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Interpretation of the Result of a Traditional Salt-Frost Scaling Test



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ABSTRACT

Frost damage on the concrete surface might be aggravated when freezing occurs in the presence of a salt solution, like sea water or de-icing salt. A possible mechanism behind this combination of frost and salt is discussed. When freezing takes place in pure water, ice formed at the surface will block inflow of water to the concrete, but it will cause drying of the concrete. When freezing occurs in salt solution, unfrozen water (brine) can enter the concrete surface and make the concrete completely saturated. When pore water freezes, it exerts pressure. The effect of air-entrainment is favourable since it reduces the stresses. A calculation is made of the air requirement for concrete with w/c-ratio 0.45.

Key words: Frost resistance, salt-frost scaling, air-entrainment, hydraulic pressure

1. SALT-FROST SCALING TEST - EFFECT OF THE EXTERNAL SALT CONCENTRATION

Concrete surfaces exposed to salt solution, like de-icing salt or sea water, in combination with exposure to frost, might be severely scaled. This will occur in a salt freeze/thaw test in the lab, as well as during exposure to natural conditions. Each new freeze/thaw cycle in a freeze/thaw test will cause additional scaling. The same is the case for the salted surface of a real structure when

this is exposed to repeated frost. When the same concrete surface is exposed to pure water in the lab, or in practice, no or marginal scaling will occur. Scaling is seldom accompanied by important internal damage.

The results of a lab test in which the surface of samples cast from the same *non-air entrained* concrete batch were exposed to NaCl-solutions of variable strength for 56 freeze-thaw cycles are shown in Figure 1 [1]. Freezing and thawing with pure water on the surface gave almost no scaling while as small salt concentration as 1 weight-% caused considerable scaling. Increasing the salt concentration to 5% gave no additional scaling. Thus it seems clear that salt-frost scaling is not a chemical but a physical effect. This is verified by earlier tests performed by Verbeck & Klieger [2] in which solutions of different types of chemicals like sodium chloride, calcium chloride, urea and ethyl alcohol caused big scaling of non-air entrained concrete at the concentration 3%, but no, scaling at concentration 0% and 8%. Probably, these results are the reason behind the commonly advocated opinion that there exists a “pessimum” salt concentration of 3% in salt-frost scaling. No tests were, however, made for other salt concentrations between 0% and 8%. And no other systematic tests like that presented in Figure 1 has been found in literature.

The average density of scaled material is about 2000 kg/m^3 . Total scaling in salt solution is of the order 1800 g/m^2 for the pre-dried concrete, which means that the average thickness of scaled material in salt solution is of the order 1 mm. Therefore, it is what occurs within the outmost millimetre of the specimens that is of primary interest in an analysis of the result. For concrete with higher w/c-ratio and low air content scaling will often be considerably bigger. Concrete that has sufficiently high amount of *entrained air* can stand also a saline environment with no or low damage. It is clear, however, that the air content must be higher for concrete exposed to salt than for concrete exposed to pure water.

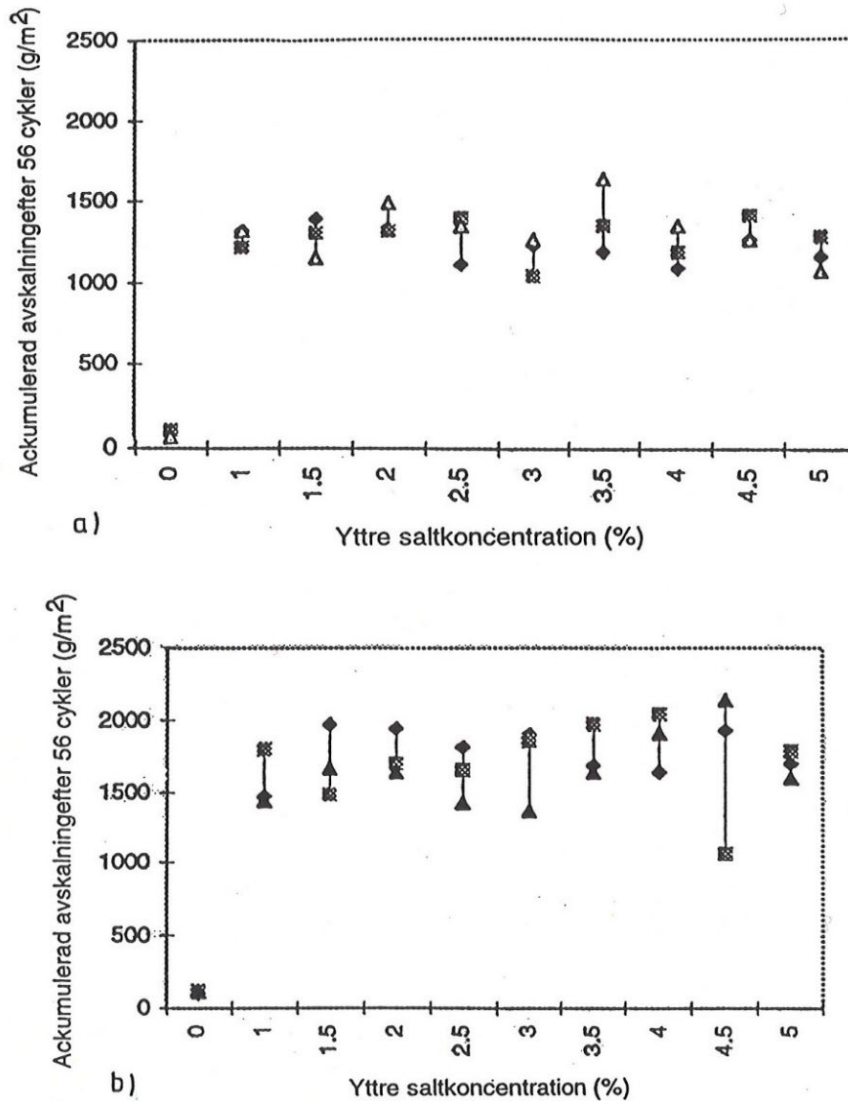


Figure 1 - Influence of the outer salt concentration on the salt-frost scaling of non-air entrained concrete with w/c-binder-ratio 0.34 and 5% silica fume [1]. (a) Non-dried before exposure to frost. (b) Pre-dried at +50°C and re-saturated. Salt concentration is weight NaCl in 1 kg of water. x-axis: outer salt concentration, %. y-axis; total scaling after 56 freeze-thaw cycles, g/m².

