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A HYPHOTHESIS ON THE MECHANISM OF SURFACE SCALING DUE TO COMBINED SALT - AND FROST ATTACK

A working paper presented at the RILEM TC 117 meeting, August 19 , 1996, Helsinki, Finland

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Abstract

A hypothesis on the mechanism of "salt-scaling" of porous building materials based on theories for frost heaving in soils and observations made by Powers and Helmuth /1953/ is described. Though the text mainly deals with cement based materials, the mechanism described should be valid for any brittle, porous material. A simplified calculation of possible scalings shows that the hypothesis predicts reasonable values. Results from a first qualitative test support the hypothesis.

Background

In /1943/, Arnfelt investigated damages observed on Swedish concrete roads and also performed some laboratory experiments which clearly showed that weak solutions of different salts would cause severe surface damages when the concrete was exposed to frost. These results also proved valid for solutions of urea and ethyl alcohol, which are both non ionic. For this reason, Arnfelt came to the conclusion that the mechanism was of physical rather than chemical nature. Brick and sandstone were tested too, but in these cases, pure water caused worse damages than did the solutions that were used. The damages observed on bricks (used for roofing) were of another kind than the ones seen on concrete, and it was not as clear that the bricks were subject to a surface attack. Sandstone showed larger scaling the less the salt concentration used. Arnfelt proposed this was due to the different pore size distribution of sandstone as compared to concrete.

Verbeck and Klieger /1957/ presented results from tests on surface scaling resistance of concrete exposed to frost attack and solutions of different de-icers. Their results showed that the combined frost de-icer attack causes much worse surface damages than does pure water. Also, it was concluded that a moderate concentration of de-icer, 2-4 percent by weight, causes worse damage than do lower as well as higher concentrations.

The results from Verbeck and Klieger are very similar to those of Arnfelt, and similar results have also been achieved later by other researchers. Some attempts have been made to explain the observed results, e.g Pühringer / 1994/, Powers /1965/, Browne&Cady /1975/, Petersson /1984/ and others, but none of them has been found fully satisfactory.

The aim of this text is to present a hypothesis based on theories for frost heaving in soils. After a short description of a classical model set up by Everett /1961/, a physical model is presented and with that model as a basis some speculations on the consequences of some variations of parameters in a testing procedure will be given.

The classic Everett-model

In figure 1, which was drawn according to Everett /1961/, two perfectly rigid containers are connected by a narrow channel of radius *r*. The pistons make it possible to adjust the volume of each container. Both containers are initially water filled, but ice formation is initiated in A, the upper one. Both phases thus exist under the same temperature and pressure. As the entropy of ice is lower than that of water, the level of free energy of the ice will be lower than that of the water and accordingly the water in the narrow channel will now "condense" on the ice surface and continue to do so until both phases reach the same level of free energy. (The radius of the containers is large enough to make surface conditions insignificant) In this way, water will be transported from B to A until equilibrium is reestablished. If the pistons are free to move, this means container B will finally be emptied. To reestablish equilibrium at constant temperature and in the abscence of solutes, a pressure difference is needed between ice and water. In the present case and under assumption of the contact angle between water and channel wall to be 0°, this pressure difference is given by the LaPlace equation:

$$\Delta P = \frac{2\sigma}{r} \tag{1}$$

in which ΔP = Pressure difference required for equilibrium, Pa
σ = Interface tension ice-water, J/m^2 (ca 0.033)
r = Kelvin radius of the meniscus, m

It is thus seen that if the radius of curvature of the meniscus is 10 nm, a pressure difference of about 6.6 MPa is needed to maintain equilibrium.

If the upper container is initially completely filled with water and the pistons are fixed in their positions, pressure will raise heavily on ice formation and the process will be stopped. On the other hand, if the degree of saturation is such that the upper one contains just a small fraction of the total water content, no pressure will arise in the ice. Instead, as water is transferred to the ice phase, container B will be partly emptied. This will give rise to a reduced pressure in the water and the requested pressure difference may be reached.

If though container B were sufficiently larger than container A, the required (reduced) pressure would not be established before the ice would start to exert a positive pressure on the container walls.

For a real, brittle material of low tensile strength, within a certain interval of saturation, equilibrium will be established as a combination of positive pressure in the ice and reduced pressure in the water. For lower degrees of saturation, no positive pressure will exist in the ice, and for higher degrees of saturation, pressure will not be reduced in the water. Somewhere within this interval, there will be a critical degree of saturation at which the material will be damaged due to

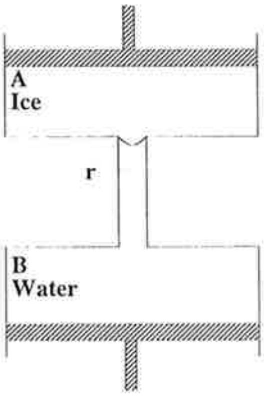

Fig 1: Ice and water at thermodynamical equilibrium (and equal temperatures), with a spherical meniscus of radius r separating the phases. Everett /1961/.

micro ice lens growth. As the isothermal compressibilities of both water and ice are quite low, this interval is likely to be rather narrow. (Obviously, for levels of saturation higher than 0.917, assuming all the water to be freezable, a normal material will be damaged simply due to in-site ice formation.)

Results from Powers and Helmuth

In /1953/, Powers and Helmuth proposed a mechanism of inner frost damage in concrete specimens, which has later been referred to as the theory of micro ice lens growth. Observations like the one shown in figure 2 formed the basis for this theory, according to which ice lenses which form in capillary pores are able to feed from the unfrozen water in nearby gel pores. This process is due to the different levels of free energy in unfrozen water and ice, which are caused by differences in temperature and pressure. The process will be active also between ice crystals of equal temperature and pressure but of different size, as surface tension adds to the level of free energy.

This harmful process will come to a stop when the levels of free energy are equal. As will be shown below, a stable temperature gradient between the pores, the presence of solved salts in the pore water or a pressure difference between the phases are different ways of reestablishing equilibrium. Obviously, any combination of these opportunities may do as well.

The first case, a stable temperature difference, is very unlikely to occur between two adjacent pores. Actually in an ordinary specimen, the temperature would have to be higher in the unfrozen portion of water and lower in the frozen one, which must be considered an impossible situation. It may therefore be considered as impossible to stop the process by the aid of local temperature differences.

