta$ ( $m^3/m^3$ )
----------------	---

The equations above can be used for a calculation of the hydraulic pressure as function of the freezing temperature. It might very well be that the maximum pressure is reached at the lowest temperature simply because the amount of ice is so high that water that is expelled from the freezing site at low temperatures cannot be forced away without causing destructive forces. These relations between the temperature and the permeability and the inner pressure are visualized in Fig 21.

Measurements of the expansion of cement mortars during freezing also indicate that the expansion increases with decreasing temperature; see Fig 22 and 23. In no case did the specimen contract when the temperature was lowered. Thus, it actually seems as if the internal pressure is higher the lower the temperature.

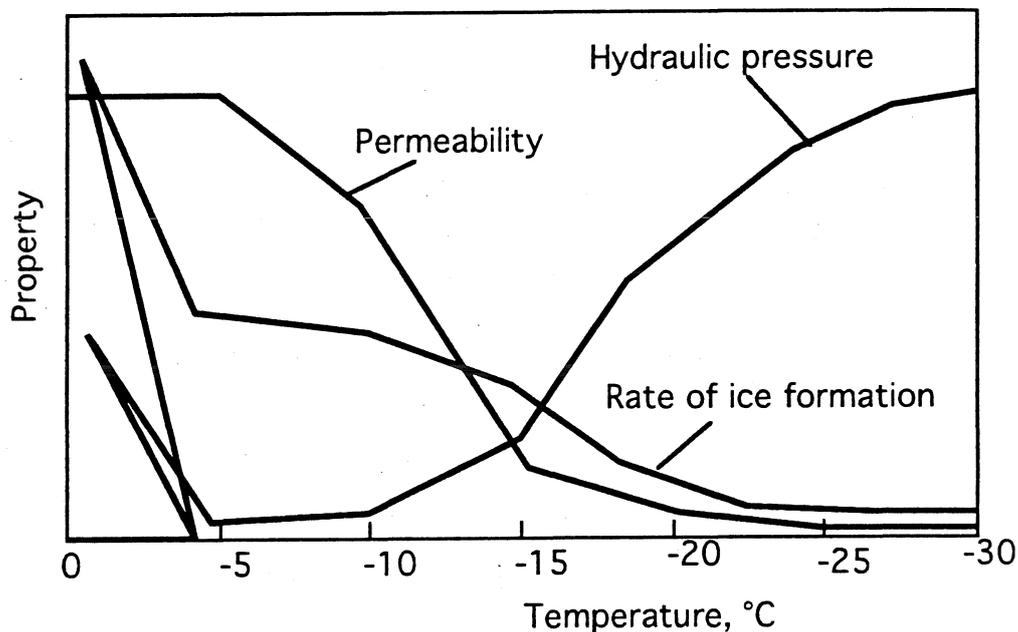


Fig 21: Hypothetical curves of the rate of ice formation, the permeability and the hydraulic pressure.

## 10. Effect of salts

### 10.1 Moisture isolated freeze/thaw

As discussed in paragraph 3 the damaging stresses might be higher when the pore water is saline. Some results are shown in Fig 22 and 23; /19/. Two cement mortars with the water/cement ratio 0,64 and 0,60 were pre-dried and then exposed to a vacuum corresponding to a residual pressure of either 150, 50 or 2 torr. Then, while the vacuum was still active, a salt solution containing either 0, 2,5, 5 or 10% of NaCl was introduced in the vacuum chamber, whereafter ordi

nary atmospheric pressure was applied. The specimens were stored in the salt solution for more than 1 month. The degree of saturation of salt solution became very high when the vacuum treatment was made at 50 or 2 torr and moderately high when the pressure was 150 torr. The salt concentration was the same throughout the mortar specimen. This was proved by the initial freezing point measured in the center of the specimen corresponding exactly to the theoretical for the actual concentration.