2. FREEZE-THAW IN PURE WATER - INTERPRETATION OF RESULTS IN FIGURE 1

2.1 Characteristics of the freeze-thaw cycle

The freeze-thaw cycle is composed of about 3 hours of lowering temperature from 0°C to -10°C and about 6 hours from -10°C to -20°C. Warming from -20°C to 0°C takes about 4 hours. Temperature is held constant at -20°C for about 4 hours. The thawed specimen surface is exposed to liquid water, or unfrozen solution, during about 7 hours each cycle.

2.2 Discussion of the damage mechanism

Almost no scaling occurred when the concrete surface was covered by pure water or ice. The reason is discussed below.

One can assume that all pores in concrete (capillary and gel pores) are completely saturated when a freeze-thaw cycle starts. Air pores, if such are present, will be partly empty provided the air pores are isolated from each other, so that air pores do not form a continuous system able to suck water. However, a certain, very slow, gradual absorption in air pores might occur during thawing since air might dissolve in the surrounding pore water and diffuse to outside air and be replaced by water. This process is discussed in [3].

The outer exposed millimetres of the concrete are of primary interest in the analysis since scaling takes place there. When freezing starts, the specimen surface will be rapidly covered by solid ice. Some ice is also formed in coarser capillaries and in air pores. Water in some capillary pores will stay super-cooled also at low temperature, see Figure 2.

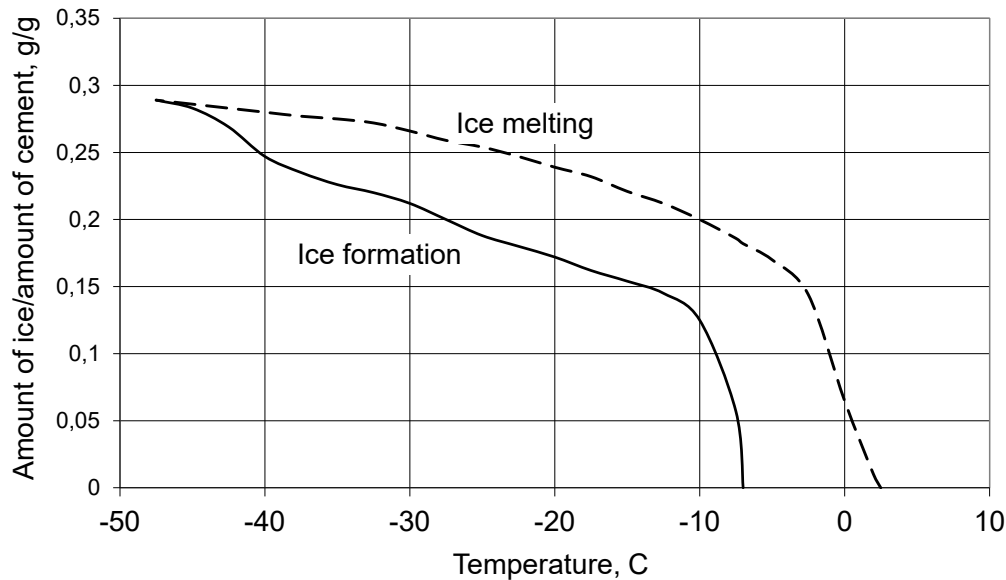


Figure 2 - Example of the hysteresis between ice formation and ice melting. Concrete with w/c-ratio 0.60. [4]. The area between the two curves is a measure of super-cooled water at freezing. (Note: temperature is measured in the calorimeter compartment and not in the specimen).

There will be a difference in vapour pressure between water and ice. The vapour pressure of ice at -10°C and -20°C is 260 Pa and 103 Pa, respectively, [5]. The vapour pressure of super-cooled water at these temperatures is 287 Pa and 126 Pa, respectively, [6]. The pressure difference between water and ice is about 27 Pa at -10°C and 23 Pa at -20°C .

The pressure difference will cause super-cooled water to move from water-filled pores towards ice on the surface and to ice in air pores. The water transfer takes part within the water-filled and unfrozen part of the pore system. The process is visualized in Figure 3.

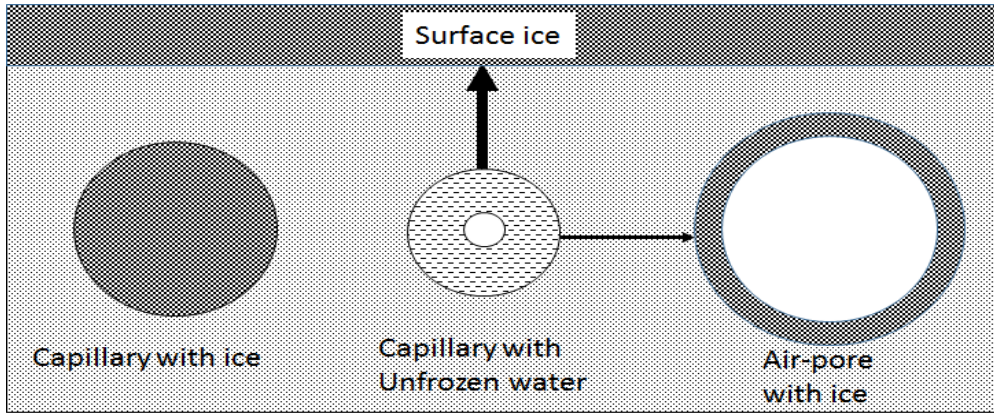


Figure 3 - Water flow in the outer millimetres of the saturated cement gel when freezing occurs in pure water. Water flow is shown by arrows to surface ice and air pore ice. The ring in the capillary symbolises drying caused by water flow. The three pores represent all pores within the surface zone.

