

SP 47-1

Freezing Effects In Concrete*

By
T. C. Powers

Synopsis: Theories as to the mechanism of freezing and thawing damage in concrete have been advanced for more than 40 years. The author discusses the evolution of these theories for cement paste, aggregate and the overall concrete. Since the author was prominent in the development of many of the theories his current views of the mechanism of freezing and thawing in concrete are of unique interest.

Keywords: aggregates; air entrainments; bubbles; cement pastes; concretes; cracking (fracturing); deicers; freeze-thaw durability; freezing; lightweight aggregate concrete; plastic shrinkage; scaling, temperature; water-cement ratio.

*Note: This paper is essentially the reply Dr. Powers gave to a letter of inquiry from ACI 201, Durability of Concrete, asking for comments on a committee draft of "freezing and thawing phenomena in concrete."

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T.C. Powers graduated from Willamette University in 1925 B.A. degree. Chemist and testing engineer for the Oregon Highway Commission, concrete technologist for Bull Run Dam and manager of a ready-mix company were his early experiences. In 1930 he joined the research and development laboratory of the Portland Cement Association where he was an outstanding researcher until his retirement. A three time recipient of the ACI Wason Research Medal 1932, 1945 and 1948, he now lives in Green Valley, Arizona.

INTRODUCTION

Specimens of concrete kept continually wet on all surfaces by spraying or immersion usually become damaged or destroyed when they are cooled well below the normal freezing point of water; if the period of soaking is long, nearly all concretes so exposed, air-entrained or not, cannot withstand freezing. On the other hand, concrete structures having at least one surface exposed to air continually show extremely various behavior, from total failure, usually localized, to apparent immunity to freezing effects. The mechanisms of freezing effects are likewise various; they have been the subject of systematic research for many years and can now be explained; only some matters of detail and certain quantitative aspects remain for conjecture or further research.

Early Hypotheses

Some early attempts to explain damage caused by freezing were based on the fact that water expands 9 percent when it freezes. If a closed vessel is more than 91.7 percent full of water, it will be stressed when the water freezes, perhaps to failure. It was assumed that damage occurs when the pores are more than 51.7 percent full at the time of freezing. On this basis, materials were supposed to have a critical saturation point of 91.7 percent, although experiments indicated that for some materials the critical point was below that level.

In 1945 Powers¹ pointed out that concrete is not a closed vessel, and that even if it were it always contains enough air-filled space to accommodate the increase in water volume caused by freezing. He advanced the hypothesis, which was further amplified in 1949,² that the destructive stress is produced by the flow of displaced water away from the region of freezing, the pressure being due to the viscous resistance to such flow through the permeable structure of the concrete; if the water content is above the critical saturation point,

such flow will take place. Since the resistance to flow at a given rate is proportional to the length of flow path, it follows that there is a critical length of flow path, or critical thickness of the body being frozen, beyond which the hydraulic pressure exceeds the strength of the material; critical thickness was defined in terms of a state of complete saturation.

Data on the probable rate of ice production at a given rate of cooling, and data on the magnitude of the coefficient of permeability of concrete, gave figures showing that the critical thickness was of the order of 0.01 in., and this seemed to account for the necessity of entrained air in concrete. The air bubbles were thought of as spaces into which the excess water produced by freezing could be expelled and then frozen without generating destructive pressure.

Earlier, a different hypothesis had been advanced by Collins,³ based on still earlier work by Beskow⁴ and by Taylor⁵ on frost heaving of soils. By this hypothesis, the stress is not produced by hydraulic pressure but by the segregation of ice into layers, the unfrozen water in the concrete flowing toward the region of freezing, rather than away from it. Powers^{1,6} considered this hypothesis, recognized its soundness as applied to certain soils, but believed it to be inapplicable to a cohesive system such as mature concrete, although McHenry and Brewer⁶ had demonstrated its applicability to concrete only 4 hr old.

After the development of working hypotheses, there followed a long systematic research which made possible firm conclusions about the nature of frost action in concrete based on experimental observations rather than theory. As is shown in the following discussion, it turned out that in general all the theories mentioned above, with some modifications, are required to account for the nature of freezing effects in concrete.

Freezing Phenomena in Cement Paste

The hydraulic pressure hypotheses described above was based on incomplete studies of the structure of hardened cement paste and quantitative measurements of the amount of water that freezes in it at various temperatures.⁷ These studies showed that a considerable fraction of the evaporable water in saturated paste is in the adsorbed state, and we now know from thermodynamic considerations as well as experiment that adsorbed evaporable water is not freezable.²⁷ The rest of the evaporable water is held in spaces called capillaries or capillary cavities, and it is freezable.

However, there is a wide range of cavity sizes, and there are as many different melting points of ice as there are different sizes of cavity in which the freezing can occur, for all these spaces are so small that the melting point of the ice bodies they can contain are significantly lower than the normal melting point, the lowering of melting point being greater, the smaller the cavity.

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The melting point of ice in cement paste is lowered also by dissolved alkali, but the effect, although significant, is not as great as that due to small dimensions.

The import of the findings just mentioned is that after cooling to a temperature in the freezing range, all the freezable water in spaces smaller than a certain size corresponding to that temperature must remain unfrozen, the lower the temperature the smaller the amount remaining unfrozen. Some of the water in the larger spaces will be frozen, but not all of it; owing to the dissolved alkalis, each cavity containing ice will contain also a relatively concentrated unfrozen alkali solution having a solute concentration determined by the requirements for thermodynamic equilibrium with the ice in the cavity. Also, as discovered by Helmuth,⁸ if the temperature was reached by cooling, the actual quantity of ice is generally much smaller than the quantity that is thermodynamically freezable at the given temperature. This phenomenon is a consequence of the fact that water will generally supercool rather than freeze unless it is seeded by an ice crystal; freezing in paste is propagated from a starting point by rapid growth of dendritic ice crystals; the ends of these dendrites are presumably larger (blunter) the higher the temperature, and vice versa; hence an isolated cavity cannot begin to freeze until the temperature is low enough to produce a crystal slender enough to penetrate an opening into that cavity. The methods used by Powers and Brownyard⁷ revealed the amounts of ice in a specimen that had been cooled to 78 C, and gave data on progressive melting as a function of rising temperature; thus they gave the maximum amounts of ice that might exist, but not the actual amounts produced during cooling. Helmuth's experiments, showing the relatively small fractions that freeze on cooling, are supported by data of Vuorinen¹² which show that at 15 C, for example, approximately one-half of the water in pores large enough to be frozen at 15C remains unfrozen. These data show that early attempts to quantify hypotheses were based on overestimates of the rates of ice production.

In 1953, Powers and Helmuth¹⁰ reported studies of the effects on specimen volume of freezing in cement paste, with special reference to the hydraulic pressure hypothesis of 1945-1949, referred to above. Although in some experiments there seemed to be clear evidence of effects due to hydraulic pressure, especially with pastes of relatively high porosity, fully saturated, there were other important observations that could not be explained on that basis; specifically, with non-air-entrained paste the hydraulic pressure hypothesis could not account for continued dilatation while the temperature was held constant, and it could not explain the shrinkage of air-entrained paste; moreover, the expected effects of changes in rate of freezing were not observed consistently. Later studies by Helmuth⁹ showed also that a slightly desiccated non-air-entrained paste will shrink during cooling after the beginning of freezing, but will expand sharply after some low temperature had been passed; this too is incompatible with the theory that expansion is caused by hydraulic pressure generated by flow away from the freezing sites.

It became evident that most of the effects of freezing in cement pastes were due to the movement of unfrozen water to the freezing sites; indeed, the reaching of thermodynamic equilibrium between the ice and the unfrozen solution, and between the concentrated solution at the freezing site and the more dilute solution in the unfrozen capillaries, required such a transfer of water.¹⁴ The initial production of ice in cavities produces a relatively concentrated alkali solution in those cavities, and therefore the movement (diffusion) of unfrozen water to these cavities is like osmosis, and the generated pressure, if any, is osmotic pressure. It is easy to show that osmotic pressure can be sufficient to account for disintegration.

It was shown¹⁴ that the process of generating pressure by diffusion of water to an ice containing cavity will operate at any solute concentration including zero, i.e., pure water. In the latter case a cavity becomes filled with ice (and a layer of adsorbed water) rather than with ice and concentrated solution, and the pressure developed from the in diffusing water could aptly be called crystal pressure due to the growth of the body of ice in the cavity. However, there is no fundamental difference between the two cases, and the discussion becomes simpler by speaking of osmotic pressure regardless of the magnitude of the solute concentration.

Whether or not osmotic pressure is generated in a cavity where freezing has occurred depends on whether or not the cavity is full of solution and ice. If the supply of unfrozen capillary water is relatively abundant, an unfilled cavity becomes expansive after diffusion has filled the cavity; before the expansive stage is reached, the paste tends to shrink as water is drawn from the unfrozen cavities to the cavities containing ice: the observed change is a resultant of the two effects.

The main function of entrained air bubbles in cement paste is to prevent the development of osmotic pressure. Moisture in an air bubble freezes as soon as any freezing in capillary cavities occurs. The unfrozen capillary water may diffuse either to the ice and solution in the air bubble or to that in the capillary cavity. If it moves to a cavity already full of ice and alkali solution, osmotic pressure develops, but if it moves into an air bubble, no osmotic pressure develops there because the air bubble is far from being full; therefore the ice and solution in the air bubble wins the competition for the unfrozen capillary water, and withdrawal of water from the cement paste produces shrinkage--a freeze-drying effect; the shrinkages per degree of cooling is about two times the normal thermal contraction per deg of cooling. If the air bubbles are close enough together, the elimination of osmotic pressure is practically total. Experience indicates that the required bubble-spacing factor^{15,28} is about 0.006 in., which corresponds to an actual spacing somewhat less than that.

An important finding of these studies is that any paste of normal composition, i.e., of any practically acceptable water-cement ratio, and made with any type of portland cement, can be made completely

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immune to damage by the freezing of the water it contains by means of entrained air. On the other hand, any paste made with any type of cement without entrained air will fail the first time it is frozen in a saturated state. Therefore, where exposure conditions require it, entrained air to protect the cement paste is prerequisite to building a durable concrete structure. However, as is shown below, air-entrainment alone does not preclude the possibility of damage of concrete due to freezing; freezing phenomena in rock particles must be taken into consideration.