The specimens were wrapped in plastic foil in order to avoid evaporation. Then, they were exposed to a freeze/thaw cycle during which the length change was measured. The results are shown in Fig 22 and 23. Only the cooling phase is shown. All specimens vacuum-treated at 50 or 2 torr expanded very much during the test. In all cases, the salt concentration 2,5% gave bigger expansion than the other concentrations. Vacuum treatment at 150 torr produced a lower degree of saturation and the expansion was none or low. Even in this case there is however a somewhat bigger expansion at 2,5% and 5% than at 0% and 10%. This can also be seen in Fig 24 where the total expansion at  $-25^{\circ}\text{C}$  is plotted versus the salt concentration for different degrees of saturation.

The measurements indicate that there exists a certain pessimum internal salt concentration. The exact value is not known but it seems as if it is closer to 2,5% than to 5%. The pessimum value is not known for other w/c-ratios than the ones tested. Neither is it known for other types of salts and de-icing agents than NaCl. Observations by Verbeck & Klieger /20/ indicate that pessimum concentrations exist also for other de-icing agents and that the pessimum concentration might be of the same order of size as for NaCl; Fig 25.

The reason for the existence of a pessimum concentration is not known. Some qualitative speculations are made in paragraph 3.

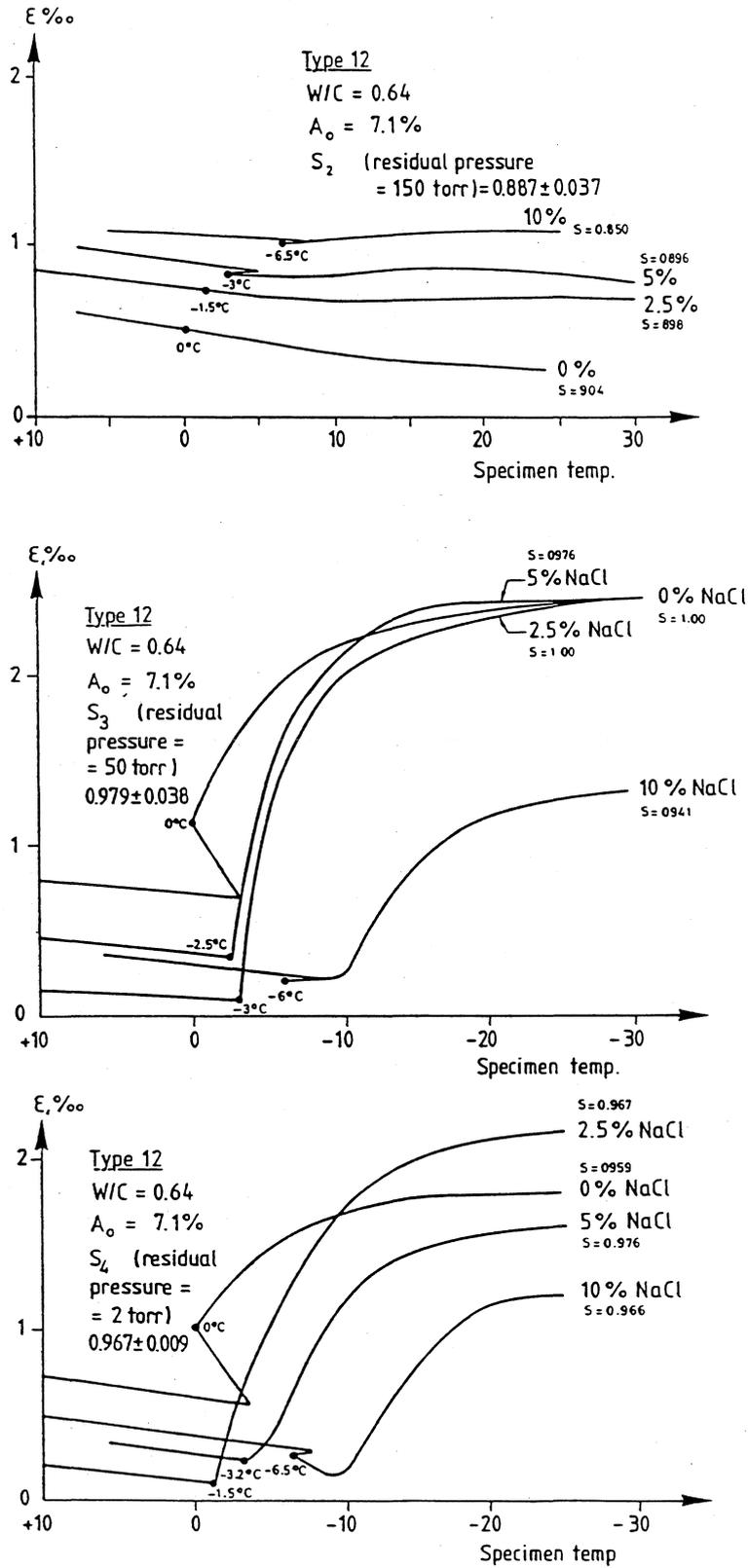


Fig 22: Length change versus temperature during freezing of cement mortar with  $w/c=0,64$ , vacuum-saturated at different residual pressures and containing salt solutions of different concentration; /19/.

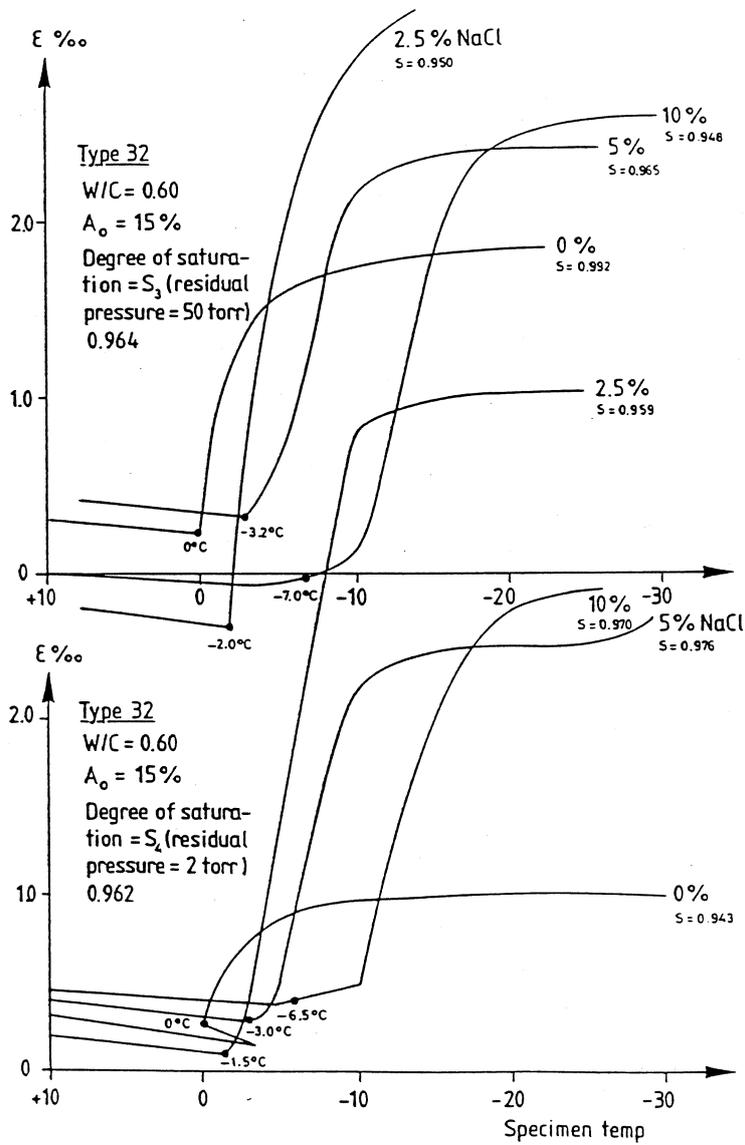
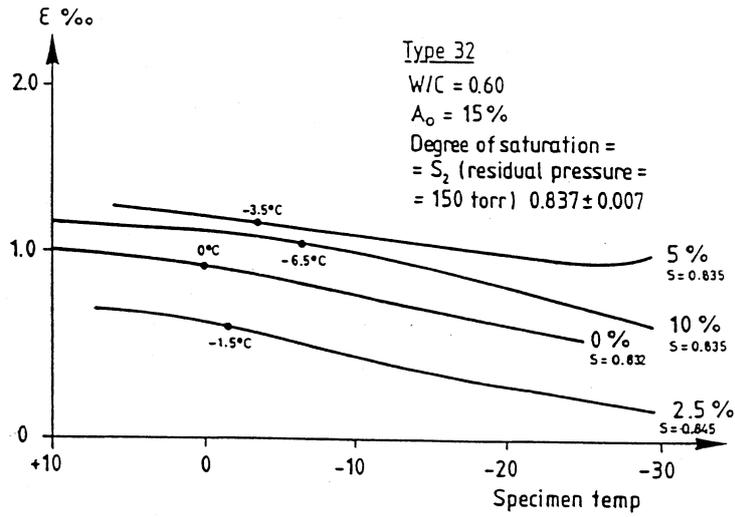