Water flow is calculated by:

$$q = \delta_p \cdot \frac{dp}{dx} \quad (1)$$

Where

- q water flow, $\text{kg}/(\text{m}^2 \cdot \text{s})$
- δ_p moisture transport coefficient, $\text{kg}/(\text{Pa} \cdot \text{m} \cdot \text{s})$
- dp/dx vapour pressure gradient, Pa/m

Values of the moisture transport coefficient as function of the humidity of concrete have been determined by Hedenblad [7]. He uses the following transport equation:

$$q = \delta_c \cdot \frac{dc}{dx} \quad (2)$$

Where

- δ_c moisture transport coefficient, m^2/s
- c moisture content, kg/m^3
- dc/dx gradient in water vapour content, $\text{kg}/(\text{m}^3 \cdot \text{m})$

The relation between δ_c and δ_p is:

$$\delta_p = \frac{\delta_c \cdot M}{R \cdot T} = \frac{\delta_c}{462 \cdot T} \quad (3)$$

Where

- M molecular weight of water, $0.018 \text{ kg}/\text{mole}$
- R the gas constant, $8.314 \text{ J}/(\text{mole} \cdot \text{K})$
- T absolute temperature, K

δ_c for high relative humidity in Ordinary Portland Cement (OPC) concrete with w/c ratio 0.35 is estimated to be about $4 \cdot 10^{-6} \text{ m}^2/\text{s}$, [7]. Then, the value of δ_p should be about $3 \cdot 10^{-11} \text{ kg}/(\text{Pa} \cdot \text{m} \cdot \text{s})$ at 260 K. Provided water in concrete is bulk, and that there is no temperature difference between super-cooled water in concrete and ice outside concrete, the maximum possible total water flow Q over the distance 1 mm during 17 hours of freeze temperature should be of the order:

$$Q = \delta_p \cdot \frac{\Delta P}{\Delta x} \cdot t \approx 3 \cdot 10^{-11} \cdot \frac{27}{10^{-3}} \cdot 17 \cdot 3600 = 0.050 \text{ kg}/\text{m}^2 \quad (4)$$

Where

$\Delta P/\Delta x$ vapour pressure gradient, Pa/m

This can be compared with the total amount of water in 1 mm of the concrete which is about $0.10 \text{ kg}/\text{m}^2$. This means that about 50 % of the water content in the outer 1 mm surface zone might migrate to the surface ice and to air-pores. For concrete with more normal w/c ratio the migration will be even higher.

Theoretically, the migration out of the concrete will be smaller than that calculated above for two reasons.

1. The vapour pressure difference over the outer mm is not constant during the entire time interval of 17 hours.
2. Drying decreases the vapour pressure of pore water. Water flow will stop when its vapour pressure has decreased to that of ice. This corresponds to the following relative humidity φ of water at -10°C :

$$\varphi = \frac{260}{287} = 0.91 \text{ or } 91\% \quad (5)$$

Where 260 and 287 are the saturation vapour pressure of ice and water at -10°C , see above. The maximum total amount of transported water is determined by the difference between the equilibrium water content within the interval 100% to 91% on the desorption isotherm. For the actual dense concrete this water content is about $0.02 \text{ kg}/\text{m}^2$, [8]. Thus, it is only about 40% of that calculated above.

During the thaw period, the emptied pores will once again become saturated.

2.3 Conclusion

Water will leave the surface zone of concrete during freezing. The surface will dry to a level where frost scaling cannot occur. Surface drying will actually make the surface zone more frost resistant than the inner parts of the concrete. This explains the findings in Figure 1. For concrete with the more normal w/c value, like 0.45-0.50, drying will increase due to the bigger water transport coefficient. An air content of 5-6% will, however, protect the surface from scaling and also protect the interior of the concrete from damage.

3. FREEZE-THAW IN SALT WATER – INTERPRETATION OF RESULTS IN FIGURE 1

3.1 Important observations

A salt concentration as small as 1% had big effect on the concrete behaviour during freeze-thaw. When the concrete was surrounded by pure water no damage occurred. When it was surrounded by 1 % solution, or more, substantial scaling took place. A plausible explanation to this behaviour is that the concrete surface is open during freezing in solution, so that water (solution) could enter the specimen during the test, and thereby keep the capillary pore system saturated.

3.2 Discussion of the damage mechanism

Vapour pressure difference

The vapour pressure of a salt solution is lower than that of pure water. It is given by Raoult's law, [9], Equation (6):

$$\frac{p}{p^*} = 1 - X \quad (6)$$

Where

p	vapour pressure of water solution, Pa
X	mole fraction of salt in the solution, mole/mole
p^*	saturation pressure of pure water, Pa

The vapour pressure of the solution is increased with reduced freezing temperature due to increased concentration of the solution when more ice is formed.

The vapour pressure of ice in pores will be equal to the vapour pressure of the pore solution, and of pore solution ice, at all temperatures and concentrations. Therefore, there is no vapour pressure difference that can cause brine to flow between solution and ice, and thereby explaining the observations in Figure 1.