Freezing Phenomena in Rock Particles

Studies of the freezing of various rocks by Thomas¹³ and others revealed the same kinds of phenomena as those observed with cement paste; therefore, results of the extensive studies of freezing in cement pastes can be applied to rocks.

The rocks commonly used for concrete aggregates contain interconnected capillaries as shown by their ability to absorb water. When saturated, a rock contains unfreezable adsorbed water, and there is a wide range of small capillary sizes, giving rise to a range of melting points when the system is frozen. However, in an ordinary rock of good quality, the amount of adsorbed water is negligible, the average capillary size is much larger than that in a typical hardened cement paste, and a relatively large fraction of the evaporable water in a saturated specimen can freeze in a narrow range of temperatures not far below the normal melting point. For this reason, most saturated rocks tend to expel water during freezing,¹⁷ and stress in rock and matrix is produced by hydraulic pressure; in other words, the hydraulic pressure hypothesis is applicable.

A given kind of rock, frozen by itself, will show a critical size below which it can be frozen without being damaged, as was demonstrated by Verbeck and Landgren.^{11,16} The critical sizes* of rock quality range upwards from perhaps a quarter of an inch, whereas the critical size or thickness of cement paste is less than 0.006 in., an observation that reflects the great structural difference between cement paste and rock quality.

When in air-entrained concrete, each particle of an aggregate is isolated by a matrix composed of cement paste and air voids. When freezing occurs, the excess water in rock particle produced by freezing tends to be forced into the matrix. If for example the porosity of the rock is 2 percent by volume, all the efflux must try to enter the matrix through only about 2 percent of the interfacial area between the rock particle and the matrix; this consideration, together with the

*Note: for warnings about oversimplifying the concept of critical size and critical saturation, see Reference 16.

lowness of the coefficient of permeability of hardened cement paste, explains the fact that an ordinary good quality aggregate is able to destroy air-entrained concrete if some of the rock particles became saturated before freezing occurs. The results of standard freezing and thawing tests prove the point: the nature of the test is such that the aggregate particles must eventually become saturated and produce failure.

On the other hand, there are some comparatively rare aggregates having capacities for freezable water so near to zero that they do not produce stress when freezing occurs, and air-entrained concrete made with such aggregate has been found to withstand more than a thousand standard cycles while suffering only superficial damage.

With ordinary aggregates, the destructive effect of freezing in air-entrained concrete is larger, the larger the particle, assuming that large and small particles have the same structure. This has been observed experimentally, and it is to be expected from consideration of the volume of water to be expelled per unit of interfacial area, as well as from the effect of critical size; a rock that would fail if frozen alone could be doubly destructive if frozen in concrete.

The role of entrained air in alleviating the effect of freezing in rock particles is minimal. There is some evidence that the air bubbles in the matrix are able to relieve the pressure from water forced out of sand particles, but not so for the larger particles.

Because of capillary size effects, and perhaps the presence of solutes, some of the water in a rock remains unfrozen at a given sub-freezing temperature. Therefore, secondary effects due to diffusion of unfrozen water to the ice are probably present but are not ordinarily observable. However, Thomas¹³ did observe some rocks to expand while the temperature was held constant, and other to shrink. Some argillaceous rocks hold considerable amounts of free capillary water in very small spaces and show freezing behavior similar to that of cement paste not protected with entrained air; some of these rocks are even worse for they can be disintegrated by water without freezing.²⁷

Dunn and Hudec²⁷ advanced the hypothesis that the principal cause of disintegration of rocks is not freezing but the expansion of adsorbed water during cooling; specific cases of failure without freezing seemed to support their more general conclusion. However, extensive studies of adsorbed water by Helmut⁹ and others gives no support to the assumption that adsorbed water expands when cooled. It is true that the cooling of a system that contains both adsorbed and capillary water will cause the relative proportion of adsorbed water to increase, but this increase produces no expansion of the system beyond its original dimensions. It now seems clear that the Dunn and Hudec experiments on certain clay-bearing rocks either involved the osmotic pressure mechanism explained above for cement paste,¹⁸ or swelling produced by the disjoining action of adsorbed water in the unbonded-clay constituent of the rock.¹⁹

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Overall Effects in Concrete

A general discussion of results of experimental investigations of frost action in concrete was given by Powers in 1955²⁵ and again in 1965.²⁶ It is now clear that the paste and the aggregate should be considered separately not only when explaining frost action, but also when making concrete for severe exposure.

If the matrix of the aggregate in concrete is composed of hardened cement paste and a sufficient concentration of air bubbles, (spacing factor not more than about 0.006 in.)²⁸ freezing the capillary water in the paste does not produce destructive stress, but without entrained air, the matrix fails as soon as the paste becomes saturated.

With ordinary "sound" aggregates, the saturated particles must expel water when freezing occurs. Consequently, air-entrained concrete is ordinarily not able to withstand stresses due to freezing when the concrete is subjected to a perpetually wet environment. This is shown by the fact that nearly all air-entrained concretes disintegrate in a standard freezing and thawing test; they disintegrate at once if the aggregate particles are saturated at the start, an unusual condition because of the effects of self desiccation during early hydration; otherwise, they disintegrate gradually as the aggregate absorbs water in the course of the test. Such failure reflects the inability of entrained air to control stress originating in the aggregate, particularly the coarse aggregate; it does not necessarily signify that the paste is inadequately protected, although such can be the case in air-entrained concrete if the void size distribution is abnormal. For extensive discussion of the air content, see Reference 23, Chapters 7 and 8.

Pressure originating in an aggregate particle may rupture the particle and the matrix, or it may cause a separation between the matrix and the particle; if the particle is near the surface of a pavement, a popout may be produced.

There are a few rocks that can contain practically no freezable water. Air-entrained concrete made with an aggregate composed entirely of such rock will withstand freezing under continually wet conditions for a long time, but it cannot do so for an unlimited time because the air bubbles eventually become filled with water, and the leaching of lime from the paste eventually destroys it even if freezing does not. Moreover, fluctuation of temperature without freezing can produce gradual swelling and eventually failure,^{21,22} at least with some materials.

Because of the rarity of "unfreezable" rock, durable structures must in general be built with intrinsically vulnerable concrete, the absorptive aggregate being the uncontrollably vulnerable constituent. The durability of most structure, made of air-entrained concrete is to be attributed, generally, to circumstances that keep the aggregate particles from becoming critically saturated. The most obvious factor is the alternation of drying and wetting periods; the rock pores cannot

become critically saturated until after the paste becomes saturated; the process is slow, and is slower the lower the coefficient of permeability of the paste. Therefore, under severe conditions rich air-entrained concrete lasts longer than lean; it may even last indefinitely as far as freezing is concerned.

An equally important factor is the phenomenon called transpiration, which in the present context is the diffusion of water away from a wet region in the concrete toward an exposed dry surface, first discussed in 1965,¹⁶ if an air-entrained concrete structure standing in water or wet soil presents one or more exposed surfaces, transpiration will usually keep the moisture content of the aggregate under the critical point at levels in the structure well below the water or ground line.

Besides being subject to the intrinsic limitations of most aggregates, concrete structures may be also vulnerable because of structural flaws that may develop spontaneously during the bleeding period because of shape of form, or horizontal bars, or faulty curing and finishing procedures. For a discussion of the nature of these phenomena, see Reference 23, Chapter 11.

Scaling Due to Deicers

The use of deicers on non-air-entrained concrete slabs usually results in localized failures near the surface, described as scaling. Experimental evidence indicates that the localized effects are severe because of the dissolved sodium chloride or calcium chloride becoming concentrated in the larger capillary pores of the paste near the surface of the slab. This augmented concentration tends to increase the magnitude of osmotic pressure that develops after or during freezing, and thus makes the destructive effect more severe. Entrained air has the same effect explained above: it prevents the build-up of osmotic pressure in the capillary cavities.

Field experience indicates that with entrained air of normal characteristics, and in the absence of improper finishing procedures, entrained air prevents scaling; however, in laboratory tests, where the concrete is denied the benefit of occasional drying, it does not always appear to be fully effective, and this is probably due to the aggregate particles near the surface becoming critically saturated. For a more complete discussion, see Reference 16.

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The Significance Of Critical Degrees Of Saturation At Freezing Of Porous And Brittle Materials

By
G. Fagerlund

Synopsis: The paper treats the problem "Frost Resistance" as a general problem for all porous materials. The basis is the undeniable fact that well defined critical degrees of saturation exist for all porous materials.

1st part--The difference between the new way of defining critical degree of saturation (as a materials constant) and the usual way (as functions of a combination of properties of material and environment) is discussed. Method of determination is shown and discussed.

2nd part--Possible definitions of moisture conditions are provided.

3rd part--By comparison of the critical degree of saturation and the actual reached in practice the frost resistance can be expressed by a plain figure which makes a rational choice of material possible. The method is exemplified. A method of determination of the actual water content is shown. Hypothesis are put forward as regards frost resistance of layered structures or particle composites and frost resistance at use of thawing salts.

4th part--On basis of the hydraulic pressure theory connections between materials properties and critical degree of saturation are derived. Measurements of amount of ice formed, rate of ice formation and length-changes together with estimations on temperature-permeability relations show the reasonableness of the hydraulic pressure theory. Connections between pore properties and actual degree of saturation are discussed.

Keywords: air entrainment; concretes; deicers; freeze-thaw durability; freezing; ice formation; mix proportioning; modulus of elasticity; moisture content; permeability; Poisson's ratio; pore water pressure; porosity; temperature; water.

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G Fagerlund is a research worker at the Department of Building Materials, Lund Institute of Technology, Sweden. He has worked as consultant engineer from 1962 to 1967. The last five years he has been working with the problem of frost resistance of building materials in general. He received his M Sc in 1962 at Royal Institute of Technology, Stockholm and became Dr Sc in 1973.