Fig 23: Length change versus temperature during freezing of cement mortar with  $w/c=0,60$ , vacuum-saturated at different residual pressures and containing salt solutions of different concentration; /19/.

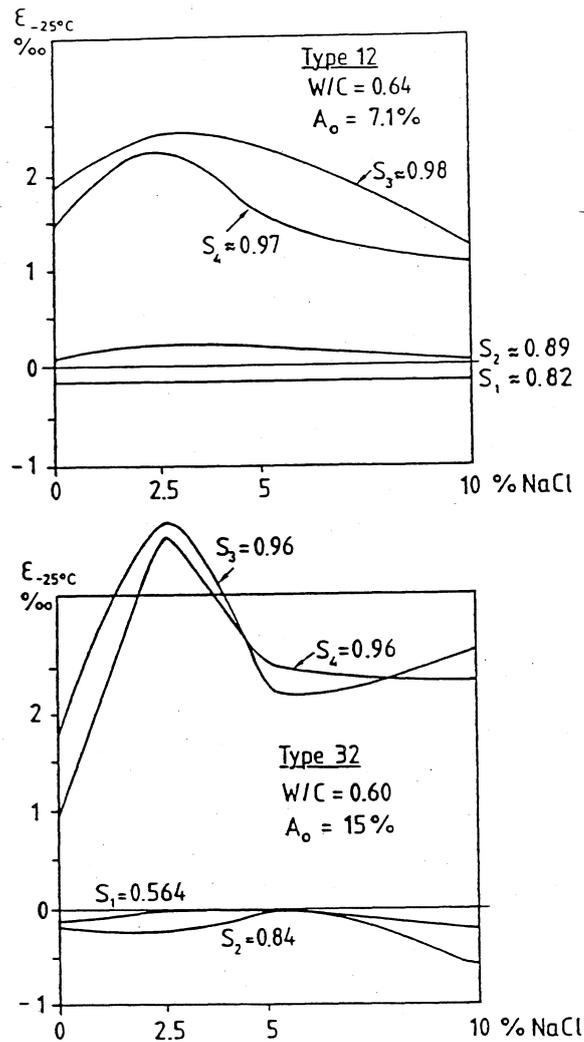


Fig 24: The dilation at  $-25^\circ C$  of cement mortars as function of the degree of saturation and the salt concentration of the pore water; /19/.

## 10.2 Unisolated freeze/thaw

The first comprehensive salt scaling studies of concrete were made by Verbeck & Klieger /20/. Their studies were made with specimens that were exposed to outer salt solutions during freezing and thawing. Thus, moisture and/or salts were able to migrate into and out of the specimen during the test. The authors found that there exist pessimum concentrations of de-icing agents. A summary of their results are shown in Fig 25. For all agents the pessimum concentration is fairly low. Only for  $CaCl_2$  there is an increased deterioration at high concentrations. This depends on chemical attack and has nothing to do with freeze/thaw. The authors also found that the deterioration is avoided if the concrete contains entrained air of sufficient quantity. This is a proof that also salt scaling is a physical and not a chemical attack.