Amount of frozen and unfrozen water

The freezing point of NaCl solutions is -0.64°C for 1% solution and -1.91°C for 3% solution. Ice formed at -10°C as fraction of the entire salt solution volume is 92% for 1% solution and 78% for 3% solution, [9]. Therefore, concrete is exposed to unfrozen salt solution during the entire freeze-thaw cycle. The gel pore system and capillary pore system in the surface zone become completely saturated by brine. Some brine also moves into the air-pore system, by replacing air in the pores. The mechanism is described in [3].

The freezable water in a water saturated concrete has been determined by Vuorinen [10]. The amount of frozen water at -20°C for the +105°C pre-dried and re-moistened concrete within the w/c-range 0.3-0.7 can be described by the following Equation:

$$W_f = C(-0.07 + 0.6 \cdot \frac{w}{c}) \quad (7)$$

Where

W_f	The amount of frozen (freezable) water, kg/m ³ or litre/m ³
C	the cement content, kg/m ³
w/c	the water-cement ratio

For w/c 0.34 the freezable water is $0.13 \cdot C$. C is about 470 kg/m³. For the actual concrete the frozen water is about $0.13 \cdot 470 = 61$ litre/m³. The scaled material consists of mortar. Therefore, the cement content and amount of freezable water in the surface zone is bigger than in concrete. The volume fraction of mortar is:

$$V_m \approx \frac{C}{3200} + \frac{W}{1000} + \frac{300}{2650} = \frac{470}{3200} + \frac{0.34 \cdot 470}{1000} + \frac{300}{2650} = 0.42 \quad (8)$$

Where

V_m	Volume of mortar in 1 m ³ of concrete, m ³ /m ³
C	cement content, kg/m ³
3200	density of cement, kg/m ³
W	amount of water in the concrete, litre/m ³
1000	density of water, kg/m ³
300	amount of fine sand, kg/m ³
2650	density of sand, kg/m ³

The cement content in mortar, C_m , is:

$$C_m = \frac{470}{0.42} = 1100 \frac{kg}{m^3} \quad (9)$$

The amount of freezable water is $0.13 \cdot 1100 = 143$ litre/m³.

When water is saline, the amount of freezable water decreases. No measurements of freezable water in concrete containing saline water have been found in literature. Some interesting measurements have been made of the non-freezable water in a bentonite clay saturated by NaCl solutions of different strength, [11]. The result, valid for temperature -20°C, can be approximately described by the following Equation:

$$UF \approx 0.3 \cdot Conc^{0.43} \quad (10)$$

Where

UF	fraction of unfrozen pore water
$Conc$	initial concentration of NaCl in pore water, mole/litre

There are two main reasons why some pore water does not freeze:

1. Hydrostatic tension of water in narrow capillaries lowering the freezing point.
2. Presence of dissolved ions.

The relative importance of these two effects on the result observed for bentonite is not known. Probably, the effect of dissolved ions dominates.

For the actual *concrete*, the total amount of pore water in the saturated concrete is about 97 litre/m³, see Equation (11):

$$W_{total} = C \cdot \left(\frac{w}{c} - 0.19 \cdot \alpha \right) \approx 470 \cdot (0.34 - 0.19 \cdot 0.70) = 97 \text{ litre/m}^3 \quad (11)$$

Where

W_{total}	total pore water content, litre/m ³
C	cement content, kg/m ³
w/c	water-cement ratio
α	degree of hydration

The total amount of pore water in the *mortar* is $97/0.42 \approx 230$ litre/m³. The amount of unfrozen water in mortar is about $230 - 143 = 87$ litre/m³. Provided the effect of salt in pore water is the same as for bentonite, the amount of unfrozen water can be calculated by Equation (10). From this, the amount of frozen water can be calculated. Data are given in Table 1.

Table 1 – Calculated amount of unfrozen and frozen pore liquid in the mortar as function of the concentration of liquid. Based on data for unfrozen liquid in bentonite, [11].

Concentration of NaCl %	Mole/litre	Unfrozen liquid at -20°C		Frozen liquid litre/m ³	Volume expansion ‰
		Fraction based on Equation (10)	Total amount litre/m ³		
0	0	0	87	143	12.9
1	0.17	0.14	99	131	11.8
1.5	0.26	0.17	101	129	11.6
2	0.34	0.19	103	127	11.4
2.5	0.43	0.21	105	125	11.3
3	0.52	0.23	107	123	11.1
3.5	0.60	0.24	108	122	11.0
4	0.69	0.26	110	120	10.8
4.5	0.78	0.27	110	120	10.8
5	0.86	0.28	111	119	10.7

NOTE: The calculation behind Table 1 is based on observations of frozen water in bentonite. Reasonably, they are not exactly valid for cement mortar. The only reason why they are presented here is that they illustrate the general effect of freezing of a saline pore solution in a mineral based material.

Volume expansion of the pore liquid at freezing is supposed to be the same as for pure water, i.e. 9%. Expansion data are given in Table 1. The calculated effect on expansion of salt concentration is small which can explain the results in Figure 1. For all concentrations, the expansion is very much bigger than the volumetric fracture strain of concrete, which is of the order 0,3 - 0,4 ‰ [12]. Maybe the fracture strain is a bit higher for mortar, but still much smaller than the calculated expansion. Therefore, in order to stop scaling, water from ice expansion must be forced towards empty air pores and towards the surface. These flows cause hydraulic pressure.

Water flow within the surface zone

The two different water flows in the surface zone are illustrated in Figure 4.