THE EXISTENCE OF CRITICAL DEGREES OF SATURATION AT FREEZING

General Discussion

The concept "critical degree of saturation" has got a rather bad reputation even by seriously working scientists. So for instance Powers writes (1):

"Whatever success such theories (about the existence of critical degrees of saturation, the authors remark) have had when applied to clay products, rock or concrete, may be ascribed to constancy of the effect of variable factors not explicitly represented in the analysis. For example, if among a certain group of materials a satisfactory correlation between degree of saturation and damage produced by freezing has been observed, factors other than degree of saturation have been constant or have had a simple, more or less fortuitous relationship to degree of saturation."

In another place Powers writes about concrete aggregates (2):

"Thus we see, that if the water is not uniformly distributed within an aggregate particle at the time of freezing, the critical saturation point for that particle based on its overall capacity might be considerably less than 91,7 % (the theoretically lowest degree of saturation). It is therefore impossible to establish any single value for the critical saturation point that would be a reliable basis for predicting the effect of freezing of aggregate particles either alone or in concrete: obviously this must be true for concrete as a whole."

By his first statement Powers evidently means that a critical degree of saturation as a characteristics of a whole family of materials could reasonably not exist. Such materials properties as porosity, pore-size distribution, strength, permeability etc must have a decisive importance for the amount of water which can be contained within a material despite risk of frost damage. Thus a general critical degree of saturation could not exist.

By his second statement Powers shows the meaninglessness in trying to define a critical degree of saturation since the water content in a specimen or a part of structure often varies across its section. He evidently looks upon the degree of saturation as a mean value throughout the whole materials volume.

Powers' categoric statements, which are representative for many scientists, might easily discourage from each further research work on critical degrees of saturation. However used in a more refined way the concept critical degree of saturation can be extremely useful. at evaluation of the connections between materials structure and frost resistance. This will be shown further on in this paper.

Of course Powers has right in his cited statements, but only from the starting-point of his own assumptions. If the concept critical "degree of saturation" should have any meaning at all it must be defined in a special way. viz. the critical degree of saturation is a materials constant that adopts individual values for each particular material. Each single value is valid for a special combination of materials properties. So for instance the critical degree of saturation for a material like concrete may vary from for instance 0,50 to 0,92 dependent on mix proportions, quality of constituents of the concrete, way of manufacturing, degree of hydration, etc. Frost damage does not occur even at a large number of frost cycles if the actual degree of saturation in a structure does not in any point of the structure exceed the critical degree of saturation in the same point.

Thus, a proper use of the principle of critical degrees of saturation demands, partly that the distribution of moisture in the structure is known, partly that the critical degree of saturation or the combination of materials properties, that determines the value of the critical degree of saturation, is known in all parts of the structure.

Such a condition that the materials properties within the same materials unit may vary throughout the unit, for instance with a layered construction, does therefore not reduce the servicableness of the critical degree of saturation as a criterion on frost resistance, as long as the critical and actual degrees of saturations are known throughout the unit.

Then, why has the critical degree of saturation got such a disrepute? Without doubt this depends on very unlogical ways of treating the concept.

Attempts have been made to find universal critical degrees of saturation that would be valid for a whole group of materials or even for all porous materials. (3), (4, 5) and others. Such attempts are absurd and can easily be rejected by experiments. (6), (7).

The critical degrees of saturation are, as far as we know, always based upon the state of moistening before the first freezing. So for instance the concept "coefficient of absorption" (S_a according to the definition in eq (1)) is often used as a concept synonymous to the critical degree of saturation.

$$S_a = \frac{w_a}{P} \quad (1)$$

All the specimens are consequently stored in water for a long time before the freezing test starts. Hence they all have the same state of

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moistening, correspondent to S_e , before the first freezing. The freezing cycles do normally involve some period where the specimens are placed in water, for instance at thawings. Hence, the degree of saturation changes all the time. Normally it increases with increasing number of cycles. Damage occurs when the increased degree of saturation exceeds the critical value. Therefore the choice of number of cycles is extremely important for the judgement of frost resistance, that is, for the judgement of critical coefficient of absorption.

On the basis of such freezing experiments same authors have tried to find correlations between the coefficient of absorption and the observed behaviour at freezing, (3), (4). Of course this is doomed to failure. There is from a logical point of view no correlation between the coefficient of absorption and the critical degree of saturation. The former is only a measure of the hydraulic properties of the material while the latter is a complicated function of strength, ductility and pore properties of material.

However, once the incompatibility of the coefficient of absorption and the critical degree of saturation is understood, things become more clear. The critical degree of saturation must be determined on specimens where the water content is constant throughout the whole test. Suitably a series of specimen are adapted to different degrees of saturation before the first freezing. This can be done by drying from a wetter condition or by wetting from a dryer condition. The specimens are sealed from water loss.

Each specimen is then frozen and thawed a couple of cycles in air with a reasonable rate of temperature lowering. The dynamic Young's modulus or length or thickness is measured before and after the freezings. The critical degree of saturation can normally be indicated as a very evident knick-point in a diagram residual Youngs modulus or dimension versus degree of saturation.

The scattering around the critical value is normally small if the tested specimens have fairly similar properties, the greater the scattering in properties, the greater the uncertainty at definition of the critical value.

The number of cycles used is without greater importance in this experiment. Since there is no water exchange with the environment, damage does not occur even at many cycles, if the specimen has a lower water content than the critical. This has been experimentally confirmed up to 165 cycles.

However, different materials are more or less ductile which means that a certain transgression of the knick-point value of degree of saturation is more or less disastrous.

In figure 1 is shown the determination of critical degrees of saturation of two almost identical concretes, one is a normal non-airentrained concrete, the other is reinforced with short pieces of steel fibre ($\emptyset$ 0,3 mm, length 25 mm). Each dot represents one specimen with size 40 x 40 x 160 mm³. 14 different specimens are used. S_e is defined according to eq (3).

The critical values, as defined at the knick-point, are the same for both materials which is expected, (eq (25)), but the reinforced specimen gets less damage if S_{CR} is exceeded because of its greater ductility. Hence, in reality the reinforced material can stand more water than the non-reinforced. It can therefore be suitable to supplement the S_{CR} value defined as the knick-point value with information of the slope of the line of $S > S_{CR}$.

The values in fig 1 are obtained after 10 - 13 cycles. In fig 2 is shown principles of the evolution of the dynamic Young's modulus with increasing number of cycles, when the water content is constant. The short time fracture character of frost damage (not fatigue character) is clear from the figure, as well as the relative ease of defining the value of S_{CR} . Often a relatively great decrease in modulus occurs at the first freezing (curves (b) and (c)) even when S is low. This is inevitable. However if no further damage occurs at the following freezings the water content in the specimen is lower than the critical. Curves (d), (e) and (f) are typical for specimen where $S > S_{CR}$.

The results in fig 1 are no exception. By the same freezing technique a large amount of different building materials, at the present more than 60 different qualities and types, have been tested as regards their critical degrees of saturation. The results are based upon more than 2000 specimens. See (8).

In no cases there has been any difficulties at indicating critical values. Therefore, the existence of critical degrees of saturation has been proved beyond each doubt. Their values defined according to eq (3) cover a range of 0,22, determined for a no fines light aggregate concrete, to 0,91 for a clay roofing tile. If consideration is taken to the fact that only a part of the water is freezable the range is further broadened.

Practical Aspects of Determinations of Critical Degrees of Saturation

Since the critical degree of saturation is regarded as a materials constant, the specimens used are as small as possible in order to assure simultaneous freezing in the whole specimen and an even moisture distribution. However, the specimens must be big enough to be representative cells of the material. Besides they must be bigger than the critical size. For a concrete the condition of representative cells gives relatively big specimens. With an aggregate size of 30 mm the diameter of a cylindrical specimen must be at least 100 mm. The need of a big specimen may however bring a conflict with the need of simultaneous freezing. When the temperature of the ambient air is lowered a temperature gradient arises in the specimen. As long as the rate of temperature lowering is moderate the temperature gradient in the specimen is limited. Since the specimen is frozen in air normally a substantial supercooling occurs. Hence, all parts of the specimen may reach a temperature equal to or lower than the ordinary freezing temperature of the pore water, before ice formation is initiated somewhere in the supercooled water. Within a few seconds from initiation of freezing the ice front has penetrated all pores with water potentially freezable at the prevailing temperature. Freezing is then seeded and

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going on simultaneously in the whole specimen even when this is relatively big. Besides most of the water is formed around 0°C without any temperature lowering worth mentioning, if the degree of saturation is fairly high. Therefore, the surface part and the inner parts of the specimen never get any great temperature difference even at big specimens. The principles are shown in fig 3 which shows halves of specimens of two different sizes. The specimen to the right is freezing almost simultaneously while the specimen to the left is freezing with a moving ice front.

It can of course be questioned whether the critical degree of saturation should not be determined on specimens freezing from one side, that is, with a moving ice-front. However, as we see it, this way of freezing brings greater difficulties to determination of the exact value of S_{CR} . Besides, the problem of moving ice front as well as the problem of moisture gradient at freezing can probably be treated theoretically once S_{CR} is known for a small volume of the material freezing simultaneously and with no moisture gradient. Eqs (15)(16).

Normally there is no important moisture gradient through the specimen when freezing starts. This has been confirmed on specimens ($30 \times 30 \times 120 \text{ mm}^3$) of different materials. Those specimens, adapted by drying to different degrees of saturation, have been placed in the deep-freezer and a normal freezing cycle has started. Immediately before 0°C -temperature the specimens were taken out and chopped in pieces. The pieces were dried at $+105^{\circ}\text{C}$. A result is shown in fig 4. The risk of moisture gradients is less the higher the moisture content. Besides the risk ought to be less if the specimens are adapted to proper water content by wetting than by drying. viz at drying the surface of the specimens might reach moisture contents lower than the average aimed at. Then, because of hysteresis wetting - drying, the outer parts of the specimen might not reach the same high degree of saturation as the inner part even at equilibrium in pore-water pressure through the whole specimen. Therefore the average water content is normally less than that in the wettest part of the specimen. The principles of this is shown in fig 5.