As described above, a pressure difference between solid and liquid phase may bring the two phases into thermodynamic equilibrium. While this pressure difference is not established, ice lens growth will proceed at a rate determined by the heat flow. If the ice phase starts to exert a pressure on the pore walls

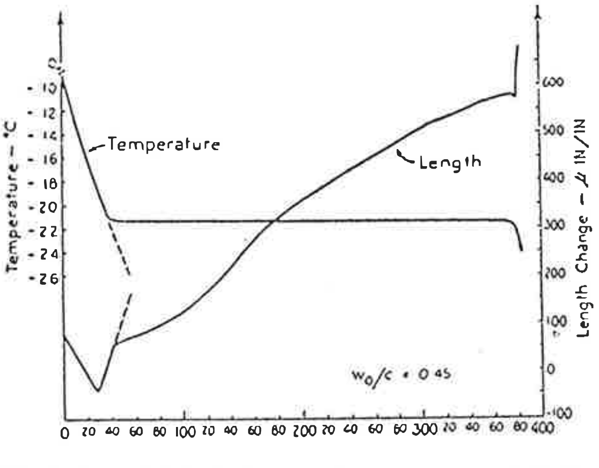

Fig. 2: Expansion of paste specimen during period of constant temperature. Powers and Helmuth/1953/.

surrounding it or if the pore system is drained to such an extent that the remaining water is subject to a reduced pressure, the required pressure difference may be obtained.

If salts are present in the pore water, the level of free energy of the water is reduced and ice will not start to form until temperature has declined to a certain extent below 0°C, a temperature which we may call T_c. As temperature continues to fall, more ice will form and the ice crystals may start to exert a pressure on the pore walls. However, the pressure difference required for equilibrium as described above is now reduced. At a certain temperature below T_c, this means that only a very small pressure difference is needed between the phases to maintain equilibrium and thus no harmful ice lens growth will occur. In a real material though, many ice crystals of different sizes are likely to be present and a slow process, aimed at minimizing the surface energies of the ice crystals, will make the larger crystals feed from the smaller ones, but still pressures in the ice crystals will be reduced as compared to the pure case without salts.

As the results of Powers and Helmuth /1953/ showed that the specimen expands during a period of constant temperature, there has to be an inner expansive pressure. This means that the amount of naturally dissolved salts in the pore system is not large enough to protect the cement paste from damage by micro ice lens growth. Instead, there is an overall competition between ice lenses for the available unfrozen water and the entire specimen volume is damaged.

Hypothesis

By combining the container-model described by Everett and the theory proposed by Powers and Helmuth, a hypothesis for the mechanism of surface scaling due to combined salt- and frost attack may be proposed. In figure 3, a principal sketch shows a small pore located a certain distance dx beneath the surface of a concrete specimen. The surface is covered with pure water. A narrow channel connects outer water and pore solution. At first, this pore solution is assumed to consist of pure water. Heat flows perpendicularly to and unidirectionally from the water surface into the air. In this way, temperature is first lowered at the upper surface. (All other edges are sealed to any kind of flow.)

Pure water on top of the specimen will start to freeze when the temperature reaches 0°C. Possibly, some supercooling may occur, but that is not very likely in a real case, and will not be considered here. This means that a meniscus will form at the upper end of the channel connecting the outer water and the solution of the pore. The exact location of this meniscus will probably be dependent on chemical composition of the pore solution and pore size distribution. As no pressure difference exists at this stage, the meniscus will initially be plane. As long as the temperature of the outer ice as well as the pore solution is 0°C, the two phases will exist in equilibrium. If now temperature were lowered in both phases, a difference in level of free energy would occur. As a consequence, the pure ice on the surface would feed from the pore solution, reducing the water content of the pore system. If the cooling is done slowly enough, water may be transported outwards at a rate high enough to prevent ice formation in the pores.

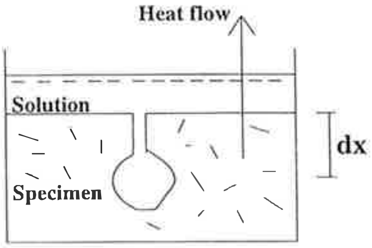

Fig 3: Model pore close to the specimen surface.

This means that pure water on the surface will act protectingly on the uppermost layer of the specimen. As the pressure in the pore solution is lowered, the meniscus will adopt a certain radius of curvature, which may be calculated as described above.

Now let heat flow in the opposite direction. In this way, the specimen is cooled before the surface water, and so the pore solution will start to freeze before the pure water on the surface does (provided the pore solution does not contain dissolved salts or something else that lowers its freezing temperature too much). Now, a meniscus will form at the lower end of the channel, with its convex side facing the channel. This means the ice formed in the pore will feed from the surface water via the channel. As the outer water volume is at constant pressure, the pressure difference needed for equilibrium must be achieved as a positive pressure in the ice. As a consequence, the ice in the pore is likely to grow and exert pressure on the pore walls. In the case of ordinary building materials, this pressure will easily be large enough to damage the material. This process is the same as that taking place in frost heaving of soils, except that everything has been turned up side down. It has also been observed, that surface scalings are more severe when a concrete specimen is tested in this way than when cooled from the surface side /Fagerlund,1995/.

If there had been no water on the surface, a meniscus between water in the channel and outside air would have formed, and on ice lens growth a reduced pressure in the water would have appeared. Under ideal circumstances this pressure reduction might have been large enough to prevent the ice from destroying the specimen. It is unlikely though that the specimen would remain completely free of damages if completely or almost completely water saturated at the start of cooling. However, the important point is that the damages would have been spread across the entire specimen volume. Actually, the surfaces should be the least damaged part, as ice lenses close to the surface would have had only half as much moisture available as the ones in the interior! Compare this with the results of Powers and Helmuth: Their specimens were isolated to moisture ingress, and so inner processes were everywhere the same (except possibly at the surfaces), causing an overall damage.

Once again, let heat flow from the specimen surface but this time replace the outer water with a salt solution with a freezing point depression ΔT. For the sake of simplicity, we shall presume the pore solution to be pure water. When temperature reaches 0°, no ice will form in the outer solution, but ice will start to form inside the specimen (certainly, 0° will be reached slightly later in the pores than in the surface water, but the delay will be very small under usual testing conditions). This time, the meniscus will form at the lower end of the channel and water transport will be directed from the narrow channel towards the ice crystal. As the outer liquid phase and thus also the remaining pore solution will remain at atmospheric pressure, the ice crystal will be able to grow unrestrictedly (provided the resistance to liquid flow in the pores is not too high). Initially, the available moisture will be the pore solution which we have said to be pure water and so it will in no way limit the lens growth. In fact, the ice lens will not stop growing until the water transported to it contains a large enough amount of solutes. Depending on the depth of the ice lens below the surface, more or less pore solution will be available before the ice crystal is surrounded by water containing solutes (from the outer solution). In this way, conditions for ice lens growth close to the surface have been drastically improved as compared to the case of pure water as well as to that of no water on the surface.