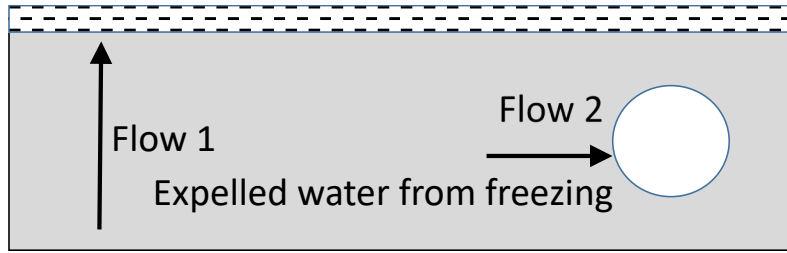


Figure 4 – Water flow in the surface zone of concrete.

Flow 1: Water flow towards the surface, causing hydraulic pressure

Hydraulic pressure caused by liquid transport upwards through the surface can be calculated on basis of the material model in Figure 5. Water cannot move towards the inner part of the concrete since this is saturated. Therefore, all expelled water from a surface zone with thickness D must move to the surface. No surface ice is blocking the flow. The hydraulic pressure is calculated below.

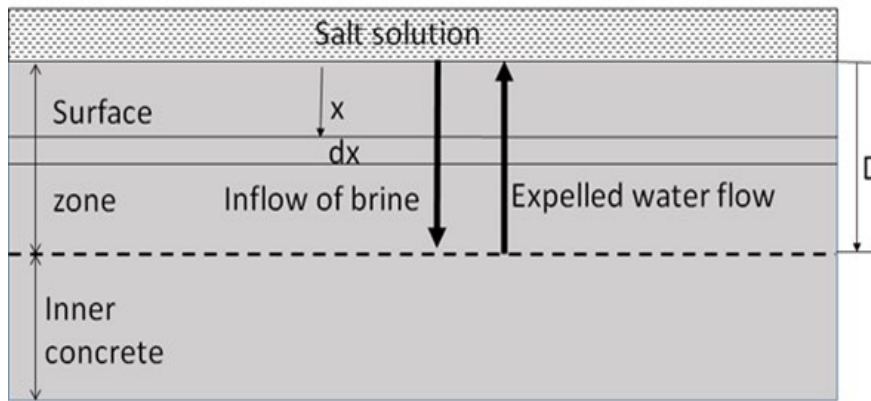


Figure 5 – Model for calculating hydraulic pressure caused by flow of expelled water towards the surface of a specimen exposed to freeze-thaw in salt solution.

Total expelled water volume from $x = D$ to $x = x$ is:

$$W = 0.09 \cdot w_f \cdot A \cdot (D - x) \quad (12)$$

Where

W	volume of expelled water, m^3
D	thickness of surface zone, m
w_f	freezable water, m^3/m^3
A	surface area of element, m^2

The flow rate is:

$$\frac{dW}{dt} = 0.09 \cdot \frac{dw_f}{dt} \cdot A \cdot (D - x) \quad (13)$$

Where

dW/dt flow rate, m^3/s

dw_f/dt rate of generation of freezable water, $m^3/(m^3 \cdot s)$

The flow gives rise to hydraulic pressure:

$$\frac{dW}{dt} = K \cdot \frac{dP}{dx} \cdot A \quad (14)$$

Where

K water permeability, $m^2/(s \cdot Pa)$

P hydraulic pressure, Pa

Combination of Equation (13) and (14) gives:

$$dP = 0.09 \cdot \frac{1}{K} \cdot \frac{dw_f}{dt} \cdot (D - x) \cdot dx \quad (15)$$

Integration over the thickness D gives the maximum pressure $P_{max,1}$ obtained at the inner part of the surface zone:

$$P_{max,1} = 0.09 \cdot \frac{dw_f}{dt} \cdot \frac{1}{K} \cdot \int_0^D (D - x) \cdot dx = 0.09 \cdot \frac{dw_f}{dt} \cdot \frac{1}{K} \cdot \frac{D^2}{2} \quad (16)$$

Spalling occurs when hydraulic pressure $P_{max,1}$ exceeds to tensile fracture strength f_t (Pa) of the mortar. Then, the thickness of the fractured surface zone exceeds its critical thickness D_{CR} (m).

The critical thickness D_{CR} of the scaled surface zone is obtained by:

$$\frac{D_{CR}^2}{2} = \frac{K \cdot f_t}{0.09 \cdot \frac{dw_f}{d\theta} \cdot \frac{d\theta}{dt}} \quad (17)$$

Where

$dw_f/d\theta$ freezable water as function of temperature, $m^3/(m^3 \cdot \text{degree})$

$d\theta/dt$ rate of temperature reduction, degree/s

Values for the parameters to be put into Equation (17) are rather uncertain. The following values for K , f_t and rate of ice formation are suggested.

1: Permeability K

According to Powers, [13], the permeability of unfrozen cement paste in darcy (K') is:

$$K' = 3550 \cdot \mathcal{E}_{cap}^{3.6} \cdot 10^{-17} \text{ cm}^2 \quad (18)$$

Where

$\mathcal{E}_{cap}$ the capillary porosity of the cement paste, which for OPC concrete is:

$$\varepsilon_{cap} = \frac{\frac{w}{c} - 0.39 \cdot \alpha}{\frac{w}{c} + 0.32} = \frac{0.34 - 0.39 \cdot 0.7}{0.34 + 0.32} = 0.10 \quad (19)$$

Where α is the degree of hydration.

The permeability in darcy becomes:

$$K' = 3550 \cdot 0.10^{3.6} \cdot 10^{-17} = 8.9 \cdot 10^{-18} \text{ cm}^2 \text{ or } 8.9 \cdot 10^{-22} \text{ m}^2 \quad (20)$$

The same value is supposed to be valid for surface mortar.