A suitable way of reaching a certain degree of saturation in a specimen is to use relatively dry specimens (drier than S_{CR}), put each specimen separately in a vacuum chamber, evacuate the pore-air to a certain residual pressure for a few minutes and then let the water into the chamber. Fig 6. In this way, by choosing suitable pressures, a spectrum of specimens of different degrees of saturation is obtained. Since every part of the specimen has reached its degree of saturation by wetting no problems of hysteresis exist.

It is, however, not quite sure that S_{CR} will get the same value for specimens dried as for specimens wetted to their water contents at freezing. Fig 5 shows two hypothetical moisture equilibrium curves. The drying curve do always correspond to a higher suction value (pF-degree). Hence, at a certain moisture ratio, the water is located in smaller pores if the moisture ratio has been attained by drying than if it is attained by wetting. It will later on be shown that this means that the critical degree of saturation is minimum when it has been attained by drying from

a complete wet condition.

Normally, the pore water pressure of a specimen is not determined by the extreme wetting- or drying curves but by a scanning curve between the two extreme-curves. Fig 5.

However, by experiments it seems as if S_{CR} is not influenced to any great extent by the way of adapting specimens to proper water contents. Besides, the effect ought to be greatest at the first freezing. After a couple of freezings moisture is probably redistributed in the specimen in about the same way despite method of adaptation.

In our test method the specimens are mounted on rotating wheels in order to facilitate the mounting of specimens in the freezing chamber, to avoid effect of temperature gradients in the ambient air and above all to avoid moisture redistribution in coarse-pored materials because of gravitational force. The wheels rotate 1 rpm. The rotational direction is changed for each full revolution in order to make temperature measurements possible.

The freezing apparatus consists of an ordinary deep-freezer. It has been provided with two fans on the lid, with a temperature sensor, with a controle cell of copper containing 25 grams of pure water and a thermocouple and with two heating elements.

The system of regulating the temperature will not be described in detail. It will be published elsewhere (8). However, described in brief: The temperature in the box is measured by the sensor. The information goes to a tyristorized temperature regulator. The actual temperature is compared with the temperature aimed at. This in turn is provided to the regulator from a potentiometer mechanically regulated by a revolving disc on which periphery the freezing cycle is cut. The freezing box is working with full capacity for which reason any divergence from the proper cycle is adjusted by the regulator supplying more or less effect to the heating elements in the box.

The disc rotates one round per 6 hours. 5 hours correspond to the freezing part and 1 hour to the thawing part of the cycle. However, by a microswitch the disc is stopped at the lowest temperature, $\approx -18^{\circ}\text{C}$, for 1,5 à 3 hours and at $\approx +5^{\circ}\text{C}$, for 3 multiples of 1,5 à 3 hours. The first stop brings the specimen down to -18°C and the last makes a complete thawing possible.

The controle cell is used as a guard of the function of the temperature regulator. viz, when corrections are made for the rapid freezing caused by supercooling of the water in the cell, it should always take the same amount of time to freeze the water. The freezing apparatus is shown in fig 6 and the cycle in fig 7.

It must be noticed, that only the air-temperature is carefully controlled. Hence the rate of temperature lowering of each specimen can be quite different dependent on its heat capacity, its total amount of water and its amount of freezable water at different temperatures. Beside its surface/volume ratio may influence the rate of temperature lowering,

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since a high such ratio causes a high rate of heat loss and consequently a high rate of freezing, cf eq(39). Hence, in order to get fair comparisons between different materials, the specimen size and form ought to be the same for all materials, or the cycle ought to be somewhat changed when the specimen size is changed. The difference in surface/volume-ratio is sometimes rather big for imaginable specimens; 0,5 for a cylinder $\varnothing$ 100 x 200 mm³ and 1,1 for a prism 40 x 40 x 160 mm³.

The rate of temperature lowering is in average 4,6 °C/h, faster at the start and the end of the freezing cycle and slower at the middle.

However, as shall be discussed later, it is not so much the rate of temperature lowering that is interesting as the absolute temperature difference between the surface of the specimen and the ambient air. This difference determines the rate of heat loss from the specimen, Eq(38)

If the degree of saturation is defined according to the physically correct eq (2) there is a need of knowledge of non freezable water contents in the specimen at the lowest temperature used. At our institution non freezable water contents have been determined for 48 different materials and qualities of materials. The apparatus used is a "relatively adiabatic" calorimeter built at the institution. The experiments are performed by thawing of specimens with different degrees of saturation frozen to -25 °C, -13 °C and -8 °C.

In order to define proper values of S, it is essential to know the total openpore-volume as accurate as possible. This has therefore been determined by vacuumtreatment of dried specimens (+105 °C or +50 °C dependent on the material). The minimum pressure is about 2 mm Hg kept for some hour after which water is let into the specimens. The specimens are then stored for many days in the water before determinations of pore-volume, volume and density.

DEFINITIONS OF CRITICAL MOISTURE CONDITIONS

The physically correct definition is:

$$S = \frac{w_f}{w_f + 1} \quad (2)$$

Sometimes it is more convenient to use the following definition:

$$S_e = \frac{w_e}{P} \quad (3)$$

Definition (2) as well as (3) needs the pore volume to be known. For some materials like cellular concretes and fines concretes with porous aggregate, the exact determination of open porosity is difficult. In this case the moisture ratio can be used.

$$u = \frac{Q_{we}}{Q_{dry}} \quad (4)$$

The three definitions are coupled together so that the existence of for instance a critical degree of saturation according to eq (2) is accompanied by the existence of a critical degree of saturation according to eq (3) and a critical moisture ratio according to eq (4).

The difference between definitions (2) and (3) is greater the greater the non freezable water contents. So for instance $S_{eq}(2) \approx S_{eq}(3)$ for a material like well burnt clay brick. For a material like a dense cement paste the difference is considerable.

USE OF CRITICAL DEGREES OF SATURATION AT EVALUATION OF FROST RESISTANCE

General Discussion

The fact that critical moisture conditions evidently exist, make a rational judgement on the frost resistance of different materials possible.

The pre-requisite condition for this is however, that the moisture conditions reached in practice are known.

Then the frost resistance is defined:

$$\text{FROST RESISTANCE} = s = S_{CR} - S_{ACT} \quad (5)$$

By using this definition all materials are treated in the same way despite their densities, porosities and non freezable water contents are quite different.

Often the non freezable water contents expressed as fraction of total pore volume are about the same for many materials. In this case the frost resistance can be expressed:

$$s_e = S_{eCR} - S_{eACT} \quad (6)$$

which equation expressed in moisture ratios is:

$$s_u = s_e = \frac{u_{CR} - u_{ACT}}{u_o} \quad (7)$$

A comparison between the frost resistance of two materials A and B can be done in the following way.

$$\frac{s_A}{s_B} = \frac{(S_{CR})_A - (S_{ACT})_A}{(S_{CR})_B - (S_{ACT})_B} \quad (8)$$

When the definition of moisture condition according to eq (3) is used, the comparison of frost resistance gets the form:

$$\frac{s_A}{s_B} = \frac{[(S_{eCR})_A - (S_{eACT})_A] [1 - K_B]}{[(S_{eCR})_B - (S_{eACT})_B] [1 - K_A]} \quad (9)$$

where K is defined:

$$K = \frac{w_{nf}}{P} \quad (10)$$

A test method is consequently divided in two parts of quite differ-

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rent character.

- part 1: Determination of critical degrees of saturation according to the principles discussed above. The same type of method is used for each material.
- part 2: Determination of actual degrees of saturation. The method should from a theoretical point of view be designed according to the actual way of using the material.

The problem of determination of frost resistance is now divided in two parts.

- part 1 principally dependent only on materials properties.
- part 2 for each material principally dependent only on properties of the environment.

One of the main difficulties of the problem of frost resistance has been its utmost complexity. This in turn is above all dependent on the problem being a coalescence between the materials own properties and properties of the environment in which the material is used.

In ordinary used freezing tests the same coalescence is maintained. So for instance consideration is taken to different ways of using a certain material by varying the "wetness" of the test or the number of cycles.

By the new way of defining the concept frost resistance, materials properties and properties of the environment are separated from each other which leads to the following advantages:

Theoretically, the test method takes consideration to different ways of using the same material.

The determination of S_{CR} is rapid since only a few cycles are needed. See above. The determination of proper S_{ACT} 's is more difficult but normally simple water uptake tests are sufficient.

The frost resistance is quantified for which reason materials can be ranked according to their durability.

The method gives great potential possibilities of making connections between materials structure and frost-resistance clear. See below. Besides, for instance the frost resistance of materials combinations and composite materials could be better understood.

A comparison by Arni & al (9) of the four methods according to ASTM of testing frost resistance of concrete is a good example of the confusions arising, when properties of materials and properties of the environment are mixed together.

In fig 9 is shown these authors result. Each pile within one test

method corresponds to one type of concrete. Evidently, the judgement of the frost resistance is completely dependent on which method was chosen.

However the result can be logically interpreted by use of the concept critical degree of saturation. For each concrete type S_{CR} is the same in all four methods (possibly there is some variation because of differences in rate of freezing, see above), but S_{ACT} varies. Evidently $S_{ACT} \leq S_{CR}$ in the methods "rapid air" and "slow air" whereas $S_{ACT} > S_{CR}$ in the methods "rapid water" and "slow water". An idea of the values of S_{ACT} in the four methods can be obtained by analysing the data in the original report. In Table 1 are listed approximative values of total time in unfrozen water, t_w , and in air, t_a , per cycle. Since the more essential drying occurs when the pore-water is unfrozen, the time in air at temperatures down to -5°C is listed in the table, t_{aw} . -5°C is chosen because supercooling of the pore water down to that temperature normally occurs.

The table shows that the specimens ought to have the highest degree of saturation at method slow water since each cycle involves 29 hours in water and the freezing are at maximum continued for 300 cycles.

The specimens ought to be driest at method "slow air" since each cycle involves 1,5 hours drying in air just before freezing.