Calculation principle

The above described micro ice lens growth cannot progress unless heat is withdrawn from the freezing site, neither will it progress if moisture access is too limited. The latter will be the case for an ice lens located too far from the surface - permeability will simply be too low to allow a large enough transport of water. Obviously, what water transport is needed will be determined by the rate of ice formation and thus there will be a level beneath the surface where ice formation balances the possible water flow. Geologists frequently use Darcy´s law for calculating this level of balance in calculations on frost heaving in soils /e.g. Knutsson, 1985/. In such calculations the pressure difference which is needed for equilibrium to be reestablished, is used as a driving potential. In the following, the calculation technique will be briefly described, then the possible pressure differences will be calculated and finally an example calculation will show the proposed mechanism to predict correct orders of magnitude of scaling.

As was said above, ice lensing will progress at a speed set by the current heat flow. The only restriction is that unfrozen water has to be available. This means that ice lensing will take place in places where heat flow balances the heat of fusion released on freezing. At the crystal surface, water condenses at a rate predicted by the heat flow, and the ice crystal grows in a direction which offers the least resistance. The transfer of water to the ice crystal may thus be thought of as a short cut diffusion process. However, when a certain volume of water is moved from the pore solution and into the ice crystal, it has to be replaced or else a reduced pressure will occur. In this way liquid phase from the surface is sucked into the pore system and consequently, there will be a flow of water in the pores. As long as the ice crystal and its surrounding pore solution are not in equilibrium, water will keep flowing. If moisture access is too reduced, either because the permeability is too low or because the available water is too far away, ice lens growth will stop and the actual heat flow will instead be used for cooling the specimen, which in turn may lead to the formation of ice crystals in smaller pores in the zone between the surface and the icelensing depth, and/or to spreading of the frost front into the specimen.

The depth of balance, the icelensing depth, dx in figure 3, may be calculated by applying Darcy's law:

$$G = B * \frac{dP}{dX} \tag{2}$$

in which G = Liquid flow rate, kg/(m²*s)
dP = Pressure difference, Pa
dX = Flow distance, m
B = Coefficent of permeability, s

The use of this equation will be demonstrated in the example calculation below, but first the possible pressure differences will be calculated.

The pressure difference needed for equilibrium in figure 1 is calculated from the chemical potential of each phase. At equilibrium, these potentials are equal:

$$\mu_l = \mu_s \tag{3}$$

where μ_l = chemical potential of the liquid phase
μ_s = chemical potential of the solid phase

Each one of these two is given from the following expressions:

$$\mu_l = \mu_l^* - S_l * (T_l - T_0) + V_{m,l} * (P_l - P_0) + RT * \ln X_{H2O} + \frac{A * \sigma_{l-pw}}{n_l} \tag{4}$$

$$\mu_s = \mu_s^* - S_s * (T_s - T_0) + V_{m,s} * (P_s - P_0) + \frac{A * \sigma_{s-pw}}{n_s} \tag{5}$$

where the subscripts l,s and pw represent liquid phase, solid phase and pore wall respectively while the symbols are

μ^* = chemical potential of each phase at the triple point
T_0, P_0 = temperature and pressure at the triple point (273,15K,101325 Pa)
T, P = actual temperature and pressure
n = number of moles of each phase
X = mole fraction of water in the liquid phase
R = gas constant, 8.314 J/K*mol
σ = surface tension, J/m²
A = contact area between the phase and its surroundings
V = molar volume of each phase

It is thus assumed that surface energies are mainly dependent on the contact surface between each phase and the walls of the pore in which it is enclosed.

The more interesting case though is the one of figure 3 where a small ice crystal grows close beneath the specimen surface. In the following, the equations will be arranged to suit this model.

Assuming the temperature of both phases to be equal (which is quite reasonable when dealing with surface scaling), rearranging the above equations yields the following expression for the equilibrium between the ice crystal in the capillary pore and the liquid phase in the narrow channel:

$$\frac{-\Delta H_{fus}}{T} * (T - T_0) + V_{m,l} * (P_l - P_0) + RT * \ln X_{H2O} + \frac{A * \sigma_{l-pw}}{n_l} = \\ = V_{m,s} * (P_s - P_0) + \frac{A * \sigma_{s-pw}}{n_s} \tag{6}$$

where ΔH_{fus} = 6008 J/mole. To go any further, we have to make assumptions on the geometrical limitations for each phase. For our purpose it seems natural to let the ice phase have the form of a spherical crystal (inside a capillary pore) of radius r_s and to let the liquid phase be enclosed in a cylindrical channel of radius r_l and length l where l may be interpreted as the distance between the specimen surface and the ice crystal. For a long cylindrical pore, the wall area and the volume are (neglecting the area contribution from the cylinder ends):

$$A = 2 * \pi * r * l \tag{7}$$

$$V = \pi * r^2 * l \tag{8}$$

where A is the area, V is the volume, r is the radius and l is the length of the pore. The number of moles present in such a pore is calculated from the mole volume:

$$n = \frac{V}{V_m} = \frac{\pi * r^2 * l}{V_m} \tag{9}$$

Thus the last term on the left side of expression (6) reduces to

$$\frac{2 * \sigma_{l-pw}}{r_l} * V_{m,l} \tag{10}$$

in which r_l is the radius of the channel containing the liquid phase. The same kind of expression is valid for a spherical shape, only the "2" is changed to "3". Inserting these expressions in (6) yields

$$\frac{-\Delta H_{fus}}{T} * (T - T_0) + V_{m,l} * (P_l - P_0) + RT * \ln X_{H2O} + \\ + \frac{2 * \sigma_{l-pw}}{r_l} * V_{m,l} = V_{m,s} * (P_s - P_0) + \frac{3 * \sigma_{s-pw}}{r_s} * V_{m,s} \tag{11}$$

The interface tension between ice and the pore wall may be estimated, as a first approximation, to be equal to that of ice against air, i.e. the pore wall does not affect the ice crystal surface /Jönsson*/. Thus, a value of 109 mJ/m² for the surface energy of the ice crystal may be adopted /Hobbs, 1974/. In the case of the liquid phase, it is much harder to estimate a reasonable figure for the interface tension liquid-pore wall. It should be clear though that it should be lower than that of pure water in equilibrium with its own vapor. Therefore, as a first rough estimate, a value of 70 mJ/m² will be used here.

Finally, the mole fraction of water in the liquid phase is needed. This is simply calculated from

$$X = \frac{n_w}{n_{tot}} \tag{12}$$

where X = mole fraction of water
n_w = number of moles of water
n_{tot} = number of moles in the liquid phase (water and solutes)

Suppose the ice crystal radius is 100 nm and that the channel radius is 5 nm and also assume the pore solution to remain at atmospheric pressure. The molar volumes of water and ice are 1.8E-5 and 1.97E-5 m³/mol respectively. Because the surrounding solution is pure water, X = 1. At a temperature of 263K and together with the values given above, this means the needed pressure difference is 23.5 MPa.