The relation between K and K' is:

$$K = \frac{K' (m^2)}{\mu (Pa \cdot s)} \quad (21)$$

Where

μ dynamic viscosity of water. $\mu \approx 3 \cdot 10^{-3} \text{ Pa} \cdot \text{s}$ when temperature is -10°C , [14]

Thus, the permeability K is:

$$K = \frac{8.9 \cdot 10^{-22}}{3 \cdot 10^{-3}} \approx 3 \cdot 10^{-19} \frac{\text{m}^2}{\text{Pa} \cdot \text{s}} \quad (22)$$

This is an unsafe value since the mortar might be somewhat more permeable than cement paste, and since the cement contains 5% silica fume which reduces permeability. Besides, ice formation in the pore system will reduce permeability.

2: Tensile strength f_t

$f_t \approx 5 \text{ MPa}$. This is about 8 % of the compressive strength of a cement mortar with w/c ratio 0.34.

3: Rate of ice formation $(dw_f/d\theta)/(d\theta/dt)$ or dw_f/dt

The value for the rate of ice formation is uncertain. Direct measurements of the maximum rate expressed in terms of dw_f/dt have been made for concrete with w/c ratios 0.40 and 0.6, [4]. The result is presented in Section 4. The values are:

$$\text{w/c} = 0.40: dw_f/dt = 1.4 \cdot 10^{-4} \text{ m}^3/(\text{m}^3 \cdot \text{s})$$

$$\text{w/c} = 0.60: dw_f/dt = 1.6 \cdot 10^{-4} \text{ m}^3/(\text{m}^3 \cdot \text{s})$$

The value for w/c 0.40 is used for the actual concrete (w/c 0.34).

Inserting values above in Equation (17) gives:

$$D_{CR} \approx \left[\frac{2 \cdot 3 \cdot 10^{-19} \cdot 5 \cdot 10^6}{0.09 \cdot 1.4 \cdot 10^{-4}} \right]^{\frac{1}{2}} = 4.9 \cdot 10^{-4} \text{ m} = 0.49 \text{ mm} \quad (23)$$

This value is valid for one freeze-thaw cycle. Each new cycle adds to the scaling. Then, according to theory, total scaling should be higher than observed. The discrepancy ought to depend on simplifications in the model used, and in errors in the data inserted in Equation (17). The freezing rate might be higher and the tensile strength lower, which will decrease D_{CR} . On the other hand, the permeability might have been overrated since no consideration is taken to the fact that ice formation in the mortar may block water flow. This would also decrease D_{CR} . Reducing permeability by a factor 10 decreases the value of D_{CR} to 0.15 mm.

The critical distance for other salt concentrations is not very different from that calculated above because the amount of freezable water probably is almost the same, c.f. Table 1

Flow 2: Water flow towards air pores causing hydraulic pressure

Water will also flow towards air pores. This will also cause hydraulic pressure. The critical Powers spacing factor L_{CR} is a measure of the maximum tolerated distance between air pores, [13]. It is based on hydraulic pressure being the destructive force, and it is calculated in similar way as the critical thickness. The material model used is a hole-sphere with radius R , air pore radius r and shell thickness L . It is shown in Figure 6. All air pores are of equal size and placed in a cubic array in the cement paste. Water is expelled from the periphery towards the air pore.

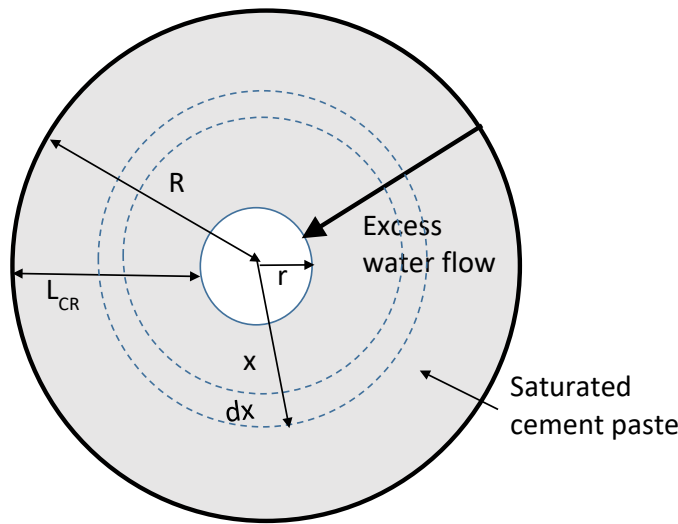


Figure 6 – Model for calculating the spacing factor.

The hydraulic pressure caused by water flow towards air pores can be calculated in similar manner as for D_{CR} . The calculation is performed in [13]. The maximum pressure $P_{max,2}$ is reached at the outer periphery of the sphere and is:

$$P_{max,2} = \frac{\frac{1}{3} \cdot \left(\frac{L^3}{r} + 1.5 \cdot L^2 \right) \cdot 0.09 \cdot \frac{dw_f}{d\theta} \cdot \frac{d\theta}{dt}}{K} \quad (24)$$

The critical Powers spacing factor $L_{CR} = (R-r)$ is obtained when $P_{max,2}$ is equal to the uniaxial tensile strength f_t :

$$\frac{1}{3} \cdot \left[\frac{L_{CR}^3}{r} + 1.5 \cdot L_{CR}^2 \right] = \frac{K \cdot f_t}{0.09 \cdot \frac{dw_f}{d\theta} \cdot \frac{d\theta}{dt}} \quad (25)$$

Where

r radius of the air pore in centre of the sphere, m

The relation between the critical thickness and the critical spacing factor for the actual concrete is found by comparing Equations (17) and (25). It is based on the assumption that the maximum hydraulic pressure is the same for flow 1 and flow 2:

$$D_{CR}^2 = \frac{2}{3} \left(\frac{L_{CR}^3}{r} + 1.5 \cdot L_{CR}^2 \right) \quad (26)$$