A comparison between table 1 and fig 9 shows the direct correlation between degree of saturation at test and damage at freezing. The result is therefore an excellent confirmation of the fact that the degree of saturation is the variable in freezing tests with dominating significance. So for instance rate of freezing seems to be quite inferior, cf table 1, which increases the possibility of a practical use of the concept critical degree of saturation.

Practical Aspects

The definition of frost resistance according to eq (5) is of course only valid for materials with $S_{CR} < 1,0$ that is for normal building materials. A material with only a few percent pores filled with freezable water has $S_{CR} = 1,0$ since the expansion at ice formation is too small to give any damage. If at the same time $S_{ACT} = 1,0$ the frost resistance according to eq (5) is zero despite the material is extremely frost resistant. Another such case is a material where the pores are so narrow that the water cannot freeze at ordinary temperatures. Even in this case $S_{CR} = 1,0$. $S_{ACT} = 1,0$ also since the pores are filled already by capillary condensation. As a consequence the frost-resistance is zero, according to eq (5). However, in those two rare cases S_{CR} can be regarded as greater than 1,0 despite this is impossible from a theoretical point of view. Hence the frost resistance $s > 0$ but its absolute value is unknown and consequently the frost resistance cannot be compared to that of other materials.

The safety term, s , is used instead of an ordinary safety factor in order not to underestimate the frost resistance of materials with high

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critical values.

Any systematic smaller error at determination of the exact pore volume, for instance use of unsufficient vacuum before saturation, is almost eliminated at use of eqs (5), (6) or (7). As mentioned earlier the exact determination of actual degrees of saturation may be difficult since this demands an exact knowledge of all data on climatic conditions. After that, the actual environment can eventually be reproduced and the moisture condition reached eventually be measured or calculated with the aid of advanced moisture mechanics.

However, the problem of determination of S_{ACT} can be substantially reduced by use of simple water uptake tests. viz. a minimum condition of frost resistance of a material used in a normal way is, that the degree of saturation reached on a dangerous depth (see below) at a short time suction from a free water surface is less than the critical.

This short time moisture condition can easily be discerned as the knick-point value in a diagram degree of saturation at a water uptake test according to fig 10 (or moisture ratio) versus root of time or log time. The knickpoint corresponds to the sudden decrease in rate of water uptake, when the water front has penetrated the total top surface of the specimen. The knickpoint value may be somewhat dependent on the thickness of the specimen. The knickpoint is easier to discern the thinner the specimen. Examples of the determination of knick-point values of certain concretes is shown in fig 11. Examples of the effect of specimen thickness on the knick-point value is shown in fig 12.

The specimen normally continues to absorb water after the occurrence of the knick-point, but with a considerably reduced rate. Hence, at a refined judgement of frost resistance not only the knick-point absorption but the rate of this later secondary stage absorption must be considered.

However, simple water uptake tests can be used as a criterion on the value of S_{ACT} after which eqs (8) or (9) can be used for a comparison of frost resistance of different materials. The pre-requisite condition for this is however that the following factors are considered.

S_{CR} can normally be defined as the knick-point value in a diagram, residual Young's modulus versus degree of saturation.

The knick-point value of S_{CR} must be supplemented with information of the effect of a transgression of S_{CR} , that is, of the slope of the curve for $S > S_{CR}$, cf fig 1.

$(S_{ACT})_{min}$ can be defined as the knick-point value in a diagram degree of saturation versus time at a capillary water uptake.

The knick-point value must be supplemented with information of the "long time absorption", and of the rate of drying after a finished absorption.

Examples of a Determination of Frost Resistance

In table 2 are shown typical results of a determination of frost resistance based upon the new principles. The materials are all no fines concretes with porous aggregate (Leca). The frost resistance is defined according to eq (7).

The degrees of saturation are calculated as if all pores were open, which of course gives somewhat too low values. The critical moisture ratio is very well defined for all 4 materials. Fig 13 shows the result for one of the materials.

The mean frost resistance of the four materials related to the resistance of type 1 at knick-point absorption is shown graphically in fig 14. Evidently the durability is reduced for all materials with increasing time of water storage. The materials 3 and 4 both get a negative safety term at 10 days storage while material 1 is very durable even after a very long time of water absorption.

All four materials show good durability in practice which they ought to do according to the test result. However, on basis of the test a use of materials 3 and 4 is not recommended in a situation where they have free access to water and where freezing might occur. In such places material 1 is superior.

Use of Critical Degrees of Saturation at Multi-layer Structures and Multi-phase Materials - Hypothesis

Fig 15 shows an example of multi-phase materials. Material A shall be combined with material B. Their critical degrees of saturation are S_{CR}^A and S_{CR}^B . At water uptake for a long time they reach different actual degrees of saturation, S_{ACT}^A and S_{ACT}^B . The condition $S_{CR}^A > S_{ACT}^A$ is valid for both materials for which reason they both have a good frost resistance when used single. Fig 15a.

The two materials shall now be combined as in fig 15b, that is, as a layered structure or as in fig 15c, that is, with material B as particle phase in a matrix of material A. Fig 15b represents for instance a rendered wall (or why not the upper part of a concrete slab with different properties of the surface layer and the normal concrete (10)). Fig 15c represents for instance a concrete with porous aggregate.

In fig 15b S_{ACT} will now get exactly the same value as when the two materials were single. Hence, there will be a jump in S_{ACT} at the interphase. In fig 15c S_{ACT}^B can be at maximum just as high as in the case single material. Normally material B is surrounded by a more dense material, for instance cement paste. Then according to eq (59) the particles could not be filled as when they are single since water in the paste pores seal the particles.

Probably S_{CR} will vary at the interphase. Water from the more dense material will be forced into the more porous and with greater ease than within the dense material itself. Hence S_{CR}^A will be raised

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locally. In material B the degree of saturation is therefore raised at the interphase. Besides water can only be forced into the interior of material B at freezing. As a consequence S_{CR} brought to decrease at the interphase. If this happens the dangerous condition $S_{CR} < S_{ACT}$ might occur at the interphase despite the two materials are frost resistant at the same moisture condition when they are isolated from each other.

The important case with a transitional zone between the two materials is discussed in (14).

Use of Critical Degrees of Saturation at Freezing in Presence of Deicing Agents - Hypothesis

It is a well-known fact that frost damage is increased in presence of deicing agents such as $CaCl_2$, $NaCl$.

This is possibly an effect of a decrease in S_{CR} and/or an increase in S_{ACT} .

The decrease in S_{CR} should be an effect of additional forces because of osmotic pressure (12). However, at high salt concentrations the effective degree of saturation according to eq (2) at a constant water content is decreased since the freezable water content is decreased. Therefore, a pessimum salt concentration can be expected. This is also confirmed by experiments in which a concentration of 3 to 5 % is normally found to be most dangerous.

An eventual increase in S_{ACT} because of thawing/surface gets wet for very long periods. The prolonged drying depends on the lowering of the vapor pressure of the water and is confirmed by experiments, (13). Another eventual " S_{ACT} -raising effect" is redistribution of water within the material. Regard a concrete slab with the same moisture content across its thickness. A salt solution is poured on the top surface of the slab. Then, because of concentration gradients a redistribution of water might occur and the surface layer gets wetter than in the original state.

Thus the hypothesis is, that in presence of deicing salts the gap between S_{CR} and S_{ACT} gets smaller than at "ordinary" freezing. Consequently the frost resistance is diminished.

USE OF CRITICAL DEGREES OF SATURATION AT EVALUATION OF RELATIONS BETWEEN MATERIALS STRUCTURE AND FROST RESISTANCE

In General

Informations on relations between materials structure and frost resistance can be gained by analysing the effect of materials properties on the values of S_{CR} and S_{ACT} . Such an analysis has been carried through more comprehensively in (15).

Influence of Materials Properties on the Critical Degree of Saturation

At first, there is a need of a model for frost damage.

A successful model used in our work is provided by Powers' hydraulic pressure theory (16).

This theory predicts the existence of critical distances at freezing. Such a critical distance is the critical thickness which is the thickest completely water saturated slice of a material that is not damaged by freezing.

The critical thickness can be expressed (15);

$$D_{CR} = \sqrt{\frac{8 \cdot \sigma_B \cdot B}{0.09 \cdot w_f \cdot \frac{d\beta}{dt}}} \quad (11)$$

If the water saturated material is situated within a specimen that is not saturated eq (11) can be expressed (15):

$$D_{CR} = \sqrt{\frac{8 \cdot \sigma_B \cdot B (1 - P (1 - S_e))}{0.09 \cdot w_f \cdot \frac{d\beta}{dt}}} \quad (12)$$

At the derivation, it is assumed that the permeability, B, is constant. This is however a wrong assumption. For materials with a minor part of non freezable water the permeability at lower temperatures is extremely reduced because of ice filling up and blocking the pores. cf eq (42).

Another critical distance is the critical wall thickness of a spherical saturated material surrounding an air filled pore. This thickness is normally the same as Powers' spacing factor, $\bar{L}$. (16). The connection between the two critical distances is (17);

$$D_{CR}^2 = \frac{8}{3} \left(\frac{\bar{L}_{CR}^3 \cdot \alpha}{3} + \frac{3 \cdot \bar{L}_{CR}^2}{2} \right) \quad (13)$$

The critical radius of a spherical freezing material, R_{CR} is related to D_{CR} through eq (14):

$$R_{CR} = D_{CR} \frac{\sqrt{3}}{2} \quad (14)$$

This later model can be used for the critical size of a saturated piece of aggregate.

Warris (17) treats the important case where an ice front is propagating into the interior of a material. The excess water created at ice formation is supposed to be forced only into the interior of the specimen. As a consequence a hydraulic pressure is created.