Example calculation
Expression (11) may now be used for studying how the model pore system of figure 3 behaves.

As an example a simplified calculation will be given which shows that the proposed mechanism predicts scaling thicknesses of correct order of magnitude. Consider figure 3 once again. Let the outer solution be a salt solution of some concentration but leave the pore solution free of salts (this may be achieved in practice by applying the salt solution shortly before freezing in the pores is commenced). In this way, there will be some liquid phase left on the specimen surface as long as the solution temperature is above the eutectic temperature of the solution. This liquid phase, as well as the ice which forms in it, will remain at atmospheric pressure throughout the test.

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* Jönsson, Bengt. Assoc. Professor, Physical Chemistry 1, Lund University. Personal communication.

When temperature is low enough, ice will start to form in the capillary pore. As was said above, the ice crystal in the capillary pore will not stop growing (i.e. will not stop feeding from the surrounding solution) until the chemical potential of the crystal itself and the surrounding solution is equal. In the uppermost millimetre of the specimen and under normal testing conditions (like in the Scandinavian Slab Test), temperature will be practically the same in the capillary pore as that in the outer solution. Thus equilibrium cannot be reestablished as a temperature effect. Instead a pressure difference is needed. This difference is calculated as described above.

At some depth dX below the surface, heat flow will balance the heat of fusion which is released on freezing of the water which flows from the surface to the ice crystal. Close to the surface of the specimen in a test like the Scandinavian Slab Test, the heat flow may be estimated from the cooling rate in the surface solution:

$$q = V * \rho * c * \frac{dT}{dt} \tag{13}$$

in which q = Heat flow, J/(m^2*s)
V = Volume of water covering the specimen surface, m^3/m^2
ρ = Density of water, 1000 kg/m^3
c = Specific heat of water, 4.2 kJ/(kg*K)
dT/dt = Cooling rate, K/s

Under normal testing conditions (as in the Swedish standard SS137244), water depth and cooling rate are 3 mm and 3 K/h, respectively. This means the heat flow is 10.5 J/m^2*s. The heat of fusion is 333 J/g, and so this heat flow corresponds to an ice formation rate of 10.5/333 = 0.0315... g/m^2*s. The water flow reaching the ice crystals thus has to be 0.0315 g/m^2*s in order to balance the heat flow.

The mean temperature during a frost cycle like the one used in SS137244, may be set to be -10°C. At this temperature, the unfrozen transportation channels will have radii of about 6 nm /Brun et al, 1977/ (provided no salts are present). From expression (11) and the figures mentioned above, we then have that the equilibrium pressure difference will be about 19 MPa.

The permeability of a frozen cement paste has to be estimated in some way. For example, one may conclude from pore size distribution measurements e.g. /Mehta and Manmohan, 1980/ or /Winslow and Diamond, 1970/ that in a cement paste in which all pores of radii larger than 6 nm are filled with ice, the remaining capillary porosity is very low, less than 0,10 cm^3/cm^3. The permeability coefficient B may then be estimated from Powers et al /1954/ to be about $1*10^{-15}$ s. Certainly, it is doubtful whether or not all pores larger than the theoretically calculated radius of the smallest pore containing freezable water actually is filled with ice and thus impermeable; Super cooling phenomena and redistribution of water between different pores during the preceding freezing process may render some larger pores open to water transport and thus the estimated permeability will be too low.

Solving for dX, we get

$$dX = B * \frac{dP}{G} = 1 * 10^{-15} * \frac{19 * 10^{6}}{0.0315 * 10^{-3}} = 0.6mm \qquad (14)$$

In the laboratory, surface scaling flakes have been measured to be up to about 0.9 mm. Of course, the exact figures shall not be focused upon too much, but this very simple calculation shows that the proposed mechanism predicts values of correct order of size. Obviously this calculation is very much simplified; In laboratory testing, the ideal ice lensing depth will vary in a very complex manner during the test depending on temperature, cooling rate, pore size distribution and many other factors. As a consequence, ice lenses will not form in just one single layer, but rather at many different depths and thus flakes will be of many different thicknesses.

Obviously, one may question the use of a non-existing pressure as a driving force for water flow and the use of a permeability as measured for water flow under an outer overpressure. However, the explanation given above (describing the process as a shortcut diffusion process) and the fact that geologists use this approach, should make it reasonable to believe these principles will hold also in the case of porous building materials. Of course this should be tested in the laboratory.

An obvious objection

It may seem unnatural that the ice lenses which form inside the specimen would be able to feed from the moisture outside, as the level of free energy is higher in the small ice crystal due to its minute size than it is in the outside liquid phase. However the mechanism is not primarily based on the possibility for the *outer* solution to *enter* the specimen and thereby add to the ice crystal growth, but rather on the fact that as the outer phase is liquid, the pressure in the pore solution will remain atmospheric and so the ice crystals may use the pore solution for growing. When the specimen is covered with pure ice or not covered at all, a meniscus will form which, when water starts to move towards the ice crystal, causes a reduced pressure in the water which in its turn will restrain or even stop further growth of the crystal.

The lowest level of free energy will however be found in the outer solution (it will of course be equally low in the outer ice) and if it was possible to cool the specimen to a low temperature and then keep temperature constant without damaging the specimen, the outer ice which had been segregated from the solution, would feed from the pore system in the long run. The specimen would thereby be drained to such an extent that the level of free energy in the remaining pore solution would be as low as that in the outer ice. But this is a very slow process and when freezing is initiated in the pores, the ice crystals and the pore solution close to them will only "feel" the local unequilibrium and act as has been described.

Consequences - Predictions

We may now turn to the qualitative predictions mentioned above. As will be evident, any single change will affect the system in many ways and as a consequence the discussion will have to be limited, otherwise it will not serve its purpose of clarifying the basic principles.

The predictions are essentially divided into two groups: Reactions caused by changes in outer circumstances, and reactions caused by changes in material properties.

Permeability

Permeability governs the water flow under conditions of constant pressure difference and flow distance. In this way, permeability plays a major role in that it decides the maximum depth at which ice lensing may take place. As mentioned above, using the permeability to water flow as measured for water flow at conditions of an outer overpressure may not be correct, but irrespective of what parameter is chosen for flow calculations, the principles given below will apply.

Permeability to water flow through discs of cement paste has been studied by many researchers. Though, as far as the author knows, no studies have been reported on water permeability of partly frozen cement paste or mortar. Such measurements are undoubtedly very difficult to accomplish, but should prove very useful for more precise predictions of the phenomenon described. In the lack of proper data, the simple relation between capillary porosity and permeability given by Powers et al in /1954/, will be used to demonstrate possible effects.