The relation depends on the size of the air pore. The specific surface of the actual air-pore system is probably quite low since the concrete is non-air-entrained. The pore radius is calculated from the specific surface of the entire air pore system by:

$$r = \frac{3}{s} \quad (27)$$

Where

s specific surface of the air pore system, mm^{-1}

The specific surface 15 mm^{-1} , which is typical for a natural air pore system, corresponds to the pore radius 0.20 mm . Then, the critical spacing factor based on the value $D_{CR} = 0.49 \text{ mm}$ becomes:

$$L_{CR} = 0.33 \text{ mm}$$

For the specific surface 25 mm^{-1} , typical for air-entrained concrete, the pore radius is 0.12 mm and the spacing factor becomes:

$$L_{CR} = 0.30 \text{ mm}$$

The effect of pore size is limited.

Minimum required air content in concrete

In a situation where the air content is exactly what is required for the critical spacing not to be transgressed, the hydraulic pressure will be the same for transport to air pores as for transport through the surface. This means that flow through the surface will be reduced, and the risk of scaling will also be reduced.

The required air content for this to happen is calculated by the following Equation, [13]:

$$a_{req} = \frac{V_m}{0.364 \left(\frac{L_{CR} \cdot s}{3} + 1 \right)^3 - 1} \quad (28)$$

Where

a_{req}	required air content in concrete, %
V_m	fraction of cement mortar in concrete exclusive of air pores, %
L_{CR}	critical spacing factor, mm
s	specific surface of the air pore system, mm^{-1}

$V_p = 42 \%$ (see Equation (8)). The required air content becomes:

For specific surface 15 mm^{-1} ($r = 0.2 \text{ mm}$):

$$a_{req} = \frac{42}{0.364 \left(\frac{0.33 \cdot 15}{3} + 1 \right)^3 - 1} = 7.3 \%$$

For specific surface 25 mm^{-1} ($r = 0.12 \text{ mm}$):

$$a_{req} = \frac{42}{0.364 \left(\frac{0.30 \cdot 25}{3} + 1 \right)^3 - 1} = 2.9 \%$$

The required air content for the non-air-entrained concrete (7.3 %) is higher than the air content of the actual concrete. Therefore, all water expelled by freezing must move towards the surface, which causes the spalling observed.

If the concrete is air-entrained with an air content of the order 3%, water flow should turn towards air pores and thereby reduce, or hinder, scaling.

Note: No consideration is taken to the fact that a certain fraction of the air pore system might have absorbed water which increases spacing between air-filled pores, and increases the required air content. A method to handle this is given in [3].

Required air content for most water to move to air pores

Equation (26) is based on the fact that the hydraulic pressure is the same for Flow 1 and 2. Therefore, water will be expelled both to the surface and to air pores. Thus, the required air content calculated above is lower than required if all water shall move to air pores, and thereby reduce pressure.

The relation between pressure caused by flow 1 to the surface and flow 2 to air pores is obtained by the following Equation:

$$\frac{P_{max,1}}{P_{max,2}} = \frac{3}{2} \cdot \frac{D_{CR}^2}{\left(\frac{L^3}{r} + 1.5 \cdot L^2 \right)} \quad (29)$$

The specific surface of the air-pore system is supposed to be 25 mm^{-1} ($r = 0.12 \text{ mm}$). $D_{CR} = 0.49 \text{ mm}$. Pressure 1 is twice pressure 2 when the following Equation is valid:

$$\frac{P_{max,1}}{P_{max,2}} = \frac{3}{2} \cdot \frac{0.49^2}{\frac{L^3}{0.12} + 1.5 \cdot L^2} = 2$$

This gives $L = 0.23$ mm.

The required air content for this spacing factor is:

$$a_{req} = \frac{42}{0.364 \left(\frac{0.23 \cdot 25}{3} + 1 \right)^3 - 1} = 4.3 \%$$

The air requirement must be increased from 2.9 % to 4.3 % if the hydraulic pressure for flow to air pores shall be reduced by a factor 2. Flow to air pores will therefore increase and reduce, or stop, scaling.

3.3 Conclusion

Low salt concentrations can cause severe scaling of non-air-entrained concrete during a freeze-thaw test. A probable reason for this is that unfrozen solution can enter the concrete through the surface, making the concrete more or less completely saturated.

The 9% increase in volume when pore water freezes produces water flow that causes inner pressure in the saturated concrete. Pressure can only be relieved by flow towards empty air pores, or flow through the concrete surface. For a non-air-entrained concrete the only possibility is flow through the concrete surface. The hydraulic pressure caused by this flow caused the spalling of the concrete surface observed in Figure 1. The scaling depth is determined by the critical thickness when the saturated surface freezes. Calculation based on material data and on estimated rate of ice formation gives a critical thickness for the actual concrete of about 0.49 mm. The calculation is particularly sensitive to the value selected for permeability and rate of ice formation.

Sufficiently high air entrainment can take care of water expelled from freezing, and thereby stop flow through the surface, and stop scaling. The amount of air-entrainment depends on the fineness of the air-pore system.

4. EFFECT OF INCREASED WATER-CEMENT RATIO - EXAMPLE

The concrete in Figure 1 has a very low w/c ratio, but despite this the scaling in salt solution is substantial. Scaling would be even higher for non-air-entrained concrete with w/c-ratio 0.45 which is a normal w/c ratio for concrete frost tested in salt solution. Important data for this concrete are given in Table 2.