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The maximum depth of water transport $(X_{us} - X)$, can be obtained from a heat balance equation in which $\dot{Q}_{us}$ neglected the heat loss at lowering the temperature (damage is supposed to occur at the major ice formation in the neighbourhood of 0°C). Then according to (15) the connection between D_{CR} and the critical "depth of unsaturation" is:

$$(X_{us} - X)_{CR} = \frac{D_{CR}^2}{8} \cdot \frac{1}{dx} \cdot \frac{w_f}{(1 - P(1 - S_e))(w_f + P((S_e)_x - S_e))} \quad (15)$$

dx is the thickness within which ice is forming simultaneously. The value of dx is dependent on the degree of supercooling and on the rate of temperature lowering. However, since the derivation av D_{CR} assumed simultaneous freezing in the whole slice, dx ought to be greater than $\frac{D_{CR}}{2}$. When there is no moisture gradient eq (15) is changed to eq (16).

$$(X_{us} - X)_{CR} = \frac{D_{CR}^2}{8} \cdot \frac{1}{dx} = \frac{D_{CR}}{4} \text{ when } dx = D_{CR}/2. \quad (16)$$

Warris (17) gives eq (16) in somewhat different form. $\frac{1}{dx}$ is replaced by the surface-volume ratio of the specimen.

Eqs (15) and (16) are oversimplified, especially since they assume that all excess water is forced only into the specimen and above all since D_{CR} in reality is determined by a permeability reduced by ice formation, while in eqs (15) and (16) the permeability is constant and equal to the permeability of the unfrozen material. Both those factors make $(X_{us} - X)_{CR}$ calculated from eq (16) too small.

The occurrence of critical distances is not only predicted by the hydraulic pressure theory but also by Powers' theory of microscopic ice lense segregation. (1,12).

The existence of critical thicknesses has been confirmed by experiments at our institution. Specimen were cut with area $30 \times 30 \text{ mm}^2$ and variable thicknesses. They were vacuum saturated, weighed, wrapped in plastic foil or put in small beakers with water and then frozen a couple of times to about -18°C . After the final thawing they were vacuum saturated again and weighed. The eventual increase in weight is a measure of volume change caused by freezing. Normally visual inspection was satisfactory. 4 types of cellular concrete, 1 type of sand-lime brick and two types of clay bricks were tested.

All specimen of sand-lime brick and cellular concretes were completely destructed, which means that the critical thickness is less than 1,7 mm. This is confirmed by freezing experiments on bigger specimens, where the surface damage at $S > S_{CR}$ is a scaling of very thin flakes or even crumbling. The crack system of the cellular concrete was mainly parallel to the surface. The distance between the cracks was about 0,5 mm.

The clay bricks had very evident critical thicknesses of about

12 - 14 mm. See fig 16. On specimens thinner than D_{CR} no damage could be observed. An ice-crust covered the specimens when they were frozen in air which confirms that ice is actually forced out of the specimen at freezing. This water was regained by the specimen at thawing.

Since critical distances at freezing evidently exist the existence of critical degrees of saturation is a necessary consequence.

The problem of finding a theoretical expression of S_{CR} is reduced to the problem of finding a geometrical connection between the distance and the degree of saturation.

A general equation for S_{CR} is (15).

$$S_{CR} = 1 - \frac{l_{CR}}{P(1 - K)} \quad (17)$$

Where the critical air content l_{CR} is coupled to the distance between air filled pores. Such expressions are given by Powers (16), Warris (17) and Larson et al (18). All those expressions suppose that the air filled pores are spherical.

Warris (17) bases his expression on the critical thickness, D_{CR} . His expression is chosen since the pores may have an arbitrary pore size distribution.

$$l_{CR} = \frac{1}{1 + \alpha \cdot \frac{D_{CR}}{2}} \quad (18)$$

Powers' (16) expression for l_{CR} is similar for $l_{CR} > 0,188$.

$$l_{CR} = \frac{1}{1 + \alpha \cdot \bar{L}_{CR}} \quad (19)$$

Insertion of eq (18) or (19) in (17) gives:

$$S_{CR} = 1 - \frac{1}{(1 + \alpha \cdot \frac{D_{CR}}{2})P(1 - K)} \quad \text{or} \quad S_{CR} = 1 - \frac{1}{(1 + \alpha \cdot \bar{L}_{CR})P(1 - K)} \quad (20)$$

Insertion of eq (12) in (20) make it possible to express S_{CR} in materials properties:

$$S_{CR} = 1 - \frac{1}{(1 + \alpha \sqrt{\frac{2 \cdot \sigma_B \cdot B(1 - P(1 - S_e))}{0,09 \cdot w_f \cdot dB/dt}})P(1 - K)} \quad (21)$$

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S_{CR} can however not be calculated from eq (20) as far as the specific surface, α , of the air filled pores is not known.

By knowledge of the pore size distribution of such pores which can be air filled, it is possible to calculate the variation of α with varying S_{ACT} .

$$S_{ACT} = 1 - \frac{l_{ACT}}{P(1-K)} \quad (22)$$

Where l_{ACT} is a certain function of α_{ACT} at a certain pore size distribution and under the assumption of a certain distribution of water between the pores.

$$l_{ACT} = f(\alpha_{ACT}) \quad (23)$$

Warris (17) has shown a theoretical method of calculation. Eq (20) can be drawn with $\alpha \cdot \frac{D_{CR}}{2}$ or $\alpha \cdot \bar{L}_{CR}$ as independent variable and with $P(1-K)$ as parameter. These functions are independent on the materials properties.

Eq (22) can also be drawn with $\alpha \cdot \frac{D_{CR}}{2}$ or $\alpha \cdot \bar{L}_{CR}$ as independent variable, which means a division of the equation with the critical distance. However this curve is quite dependent on the materials properties via the function (23) and on the properties determining the value of the critical distance, $\bar{L}_{CR}$ or D_{CR} .

The intersection of the two curves gives the value of S_{CR} . An example is shown in fig 17. $(S_{CR})_{min}$ is obtained when the pore water is located in the smallest pores since α is minimum in this case.

If the aim is to study the influence of one single structural parameter on S_{CR} , it must be observed, that each change, that according to eq (21) increases the value of S_{CR} , as a consequence of this, contributes to a decrease of α , that is, to a decrease of S_{CR} . So for instance a doubling of tensile strength can never correspond to an increase of S_{CR} according to eq (21) with all parameters except σ_B constant.

An example is shown in fig 17. The doubling of σ_B gives an increase of D_{CR} by a factor 1,41 according to eq (11). Then according to eq (21) S_{CR} is increased from 0,34 to 0,50. However because of the increase in D_{CR} the curve $S_{ACT} = f(\alpha)$ is displaced towards the right with a factor 1,41. The new intersection between the curves of S_{CR} and S_{ACT} give the new value of $S_{CR} \approx 0,39$.

In the same manner an already exploited part of the strength does not influence the value of S_{CR} in the same proportion that the residual strength is influenced. (However it might influence S_{ACT}).

A proof of the correctness of eqs (17), (18) and (19) can be obtained by knowledge of the critical degree of saturation, and the specific

surface of the air filled pores. Approximate specific surfaces of the coarse pores have been measured for two of the cellular concretes and the two clay bricks for which D_{CR} and S_{CR} were experimentally determined. The water was assumed to be present in the smallest pores at all degrees of saturation. The measurements were made with linear traverse technique on magnified photographs of ground surfaces. Then equations from (16) were applied in order to determine the connection between air content, l_{ACT} , and specific surface, α_{ACT} , (eq (23)). Those equations are based on spherical pores whereas the pores in the clay bricks were more elliptical. Eq (19) was used for calculation of L_{CR} after which D_{CR} was calculated from eq (13). The calculated values of L_{CR} and D_{CR} are given in table 3 together with experimental values of D_{CR} .

The theoretical critical thicknesses are about the same for both types of cellular concretes which is expected because of the same structure of the materials. Besides the values are reasonable since thin slices, 1.7 mm, have been delaminated at freezing.

The calculated D_{CR} -values of the two bricks are of the same order of size as the measured values. For the underburnt brick the agreement is perfect. The slight deviation may for instance be dependent on the assumption of spherical pores. Use of eq (18) instead of eq (19) give about the same D_{CR} values for the cellular concretes but smaller values for the bricks.

The validity of eq (21) is limited by the following condition based on the ductility of the material (15).

$$S_{CR} \leq 0.917 + \frac{\epsilon_B \cdot 3(1 - 2\nu)}{1.09 \cdot P(1 - K)} \quad (24)$$

For a completely brittle material, $S_{CR} \leq 0.917$. For the surface layer with thickness $D_{CR}/2$ of a materials unit or for a materials unit smaller than the critical size, $S_{CR} = 1.0$.

In the following the connections between materials structure and the parameters determining the values of S_{CR} and S_{ACT} are discussed very briefly.

Specific Surface--The specific surface, α , of the air filled pores is one of the most important properties determining S_{CR} which is clear from eq (21). The smaller the air filled pores the higher the value of S_{CR} at constant materials properties. This has also been confirmed by experiments. See for instance table 3 where the two cellular concretes have about the same materials properties except the size distribution of coarse pores expressed by α_{CR} .

Thus, the often noticed positive effect as regards frost resistance of diminishing the size of air bubbles in concrete is probably a result of the rise of the value of S_{CR} at the same time as S_{ACT} is constant if the air content is constant.

For a concrete with no air entrainment the coarse compaction pores

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are distributed so far from each other that they could not serve as recipients, $L > L_{CR}$. On the other hand the capillary pores are very small ($< 0,1\mu$). Hence their specific surface is very high ($\alpha > 60000 \text{ mm}^{-1}$). As a consequence, S_{CR} of the material is determined by the condition: $S_{CR} = 0,917$ for the material that is left when the compaction pores are omitted.

The following equation can be derived for S_{CR} of a non air entrained concrete (15). The basis is wellknown data on the physical properties of cement paste (20).

$$S_{CR} = \frac{w_o/c - \beta(0,19 + 0,25 \cdot k)}{1,09(w_o/c - \beta(0,19 + 0,25 \cdot k) + 1000 \cdot l_o/c)} \quad (25)$$

Where k expresses the amount of non freezable water content as multiple of the amount of non evaporable water (15).

$$K = k \cdot \frac{0,25 \cdot \beta}{w_o/c - 0,19 \cdot \beta + 1000 \cdot l_o/c} \quad (26)$$

S_{CR} calculated from this equation adjusted to $(S_e)_{CR}$ is marked out in fig 1. The agreement with measured values is excellent. The same good agreement have been measured for cement mortars (7).