As is seen in figure 4, permeability may be described in terms of capillary porosity. When calculating the depth of balance between heat flow and water flow, either one of two simple ways of estimating permeability at temperatures below 0°C may be used. The first and simplest way certainly is to estimate, for the water to cement ratio in question, a mean permeability, likely to be valid throughout the period of freezing. The second way is to reduce capillary volume by the volume of ice formed in the pores. This is doubtful though in that we do not know exactly how much ice has formed, neither do we know where it has formed: If it forms only as micro ice lenses growing in relatively coarse capillary pores (or even entrained air pores), a case which will be possible under conditions of slow cooling, the remaining capillary porosity is unchanged and thus permeability is likely to remain constant too. In this case permeability may be chosen directly from figure 4 for the particular water to cement ratio. On the other hand, if the material is cooled rapidly, ice is more likely to form in site in the capillary pores, causing a large decrease in permeability.

According to the equations given above, a lower permeability will reduce the possible maximum depth of ice lensing, and so scaling will be reduced. Here a first complication on predicting effects of different frost cycles may be discerned: Depending on the foregoing cooling rate, conditions for ice lens growth at different depths will differ throughout the frost cycle at subsequent temperatures and cooling rates.

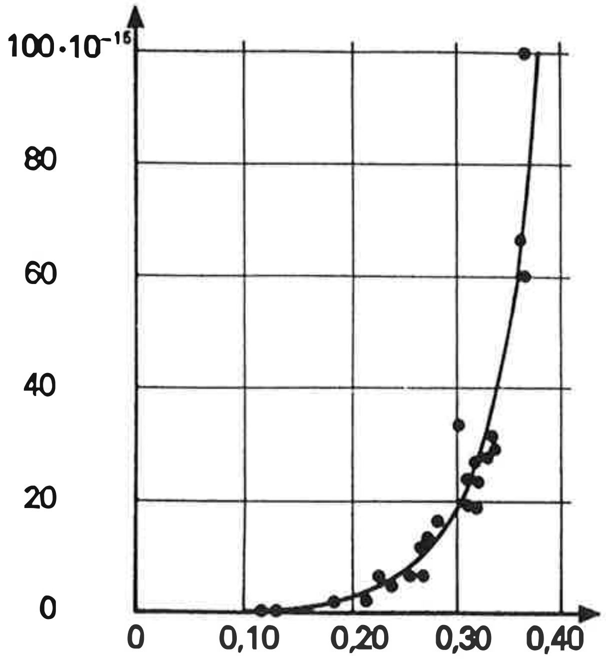

Fig 4: Water permeability (B, unit: second) vs. capillary porosity. From /1982/ after Powers et al /1954/

Permeability may also be affected by temperature. Probably though, these effects are small and as a first approximation they may be omitted.

Pore size distribution

Three main types of pore size distribution will be treated: Uniformly coarse distributions, uniformly fine distributions and finally well spread distributions comprising a wide range of sizes. Permeability is closely related to pore size distribution, but will be discussed only briefly in the following.

In a material with coarse pores of one single and quite large size (larger than 100 nm), all water will freeze almost simultaneously just slightly below 0°C. After that, no pores will be open and no water transport may take place any more. This means the proposed mechanism will not be active.

A material with a pore size distribution of this kind will be very sensitive to anomalies in its pore size distribution. If it is possible for ice to form in some pores while some others remain open to water transport, permeability will still be high and thus conditions for continued growth of the crystals formed in these pores will be very good.

In the case of uniform and very fine porous materials (pores smaller than 2 nm), very low temperatures will be needed for any ice formation at all to take place. Once ice crystals have started to form, permeability will be reduced just as in the former case, and thus the possibilities for micro ice lens growth are once again strongly restricted, but just as in the former case this pore system too will be sensitive to anomalies. Due to its very minute pores, permeability of the fine porous system will be very much lower than that of the uniformly coarse pore system, and thus such a fine porous system with some anomalies in it will not be as badly damaged, as the depth of balance between heat- and water flow can not be very large.

The two cases described are impossible, though, as it is presumed that their pore size distributions are perfectly uniform. This will never be the case in any real kind of building material. Instead in reality the suggested anomalies will always be present more or less pronouncedly and thus a coarse porous material will probably not be able to withstand a combined de-icer and frost attack. The fine porous one might suffer no or only very limited damage as ice will not start to form unless very low temperatures are applied and when that eventually happens the limited permeability of such materials should set limits on the ice lensing depth.

The third pore system contains all pore sizes between the two extreme cases treated above. In such a pore system, ice will start to form when temperature is lowered slightly below 0°C but still a lot of water will remain unfrozen at temperatures well below those normally occuring either in the laboratory or in nature. In such a pore system, permeability may still be quite high even after extensive ice formation has occured. This will make it possible for ice lensing to occur even at relatively large depths. As a consequence scaling may be severe, depending on the cooling rate.

Pore solution

Generally, the described scaling mechanism is favoured if the pores contain pure water, as any presence of solutes will reduce the pressure difference needed for equilibrium and thus will reduce the maximum possible pressure that ice lenses may exert. For example, Sellevold and Farstad /1991/ performed scaling tests on concretes which had been dried and resaturated with NaCl-solutions of various concentrations (0-12%) and found that scalings would be the worst when the specimens were resaturated with pure water and that scalings decreased the higher the salt concentration. (In all cases the outer solution was a 3% NaCl-solution)

Outer de-icer concentration

This is perhaps the most interesting question as any hypothesis put forward on the mechanism of salt-frost scaling has to be able to explain the maximum in damages at a solute concentration of about 2-4 percent by weight observed by many researchers. Unfortunately, the hypothesis does not provide any simple explanation. From the foregoing it is evident though that scalings are likely to increase the lower the de-icer concentration in the pores, while as a de-icer has to be present in the solution covering the specimen surface for any scaling to be possible at all. Before commencing any detailed analysis, it may therefore be concluded that maximum scalings are likely to occur when a test is performed in such a way that de-icers do not enter the pore system and in such a case scaling will also be independent of saltconcentration, provided there is always a large enough amount of moisture available. (As temperature drops, ice will be segregated from the solution and so the available liquid phase will be reduced. In the extreme case all this liquid may be consumed by the ice crystals and as a consequence ice lens growth due to the presence of an outer liquid phase will be stopped. This extreme case may be realized if the de-icer concentration is too low in comparison to the initial amount of solution applied.) Such a test has been carried out and the results will be shown below.

Possibly, the maximum in damages caused by a 3% solution is simply the result of these two conflicting requirements. It should be remembered however that damages do not disappear completely when stronger concentrations are used!

What amount of de-icer will be present at any given depth in the specimen is mainly a question of what time is avilable for diffusion (or any other transfer mode) of the de-icer into the pores to take place before freezing starts. Certainly, some diffusion may take place even after freezing has been initiated, but the main conditions will already be set by then. This means we may distinguish three principally different cases: In the first one no de-icers have entered the pore system, in the second one the de-icer is uniformly distributed in the entire pore system and in the third case their is a concentration gradient close to the surface. In all three cases it is presumed that the de-icer concentration in the outer solution is such that de-icers do not leave the pores.