Table 2 - Data for a concrete with w/c ratio 0.45.

w/c	C	α	$\mathcal{E}_{cap}$	V_m	w_f	K'	K	ft
	kg/m ³		m ³ /m ³	m ³ /m ³	m ³ /m ³	m ²	m ² /(Pa·s)	MPa

Eq (19)			1)	Eq (7)		Eq (20)	Eq (21)		
					in concrete	in mortar			
0.45	390	0.8	0.18	0.41	0.078	0.190	$7.4 \cdot 10^{-21}$	$2.4 \cdot 10^{-18}$	3
1) Volume fraction of cement mortar m^3/m^3 ($V_m = 390/3200 + 175/1000 + 300/2650 = 0.41$)									

The rate of ice formation in concrete with w/c ratio 0.40 and 0.60, expressed as dw_f/dt , has been measured in [4]. When the surrounding temperature was lowered by 3.6 degree/hour, the maximum rate of ice formation was about $4 \cdot 10^{-4}$ and $6 \cdot 10^{-4}$ g ice/(g cement·s), respectively. The amount of cement was 400 and 300 kg/m³ or $4 \cdot 10^5$ and $3 \cdot 10^5$ g/m³, so the rate of ice formation was $4 \cdot 10^{-4} \cdot 4 \cdot 10^5 = 160$ g/(m³·s) and $6 \cdot 10^{-4} \cdot 3 \cdot 10^5 = 180$ g/(m³·s). 1g ice corresponds to about $0.9 \cdot 10^{-6}$ m³. The rate of ice formation is $160 \cdot 0.9 \cdot 10^{-6} = 1.4 \cdot 10^{-4}$ m³/(m³·s) and $180 \cdot 0.9 \cdot 10^{-6} = 1.6 \cdot 10^{-4}$ m³/(m³·s).

For w/c 0.5 the mean value ($1.5 \cdot 10^{-4}$) might be valid.

Inserting data in Equation (17) gives:

$$D_{CR} \approx \left[\frac{2 \cdot 2.4 \cdot 10^{-18} \cdot 3 \cdot 10^6}{0.09 \cdot 1.5 \cdot 10^{-4}} \right]^{\frac{1}{2}} = 1.0 \cdot 10^{-3} \text{ m} = 1 \text{ mm} \quad (30)$$

The critical spacing for an air-entrained concrete with specific surface 25 mm⁻¹ is, (Equation (26)):

$$L_{CR} = 0.51 \text{ mm}$$

Probably, this value is too high. It is contradicted by freeze-thaw tests. A plausible reason for this discrepancy is that the effect of ice formation on permeability is neglected.

The required air content for flow 2 being the same as flow 1 is:

$$a_{req} = \frac{41}{0.364 \left(\frac{0.51 \cdot 25}{3} + 1 \right)^3 - 1} = 0.8 \%$$

Higher air content is required if the concrete shall be completely protected and flow 2 be dominant. Hydraulic pressure for flow to the surface being three times as high as for flow to air pores gives the following spacing factor: see Equation (29):

$$L = 0.34 \text{ mm}$$

The required air content is:

$$a_{req} = \frac{41}{0.364 \left(\frac{0.34 \cdot 25}{3} + 1 \right)^3 - 1} = 2.1 \%$$

The real required air content is higher, since part of the air pore system is inactivated by earlier water absorption. The effect of this is treated in [3].
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5. CONCLUDING REMARKS

Low concentration of salt in water surrounding the concrete might cause severe frost scaling of concrete having inferior air-entrainment. On the other hand, when the same concrete is surrounded by pure water, low or no scaling will take place, Figure 1. The reason behind this behaviour is discussed. When freezing takes place in pure water, the frozen concrete surface will be covered by ice. Unfrozen (super-cooled) water will leave the outer millimetres of the concrete surface and move towards the surface ice. Water flow depends on the vapour pressure difference between water and ice. This is 27 Pa at -10°C . The flow is found to be of the order $5 \cdot 10^{-2} \text{ g/m}^2$ for the outer mm of the dense concrete in Figure 1 during one freeze-thaw cycle. Thus, the surface zone of concrete will dry during freezing periods, and no scaling occurs. Drying will stop when the difference in vapour pressure is zero. This corresponds to the relative humidity in concrete of 91%.

When freezing takes place in salt water, part of this is unfrozen. Therefore, unfrozen brine can be taken up by the concrete, and make the surface zone completely saturated. The 9% expansion when water in the surface zone freezes creates water flow towards the surface and towards air pores. The actual concrete is non-air-entrained. Therefore almost all water has to move across the concrete surface, which causes spalling. It is demonstrated that air-entrainment might turn the flow towards air pores, thereby relieving pressure and stop spalling.

It is demonstrated how the required air content can be calculated theoretically. Obstacles, however, are lack of reliable information on:

1. effect of ice formation on the water permeability of frozen concrete.
2. maximum rate of ice formation.

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ADDENDUM

In this paper, it is demonstrated that hydraulic pressure might explain results of salt-frost tests. There is an alternative mechanism of interest, viz. pressure exerted by slowly growing ice. The mechanism is treated in [15], and is shortly described below.

Freeze/thaw in pure water.

Surface ice is blocking water flow into the concrete. Therefore, freeze/thaw is *isolated*. During freezing, water (brine) will move from capillaries in the concrete towards capillary ice where it freezes, and exerts pressure. But, this transport causes the pore system to dry, which finally stops ice growth. Air-entrainment is not required.

Freeze/thaw in salt solution

This is *open* freeze/thaw. During freezing, pore ice will be fed by unfrozen brine transported into concrete. Considerable pressure can be built-up. Probably, pressure is relieved by air-entrainment. However, it is not possible to derive formulae for calculating the pressure and distribution of pressure inside the concrete, as was the case for the hydraulic pressure mechanism.

Hydraulic pressure is favoured by rapid freezing, like in a salt-frost test.