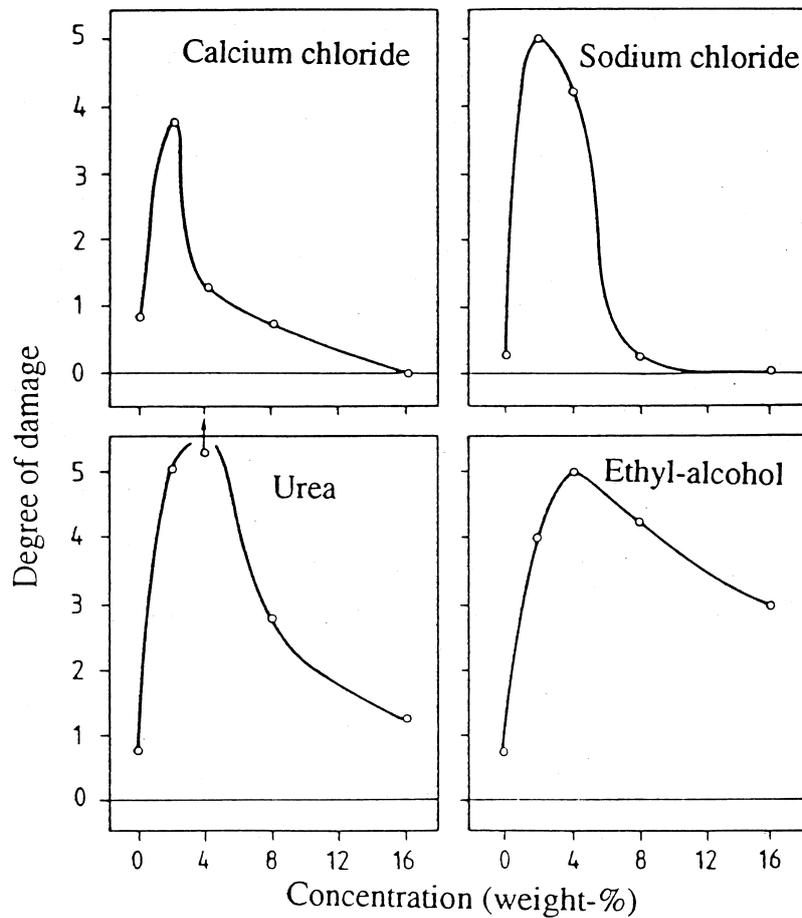


Fig 25: The degree of scaling as function of the concentration of de-icing agents poured on top of the concrete specimen; /20/.

New studies have been made of the effect of different combinations of inner concentration and outer concentration of NaCl; /21/. The concrete specimens with the water/cement ratio 0,40 and some air entrainment were stored for half a year either in pure water or in 3% or 6% of NaCl-solution. Then, they were freeze/thaw tested according to the principles of the Swedish standard method for testing the salt scaling resistance. This means that the specimens were heat insulated on all sides except the top surface. This was covered with either pure water or with NaCl-solutions with the concentrations 3% or 6%. This means that all 9 possible combinations of outer and inner concentrations were investigated. Four different freeze-thaw cycles were used for every combination of outer and inner salt concentration; see Fig 26. The freeze/thaw cycle always had a duration of 24 hours out of which the thawing phase was 8 hours.