The first case is the same as the situation described above where the pore solution consists of pure water. This means ice lens growth may take place anywhere in the pore system and also that no limits are layed upon maximum ice pressure.

In the second case where a strong concentration is present everywhere, ice lenses will not start to form until a certain temperature T_c below 0°C is reached. This temperature T_c is dependent on the salt concentration. For temperatures lower than T_c, the maximum pressure that an ice crystal may exert is reduced. For example if the relative vapour pressure of water is reduced from 100% to 96% by adding salt (about 6.3% by weight NaCl), the equilibrium pressure difference will be reduced by about 4.5 MPa (the effect will be dependent on temperature). If the requested pressure difference has to be established as an overpressure in the ice phase (assuming the liquid phase to remain at atmospheric pressure) the overpressure at -10°C may be calculated to be about 11.6 MPa. When the salt is added this is reduced to about 7.1 MPa. Possibly, an ice pressure of 7.1 MPa will still be enough to damage the pore walls, but it is clearly seen how salts in the pore water reduce the damaging effect of ice lens growth.

In the third case in which the de-icer is not uniformly spread there is reason to believe ice lens growth will occur: When ice starts to form in one pore there will always be nearby pores containing cleaner water from which the ice crystals may feed. Especially, it is likely that pores of different sizes will contain different amounts of dissolved salts after a given, short period of salt ingress.

The maximum in damage observed at about 3% by weight concentration of NaCl is possibly explained by the fact that the maximum pressure that an ice crystal may exert is not reduced too much while the depth of ice lensing is still quite large.

Cooling rate

Generally, slow cooling, i.e. low heat flows, will promote ice lens growth, but at low cooling rates, the ice lens growth will take place closer to the surface than the permeability would permit and thus scaling will not be the worst possible. Such low heat flows may be named suboptimum heat flows, as there is a certain heat flow, which will make full use of the available permeability. The optimum heat flow on the other hand, is likely to vary with temperature in the case of a material with a wide, unevenly spread pore size distribution as the amount of freezable water varies with temperature in such a material.

Suboptimum heat flows though has another advantage: After flaking off a first layer, another level of ice lens growth may be established and in this way multiple flakings may occur during one single frost cycle. Whether this outweighs the negative effect of a seemingly suboptimum heat flow is impossible to say at present.

Minimum temperature

In ordinary testing minimum temperature varies in the range -15 to -22°C. For a material with a certain spread in pore size distribution (like cement paste) it follows that the lower the temperature, the more ice crystals will form. In this way there will be more sites in which ice lenses may start to grow. Thus lower temperature generally should mean a more severe frost attack.

However, due to the very dynamic behaviour of the process it can not be said for certain on beforehand that ice crystals actually will form in the very minute pores. For example they may, during the preceeding process, have been filled with a solution so rich in solutes that ice can not form in them unless temperature is lowered even more. In such a case the number of ice crystals may not increase below a certain temperature, but instead the minute pores will be open to liquid flow.

Depth of solution covering the specimen surface

Provided cooling is kept constant, depth of the surface solution will play only a second role. It was calculated above that water flows into the specimen will be something like 100 g/m^2*h. Very probably, large deviations from this figure may occur. Anyway, it still is interesting as it indicates that under some circumstances, all available liquid on the specimen surface may be consumed and thus ice lens growth will be interrupted. For example with an initial amount of $3l/m^2$ of 3% NaCl solution, there will remain 0.6 l/m^2 of liquid phase at -10°C. If nothing else would change and all of this solution would be available for ice lens growth, it would take 6h at -10°C to consume it all. Of course conditions will not be this ideal (for instance the mechanism will not be active and thus water flow will be nonexistent if there is no heat flow) but the calculation indicates that the total amount of solution on the surface specimen at the beginning of a test might be important.)

RESULTS FROM AN INITIAL TEST

As was mentioned above, damages should be independent of salt concentration if an ordinary scaling test were carried out in such a way that no salts were present in the pores. Therefore, such a test was run as a first test of the hypothesis. Only a short review of the test will be given here; For a complete report, the reader is referred to our department.

The main interest thus lay in using different saltconcentrations. This was accomplished by pouring 26 ml of pure water on the specimen surfaces at +20° and then when the temperature of the surface solution had reached 0°, another 13 ml of different cooled NaCl-solutions were added. By using NaCl-solutions 3 times more concentrated than the desired ones, the solution covering the surface would be correct after dilution.

Three cement mortars of different water-cement ratios (0.45, 0.50, 0.65) were used. The air contents were 6.6, 6.2 and 6.7% respectively. The total paste content was about 45% and thus a moderate or low frost resistance was expected. Maximum aggregate size was 3 mm.

Specimens were circular discs with a diameter of 127 mm and a thickness of 25 mm. The specimens were heat isolated as shown if figure 5 and a lid was put on to prevent any evaporation.

All specimens were water cured for at least 6 weeks. Half of the specimens were slightly dried in a climate chamber (60%RH/18°C) for two days and were then water stored another three days before starting the test.

Because the specimens of water cement ratio 0.50 were run as a pre-series, these were treated slightly different than the others. As the differences are generally believed not to influence very much on the principal results, they will not be commented upon here, all such details are given in the complete report. There is one major difference though: The 0.50s were tested with salt solutions with concentrations of 0, 1.1, 2.3 and 5.6% respectively, while as the others were tested with 0, 1, 3 and 7.5%.

The specimens were run through 7-10 frostcycles. The temperature cycle is given in figure 6. The salt solutions were immediately removed and replaced with pure water when temperature once again reached 0°C. In this way, no salt solution was present during the hours when temperature was above 0°C.

The main results are given in figures 7-9.

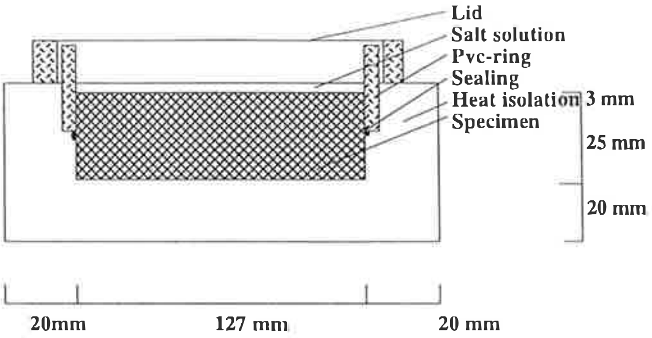

Fig 5: Test setup for salt-scaling tests.