Strength--The strength of a porous material is intimately coupled to its porosity, its pore size distribution, its grain size distribution and also to its age at constant porosity (for instance different strength-porosity connections must be valid for concretes at different degrees of hydration). For a heterogenous material like concrete it can easily be proved that the amount of dispersed particles (aggregates), size of the particles, affinity between the particles and the matrix and the elastic properties of the matrix and particles highly influence the strength-porosity relationship. All those parameters have been extensively discussed in (14).

Equations which express the strength-porosity relatively good are (14).

In the neighbourhood of the critical porosity, (for instance as a measure of effect of hydration on strength) it is valid.

$$\sigma = \sigma_o \left(1 - \left(\frac{P}{P_{CR}} \right)^n \right) \quad \text{where } n \approx 1,0 \quad (27)$$

$$\text{or} \quad \sigma = q \cdot \ln \frac{P_{CR}}{P} \quad (28)$$

Where P_{CR} for a concrete is a function of the mix proportions (14): For an ordinary concrete or cement paste P_{CR} is:

$$P_{CR} \approx 0,913 \cdot C \cdot w_o/c + 1 \cdot 1000 \quad (29)$$

σ_0 or q is a fictive value. It is determined by the amount of aggregate, size of aggregate etc. Normally σ_0 is reduced with increasing amount of aggregate.

For concretes with the same degree of hydration, the same type and amount of aggregate the following equation can be used over a greater porosity range:

$$\sigma = \sigma_0 (1 - P)^k \quad (30)$$

More nuanced expressions are given in (14).

Theoretically it is the strength of the water saturated material that should be inserted in eq (21). Besides it is the residual strength after reduction because of an eventual exploited part that should be used.

Ductility--The ductility of a material can be expressed:

$$\epsilon_B = \frac{\sigma_B}{E_B} \quad (31)$$

σ_B as well as E_B are functions of the porosity and pore structure. σ_B is even a function of pore size and general structure of the material.

A simple connection between porosity and ductility is:

$$\epsilon_B = \frac{\sigma_0 (1 - P)^{k_1}}{E_0 (1 - P)^{k_2}} = \epsilon_0 (1 - P)^{k_1 - k_2} \quad (32)$$

Where $k_2 \approx 4$ for a well cured concrete (14) and $k_2 \approx 3$ for a cement paste (14).

k_1 is quite dependent on the pore structure etc. However normally $k_1 > k_2$. $k_1 \approx 6$ is not impossible for a concrete (14). Hence the ductility is increased with decreasing porosity. Increasing degree of hydration and decreasing water cement ratio are therefore favourable as regards ductility and S_{GR} . This is also confirmed by experiments (14).

Poissons ratio--Poissons ratio is almost independent on porosity as far as this adopts normal values.

Non freezable water content--The freezing point of water in a pore is a function of the pore radius. On basis of the theory of capillary condensation the following simplified equation can be derived (19). It is valid for a material in equilibrium with a high relative humidity

$$r = -\omega \cdot \frac{2 \cdot \sigma_{LG} \cdot M}{\rho_L \cdot \Delta H} \cdot \frac{1}{\ln\left(\frac{T_0 - \Delta T}{T_0}\right)} + 19,6 \cdot 10^{-10} \cdot \sqrt{\frac{1}{\Delta T}} \quad (33)$$

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Where the second term is the thickness of the adsorbed layer and the first term is the "Kelvin radius". ΔH is a function of temperature (19). Thus the smaller the pore, the lower the freezing point. In fig 18 is shown the pore size distribution calculated from freezing point depressions determined by adiabatic calorimeter thawing experiments and two determinations by mercury porosimeter. The material is sand lime brick. The disagreement could be an effect of hysteresis absorption-desorption since mercury porosimeter is an absorption process.

Since the adsorption isotherm is a function of the pore size distribution there must be some connection between the isotherm and the non-freezable water content. Such an approximate expression is:

$$\Delta T = - \frac{R \cdot T_o (T_o - \Delta T)}{\Delta H} \cdot \ln p/p_s \quad (34)$$

Thus by knowledge of the amount of water absorbed at different relative humidities, the non freezable water content at different temperatures can be determined (19), (20).

In fig 19 is shown the upper part of the absorption and desorption isotherm determined by experiments (21) and calculated by use of eq (33). The material is the same sand lime brick as in fig 18. The agreement with the adsorption isotherm is satisfactory. However, since it is very difficult to experimentally obtain the isotherm in the high pressure range in question it is easier to make the determinations of non freezable water content via special experiments. (Perhaps the knowledge of non freezable water contents could even be used as a very easy means of calculating the isotherm in the high pressure range).

Owing to pore size restrictions on ice formation, pore water in isolated capillaries could be unfrozen at low temperatures because of supercooling (22). This is confirmed by thawing experiments on specimens frozen to -25°C and -6°C . Fig 20 shows an example of this. Eq (33) is therefore somewhat limited especially for dense concretes where the waterfilled cement gel could not freeze until ice formation is nucleated in the pore at temperatures lower than the normal freezing temperature. If the surrounding pores are very narrow the ice in these isolated pores could be formed by homogeneous nucleation at $\approx -40^{\circ}\text{C}$ (23). Then at this temperature a large amount of ice would be formed almost simultaneously and the specimen destructed since its permeability is low at this stage.

Rate of ice formation--The ice formation can be divided in two or three stages:

Stage 1--Rapid ice formation when supercooled water is nucleated. The temperature of the specimen is then normally raised if the amount of large pores is great. If the process is adiabatic the following mean rate of ice formation is obtained:

$$\frac{d\beta_o}{dt} \cdot w_f = \frac{\Delta T_o}{\rho_w \cdot \Delta h \cdot \Delta t} (\gamma_p \cdot c_p + S_e \cdot P \cdot \rho_w \cdot c_w) \quad (35)$$

Where Δt is the time needed in order to raise the temperature of the specimen. Rate of ice formation is however greatest close to the spot of nucleation. The mean rate of ice formation is therefore dependent on the size of specimen. According to (22) the rate of ice front propagation at nucleation is about $10 \text{ mm} \cdot \text{s}^{-1}$. The interval Δt can therefore be expressed as a function of size of specimen (15).

$$\Delta t = \frac{R}{v_{\text{ice}}} \approx 100 \cdot R \approx 300 \cdot \frac{V}{A} \quad (36)$$

It seems logical not to take the whole specimen in consideration when Δt is calculated but only the critical sphere of the material eq (14). By use of eqs (14) and (36) eq (35) is changed to;

$$\frac{d\beta_o}{dt} \cdot w_f = \frac{\Delta T_o \cdot 2}{\rho_w \cdot \Delta h \cdot 100\sqrt{3} \cdot D_{CR}} (\gamma_p \cdot c_p + S_e \cdot P \cdot \rho_w \cdot c_w) \quad (37)$$

Note: the permeability at this early freezing is considerably greater than at the subsequent freezing. This influences the value of D_{CR} .

Stage 2--Normal ice formation. The rate of ice formation in this stage is proportional to the temperature difference between ambient air and specimen surface.(8).

$$w_f \cdot \frac{d\beta}{dt} = k (\theta_{\text{SPEC}} - \theta_{\text{AIR}}) \quad (38)$$

Where the konstant k is dependent on convection of the air and of the surface-volume ratio of the specimen.

A heat balance equation for the already frozen zone like the one leading to eq (15) leads to:

$$w_f \cdot \frac{d\beta}{dt} = \frac{1}{\Delta h \cdot \rho_w} \{ \gamma_p \cdot c_p + \rho_w \cdot K \cdot P \cdot c_w + \rho_w \cdot P (S_e - K) c_i \} \frac{d\theta}{dt} \quad (39)$$

In this expression γ_p and c_p both decrease proportional to porosity.

Calculations show that ice formation in stage 1 is 4000 à 6000 times greater than in stage 2 if $d\theta/dt \approx 6^\circ\text{C}/\text{h}$. However in this latter stage permeability is gradually decreased.

Stage 3--This stage is the eventual homogeneous nucleation of supercooled water in isolated capillaries at $\approx -40^\circ\text{C}$.

Eq (35) can be used if consideration is taken to earlier transformation of some water into ice. In this stage permeability can be almost zero.

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Permeability--The following simplified expression for coefficient of permeability can be derived: (15).

$$B = \frac{P^3}{T^2 \cdot Y^2 \cdot \mu} \quad (40)$$

Where P is the "waterfilled" porosity.

According to eq (33) and fig 18 the amount of ice at each temperature is dependent on the pore size distribution. Hence it is suitable to modify eq (40) by dividing the porosity in different pore size classes:

$$B = \sum_n \frac{P_n^3}{T_n^2 \cdot Y_n^2 \cdot \mu_n} \quad (41)$$

Where P_1 for instance corresponds to pores with freezing points between 0°C and -1°C . The viscosity of ice is negligible to that of water which means that an ice filled pore does not contribute to the permeability. Hence the following simplified expression for the variation of coefficient of absorption with temperature can be derived.

$$B_0 = (w_{nf})_0^3 \cdot \frac{1}{T_0^2 \cdot Y_0^2 \cdot \mu_0} \cdot \text{const} \quad (42)$$

Where also T and Y are functions of temperature since they are dependent on w_{nf} . Y is increasing substantially with decreasing temperature.

Eq (42) is only valid for a material where all the water-filled pores are "permeable". In reality it is however possible that the frozen water blocks the pores so that water at low temperatures is frozen as in a closed container. The blocking may eventually be caused by the first small amount of ice formed. In such a case the variation of permeability with temperature is dependent on the amount of ice formed but also on the degree of saturation in the specimen. A possible equation is:

$$B_0 = B_0 - \beta \cdot w_f \cdot f(S) \quad (43)$$

The function $f(S)$ is determined by the shape of the pore system. In special cases $B_0 = 0$ when a certain amount of ice is formed. Then the continued freezing occurs in an almost sealed container.

Test of the hydraulic pressure theory

Eq (21) assumes that the mechanism of frost deterioration is mainly hydraulic pressure for all materials. This has been criticized, since in this case a highly permeable material like clay brick could not be destroyed by frost (24). The fact is however, that critical thicknesses as those predicted by eq (11) have been found even for clay bricks. Eq (42) brings an explanation for this. Even if T and Y

are considered constant, the amount of non freezable water is so low in clay brick that the permeability is enormously reduced.