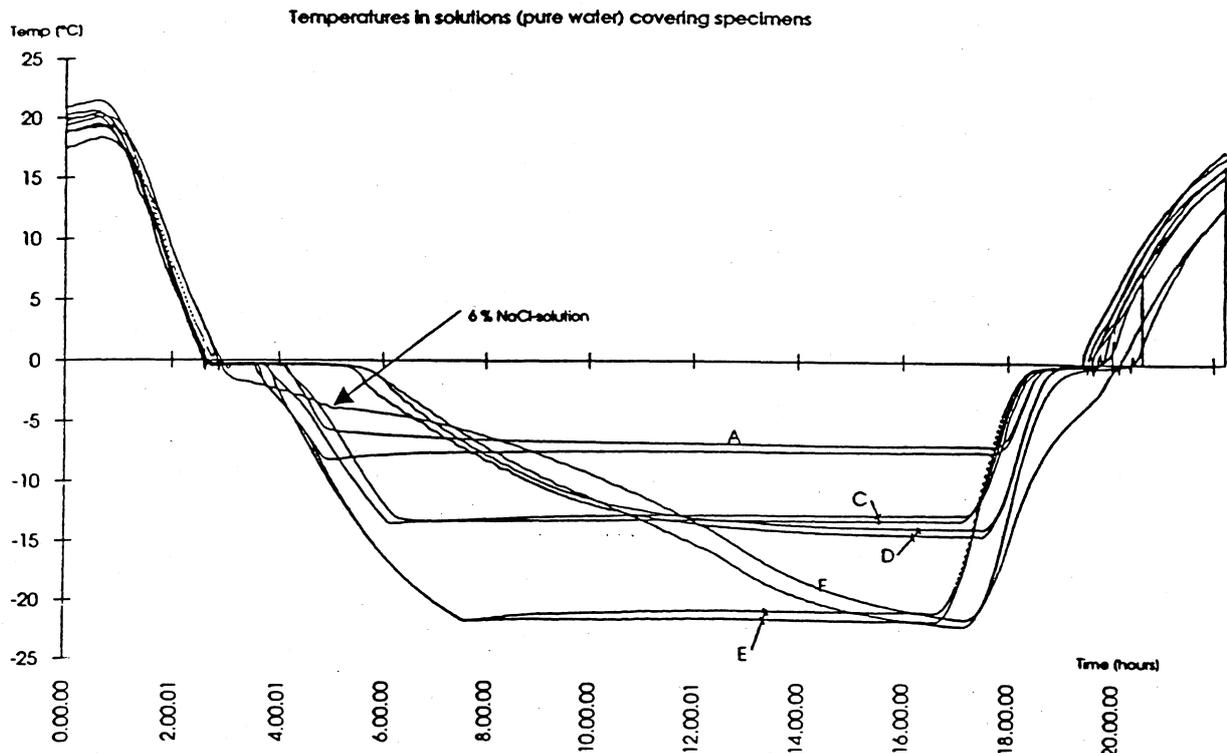


Fig 26: The freeze/thaw cycles used in the salt scaling tests accounted of in Fig 27-30; /21/.

The results of the test are summerized in Fig 27-30. It was found that the outer concentration 3% almost always gave the most severe scaling irrespectively of the inner concentration. It was also found that the minimum temperature  $-22^{\circ}\text{C}$  gave much more scaling than the minimum temperatures  $-7^{\circ}\text{C}$  or  $-14^{\circ}\text{C}$ . The rate of temperature lowering also had an considerable effect. The more rapid freezing gave the most severe scaling.

It is not known whether the real pessimum occurs at another salt concentration not investigated in the study. Besides, it is not known whether the pessimum concentration is different for other types of concrete containing mineral admixtures or having other water/cement ratios. Investigations on this problem is going on at our department.