Specimens are identified by their water cement ratio, next with a letter combination (D or ND) indicating whether the specimen has once been dried and remoistened or not, after that the salt concentration that was applied to it and finally a letter to show which one of two identical specimens is in question. 45ND3A thus means water cament ratio 0.45, Never Dried, 3%, specimen A.

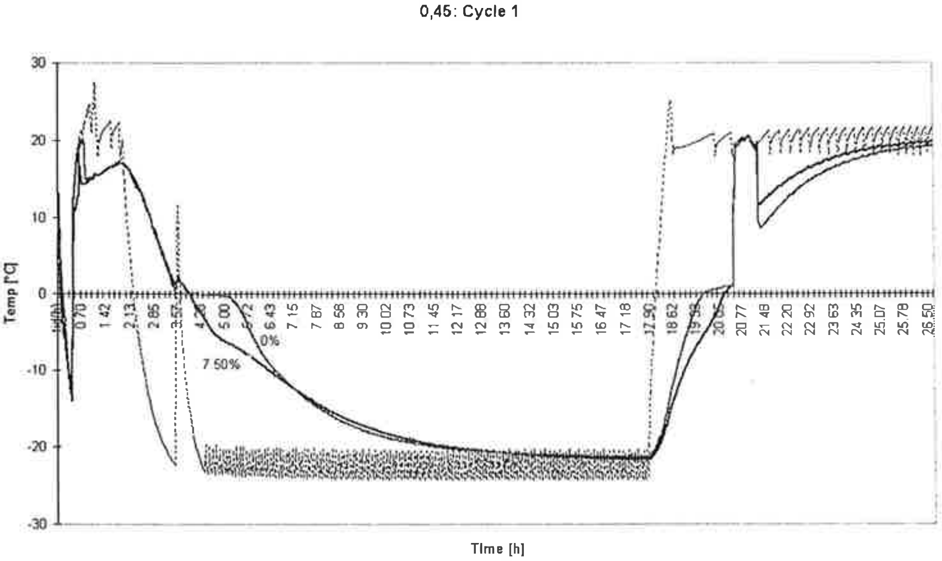

Fig 6: Temperature cycle as measured in the solution covering specimen surfaces. (Dashed line shows air temperature)

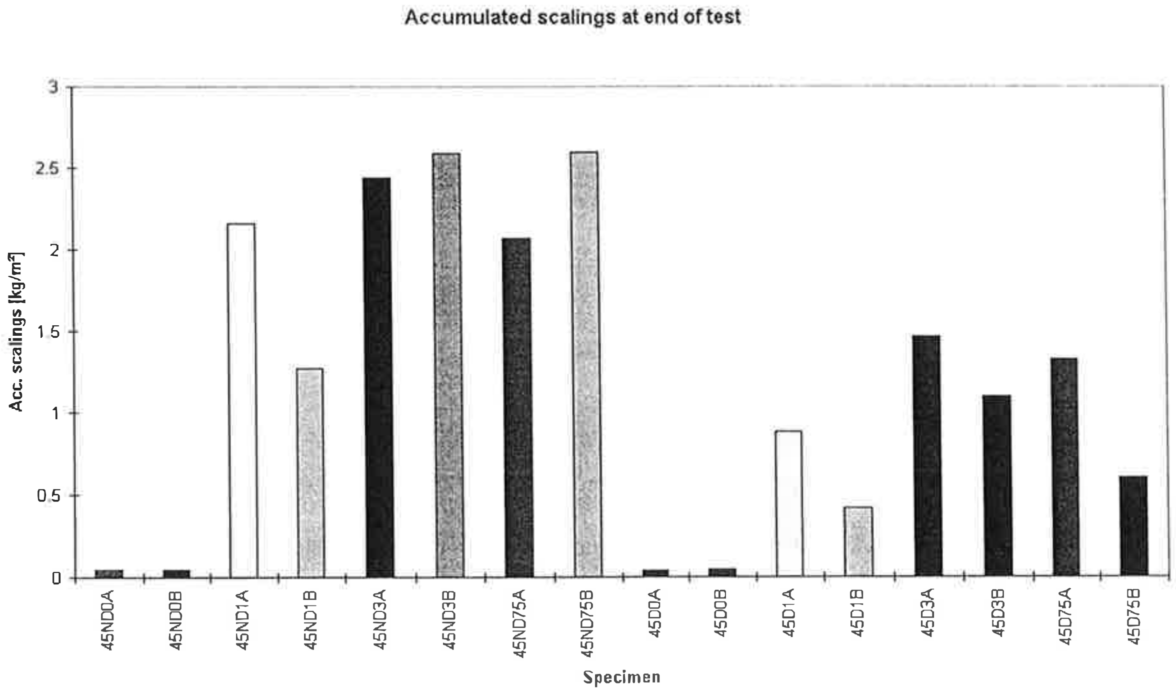

Fig 7: Final accumulated scalings (W/C 0.45,. 10 cycles)

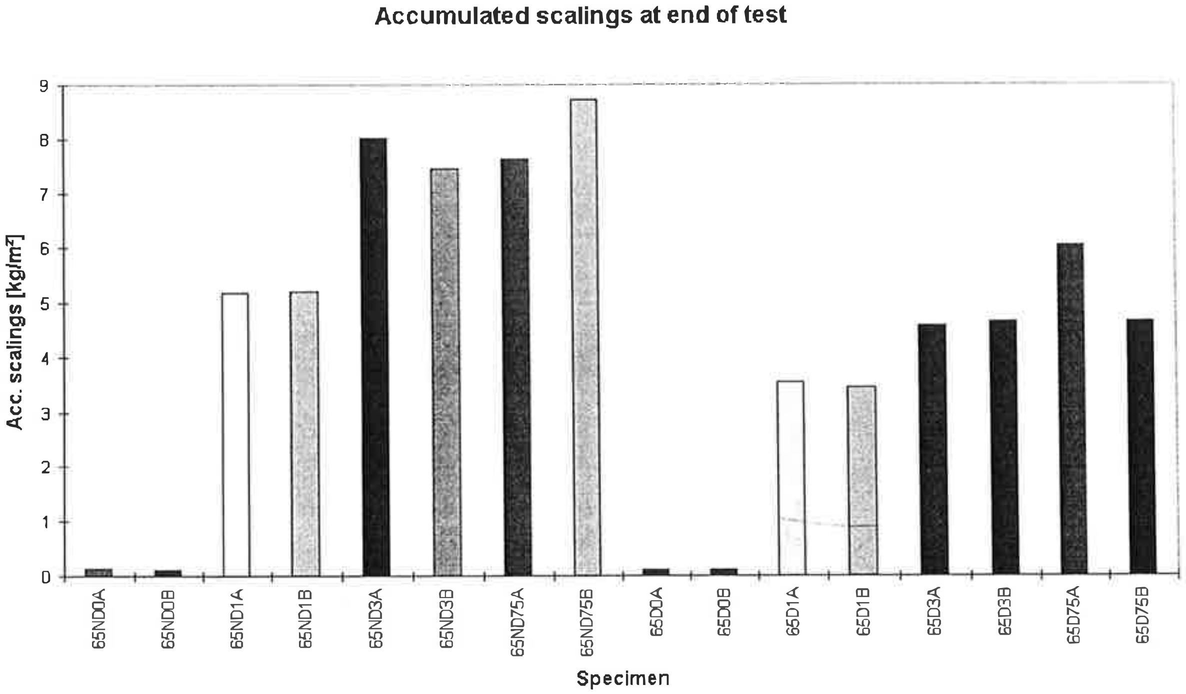

Fig 8: Final accumulated scalings (W/C 0.65, 9 cycles)

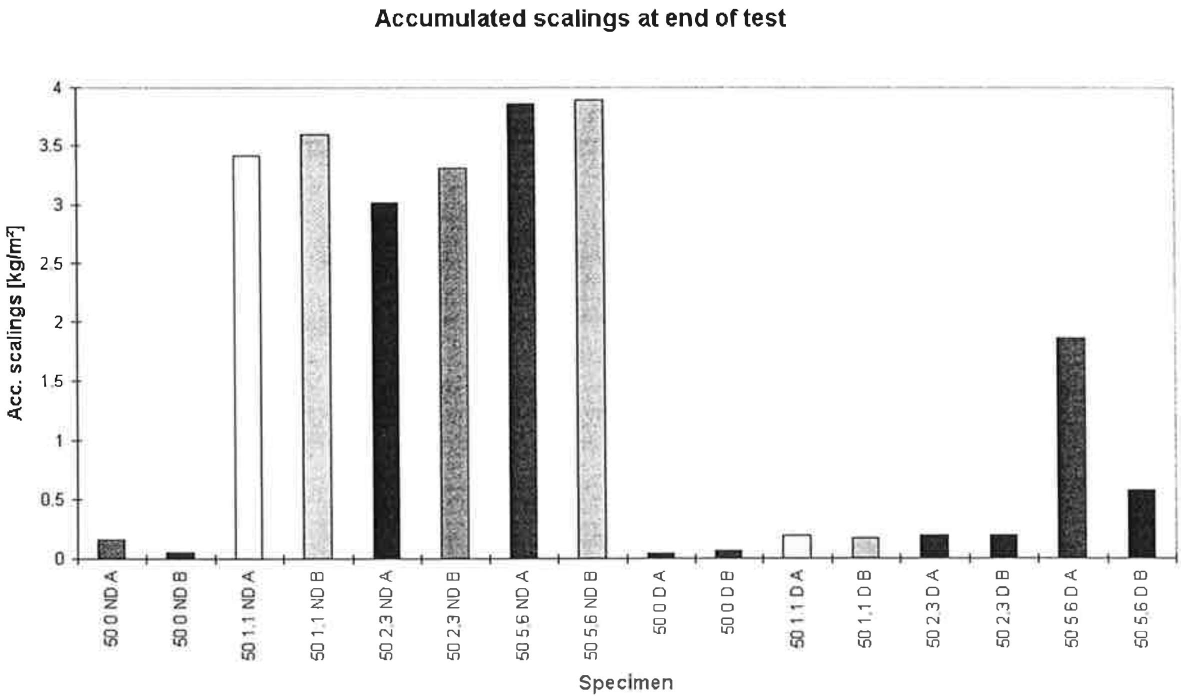

Fig 9: Final accumulated scalings for the pre-series (W/C 0.50, 7 cycles)

For specimens that were never dried, it is clearly seen that there is no damage maximum at a concentration of about 3%. Rather, damages seem to be independent of salt concentration.

Results from a test of this kind should be treated with great care as there are so many other variables which also affect the results. Nevertheless, from previous experience it was expected for a mortar of this kind to show a clear damage maximum at the 3% concentration. Therefore it seems reasonable to state that these results support the hypothesis.

One interesting observation was made during the test: Specimens that had once been dried and remoistened, were able to withstand a few cycles but when scaling finally commenced, the complete surface was scaled off in almost one single, coherent layer, about 0.8 mm thick. This behaviour was repeated in subsequent cycles, although less pronounced. Specimens that were never dried did not show the same "one-single, coherent-layer"-behaviour. Still the flakes measured up to about the same thickness.

References

1943 Arnfelt, H: "Damage on concrete pavements by wintertime salt treatment" Meddelande 66, Statens Väginstitut, Stockholm 1943 (In Swedish)

1953 Powers, T C, Helmuth, R A: "Theory of volume changes in hardened portland-cement paste during freezing", Higway Res. Board, Proceedings, 32/1953.

1954 Powers, T.C, Copeland, L.E, Hayes, J.C, Mann, H.M: "Permeability of portland cement paste", ACI Proceedings V26, No 3, Nov. 1954

1957 Verbeck, G and Klieger, P: "Studies of "salt" scaling of concrete", Higway Res. Board, Bull. 150, 1957 Washington DC.

1965 Powers, T.C: "The mechanism of frost action in concrete". Stanton Walker Lecture Series, Lecture No. 3, Presented at University of Maryland, Nov.1965

1970 Winslow, D. N, Diamond, S: "A mercury porosimetry study of the evolutionof porosity in portlan cement paste", Journal of Materials 5, 1970.

1974 Hobbs, P. V: "Ice Physics" Clarendon Press, Oxford 1974

1975 Browne, F.P, Cady, P: "Deicer scaling mechanisms in concrete", ACI Special Publication 47-6

1977 Brun, M, Lallemand, A, Quinson, J-F, Eyraud, C: "A new method for the simultaneous determination of the size and the shape of pores: The thermoporometry", Thermochimica Acta, 21, 1977

1980 Mehta, K, Manmohan, D: "Pore size distribution and permeability of hardened cement pastes", 7th International Congress on the Chemistry of Cement, Paris 1980

1982 Betonghandbok Material, Svensk Byggtjänst.

1984 Petersson, P-E: "Inverkan av salthaltiga miljöer på betongs frostbeständighet", Statens Provningsanstalt, SP-Rapp 1984:34 ISSN 0280-2503

1985 Knutsson, S: "Några synpunkter på tjälningsprocessen och dess termodynamiska bakgrund", 85:08, Avdelningen för Geoteknik, Tekniska Högskolan i Luleå. (In Swedish)

1991 Sellevold, E. J, Farstad, T: "Frost/salt testing of concrete: Effect of test parameters and concrete moisture history", Nordic Concrete Research 1991

1994 Pühringer, J: "Zur materialzerstörung durch tausalzfrostwechsel - über die 3%ige NaCl-lösung"

1995 Fagerlund, G: Personal communication.