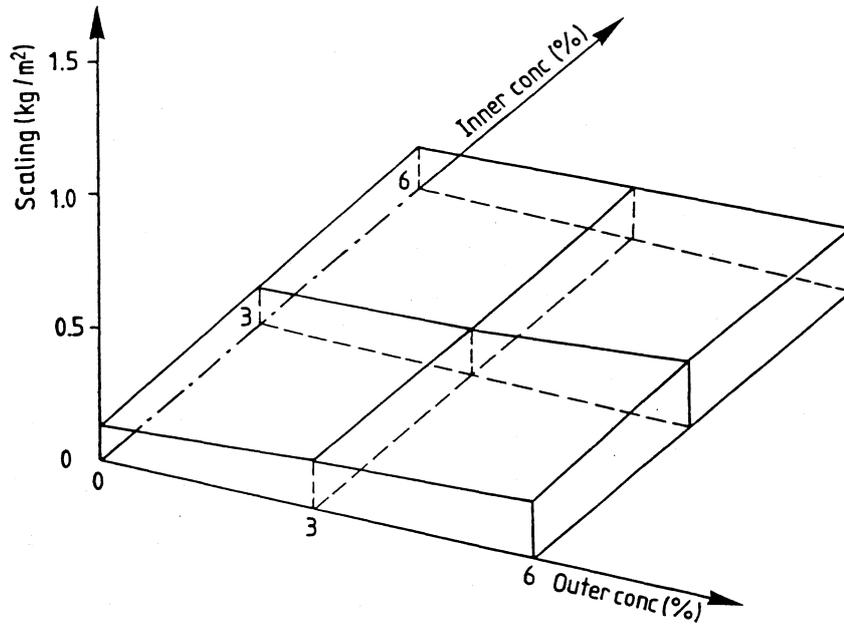


Fig 27: Salt scaling after 56 freeze/thaw cycles as function of the inner and outer salt concentrations. Minimum temperature  $-7^{\circ}\text{C}$ . Rapid freezing; /21/.

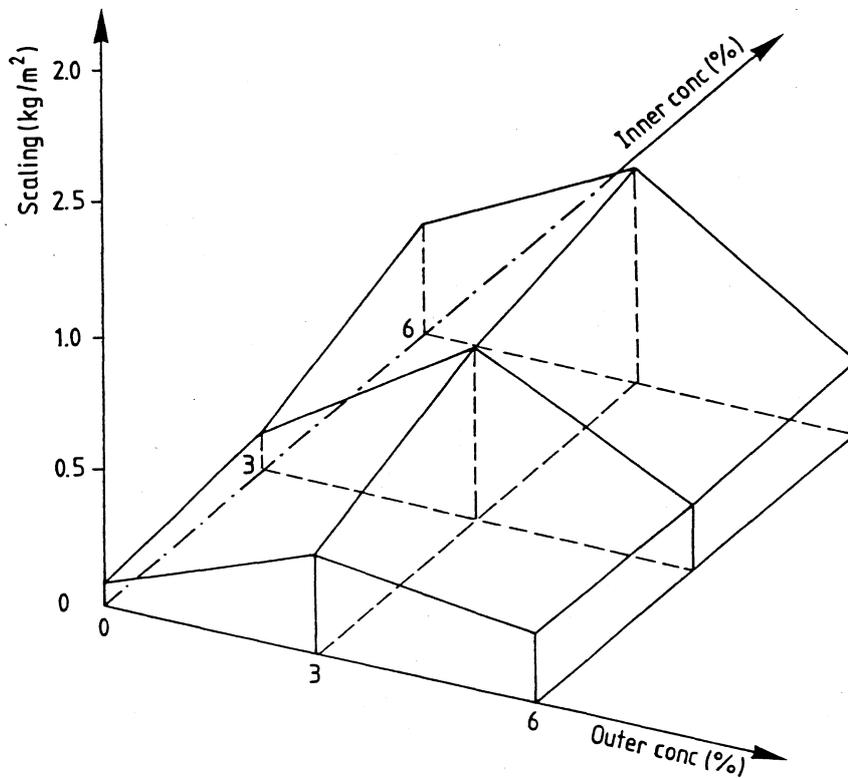


Fig 28: Salt scaling after 56 freeze/thaw cycles as function of the inner and outer salt concentrations. Minimum temperature  $-14^{\circ}\text{C}$ . Rapid freezing; /21/.

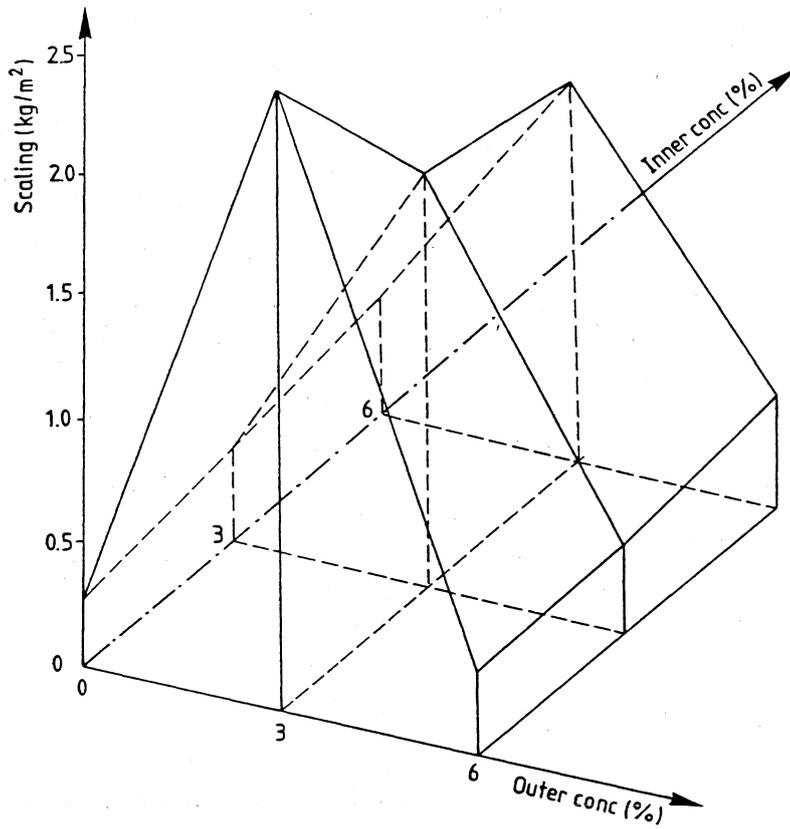


Fig 29: Salt scaling after 56 freeze/thaw cycles as function of the inner and outer salt concentrations. Minimum temperature  $-22^{\circ}\text{C}$ . Rapid freezing; /21/.

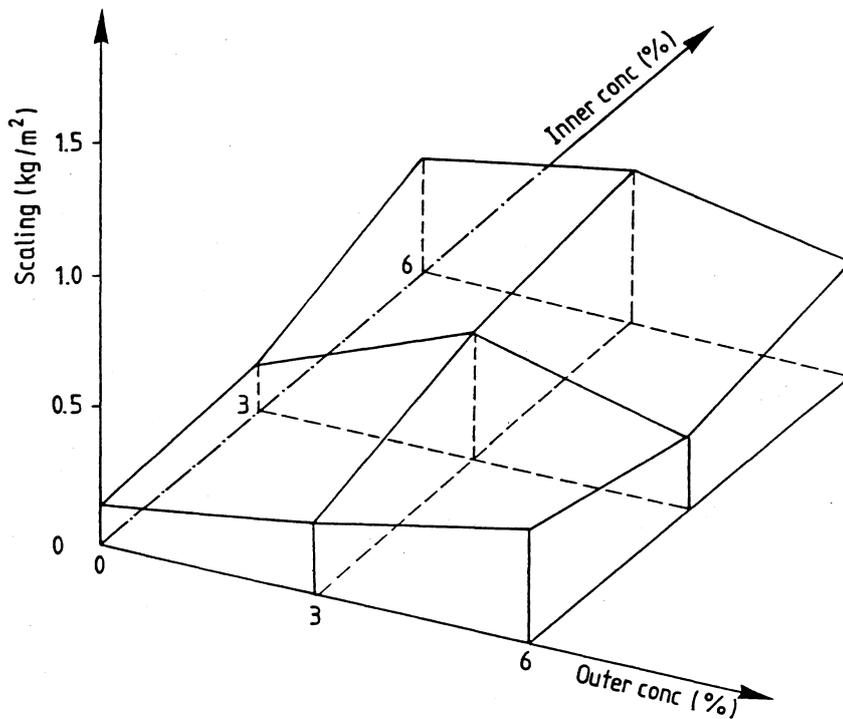


Fig 30: Salt scaling after 56 freeze/thaw cycles as function of the inner and outer salt concentrations. minimum temperature  $-22^{\circ}\text{C}$ . Slow freezing; /21/.

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