For the well burnt clay brick mentioned earlier $\frac{w_{nf}}{w_e} \leq 0,062$ at the final freezing. Then B is reduced to at least: $0,0625^3 = 2,4 \cdot 10^{-4}$ of its original value. This in turn is not the permeability of the material but the permeability of the waterfilled part of the material which can be considerably lower.

If the hydraulic pressure theory is valid the expansion of a specimen ought to follow an expression of type

$$\epsilon \approx \text{const} \cdot \frac{w_f \cdot d\beta/dt}{B} \quad (44)$$

ϵ is however limited to a value correspondant to the water expansion at ice formation. This limitation is essential at low permeabilities, "closed container":

$$\epsilon \leq \frac{1}{3(1-2\nu)} \cdot \frac{\Delta V}{V} = \frac{1}{3(1-2\nu)} \cdot 0,09 \cdot w_f \cdot \beta \quad (45)$$

Hence, by experiments where the expansion, the rate of ice formation and the permeability are measured, the validity of the hydraulic pressure theory might be confirmed through eq (44).

Such experiments are done at our institution. The apparatus is a calorimeter-extensometer the principle of which is shown in fig 21. A similar apparatus have been described in (25). The specimen, size $30 \times 30 \times 120 \text{ mm}^3$ is adapted to a certain degree of saturation, and mounted in the specimen chamber. The total assembly is immersed in a kerosene bath with constant low temperature. The length changes, heat flow and specimen temperature are measured automatically. By knowledge of the calorimeter constant and the heat capacity of the assembly, the amount of ice formed can be measured.

An apparatus for permeability measurements at low temperatures has been built. Reliable experiments have however not been performed so far.

Fig 22 shows such a freezing experiment for a non air entrained cement very porous paste. The degree of saturation in the specimen, is less than the critical value calculated from an equation of type (25).

Fig 23 shows the same specimen after 2 months prolonged curing in lime water which makes the degree of hydration somewhat higher. Besides in this experiment $S > \text{calculated } S_{CR}$.

Fig 24 shows the result of freezing of a clay brick with a degree of saturation exceeding the critical, which has been determined in the normal way mentioned earlier.

In all three experiments the pore-water is supercooled to -4 à -5°C . Then, freezing is initiated and the specimen temperature rises. The specimens expand because of hydraulic pressure arising when the first ice is formed.

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Then, for both the specimens where $S > S_{CR}$, the expansion continues as long as ice is formed. Hence, the cement paste expands all the time while the clay brick begins to contract when almost all ice is formed at -5°C .

The dryer cement paste contracts all the time despite the amount of ice formed is as high as in the case where $S > S_{CR}$. The contraction for the cement paste as well as for the clay brick exceeds the normal thermal contraction (broken line). At melting the slope of the line length-change-temperature is about the same as for freezing. Since the melting is not accompanied by any hydraulic pressure expansion, it seems reasonable to assume that the measured slope at melting is the real thermal expansion for the mixture porous material-ice. The coefficient of thermal expansion for a two phase material can be expressed.

$$\alpha = \frac{\alpha_1 \cdot V_1 \cdot K_1 + \alpha_2 \cdot V_2 \cdot K_2}{V_1 \cdot K_1 + V_2 \cdot K_2} \quad (46)$$

Where K is bulk modulus and the indices 1 and 2 represent ice and solid material.

α_{ice} is about $52 \cdot 10^{-6}$ at 0°C but decreases with decreasing temperature. α (solid phase) is about $5 \cdot 10^{-6}$ for a ceramic material. $K_1 \approx 10^5 \text{ kp/cm}^2$ for poly-crystalline ice at -5°C (22). $K_2 \approx K_0 (1-P)^3$ for a porous material (14) where $K_0 \approx 600\,000 \text{ kp/cm}^2$.

P is the total porosity since there is no adherence between the ice body and the pore wall.

V_1 is the volume of ice after freezing. Then according to eq (46) the following ratios of coefficients of thermal expansions at freezing temperatures and at ordinary temperatures are valid.

$$\text{For clay brick:} \quad \frac{\alpha < -5^{\circ}\text{C}}{\alpha > 0^{\circ}\text{C}} = 3,3 \quad (\text{measured value} \approx 3,1)$$

$$\text{For cement paste:} \quad \frac{\alpha - 5^{\circ}\text{C} \rightarrow -10^{\circ}\text{C}}{\alpha > 0^{\circ}\text{C}} = 2,4 ; \quad \frac{\alpha - 10^{\circ}\text{C} \rightarrow -20^{\circ}\text{C}}{\alpha > 0^{\circ}\text{C}} = 2,7$$

(measured values $\approx 3,0$).

Hence, the often noticed increased thermal contraction at a freezing can also be explained theoretically as a purely mechanical effect. The usual explanation is shrinkage caused by migration of unfrozen water to ice bodies in the pores (12). The experiment with the clay brick shows however the same characteristics as the paste experiment despite the brick has almost no unfrozen water ($K_{-10} \approx 0,05$) while the paste has considerable amounts ($K_{-10} \approx 0,51$). Besides, a clay

brick shows almost no shrinkage at water loss.

The thermal contraction at freezing is however somewhat smaller than the expansion at thawing. This can eventually be explained by hydraulic pressure acting during freezing.

The clay brick and the paste at high degree of saturation show great expansions as long as ice is formed. Those expansions can not be explained as in situ freezing in a closed container. viz expansions calculated from eq (45) are up to 15 times greater than the measured. Hence, water must be forced through the specimen from the freezing site. A hydraulic pressure must occur. The question is whether this pressure is big enough to expand the specimen in the observed way. If not, the expansion must be a consequence of some other phenomenon, ice lens segregation (1,12) or some other mechanism (24,26).

Since the very rapid freezing caused by supercooling expands the specimen less than the continued freezing which occurs with considerably lower rate, the permeability must be enormously reduced if the mechanism should be hydraulic pressure.

In the following an attempt is made to in a very simplified way calculate in which way the permeability is changed when the temperature is lowered.

If the tortuosity is constant the permeability at $\theta^\circ\text{C}$ compared to that at 0°C is:

$$\frac{B_\theta}{B_0} = \left(\frac{w_{nf}}{w_e}\right)^3 \cdot \left(\frac{Y_0}{Y_\theta}\right)^2 \quad (47)$$

But for spherical pores the specific surface can be expressed.

$$Y_0 = 3 \cdot \frac{w_{nf}}{r} \quad (48)$$

Where r is the radius of permeable pores.

r is coupled to the freezing point depression according to eq (33) which can be simplified to (19).

$$r \approx \frac{1}{8,061 \cdot 10^6 \Delta T - 6,12 \cdot 10^4 (\Delta T)^2 + 2 \cdot 10^2 (\Delta T)^3} \quad (49)$$

But w_{nf} is a function of ΔT .

$$w_{nf} = f(\Delta T) \quad (50)$$

Then by use of eqs (47) - (50) the change of permeability with temperature can be calculated.

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For the cement paste eq (50) is: (see fig 23)

$$w_{nf} \approx 5 \cdot \Delta T^{-1/2} \quad (51)$$

Hence eq (49) gets approximately:

$$r \approx k \cdot w_{nf}^2 \quad (52)$$

By use of eq (52) and eq (48) eq (47) is changed to:

$$\frac{B_0}{B_o} \approx \left(\frac{w_{nf}}{w_e} \right)^5 \quad (53)$$

The measured rate of ice formation can be divided by the calculated permeability which according to eq (44) gives the expansion. This theoretical expansion have been calculated and is indicated in fig 25 where the experiment in fig 23 is rewrit with time as independent variable. The constant in eq (44) is chosen so that calculated and measured expansion coincide at -19°C . The agreement between the two expansions is fair bearing in mind the approximate calculation of permeability. The expansion around 0°C is very difficult to calculate since the rate of ice formation is uncertain. It must be observed that no consideration is taken to thermal contraction in the calculated curve.

In the brick almost all ice is formed around 0°C . Hence, the specific surface is considered constant and the relative permeability gets the form.

$$\frac{B_0}{B_o} = \left(\frac{w_{nf}}{w_e} \right)^k \quad (54)$$

Where $k \approx 2,0$

This equation have been used for calculation of expansion in the same way as above. The result together with experimental curves is shown in fig 26. The agreement down to -5°C is excellent. The same good agreement is obtained even when the exponent k in eq (54) is 3 or 4. At temperatures lower than -5°C the specimen contracts thermally from the expanded state. The hydraulic pressure theory at use of eq (54) indicates however that the specimen ought to contract drastically because ice formation is almost finished. See ϵ_{CALC} eq (44) in fig 26. However the permeability gets very low for which reason it is possible that the late freezing is a freezing in a closed container. Eq (45) shows however that this would mean a substantial expansion. See ϵ_{CALC} eq (45) in fig 26. Hence it seems as if the expansion caused by hydraulic pressure in the range $0 \rightarrow -5^\circ\text{C}$ is locked by ice formed in the expanded specimen. Then, at the continued freezing the expanded specimen contracts thermally according to eq (46) from its expanded state. The thermal contraction is however reduced by the continued hydraulic pressure according to eqs (44) and (54). This can be the explanation

of the discrepance between thermal contraction and expansion in fig 24.

The maximum reduction in permeability for the cement paste is $1,3 \cdot 10^{-3}$ according to eq (53). For the clay brick it is $4,8 \cdot 10^{-3}$ according to eq (54) at maximum expansion. With the perhaps more reasonable exponents 3 or 4 in eq (54) it is however $3,4 \cdot 10^{-4}$ or $2,3 \cdot 10^{-5}$. In this case the effect on permeability of blocking the pores with ice is 25 à 175 times greater for clay brick than for cementpaste.

Thus, it seems as if the hydraulic pressure theory can explain all the phenomenons seen at a freezing even for two so different materials as cement paste and clay brick. This is very essential since in this case connections between materials properties and critical degrees of saturation can be derived in the way indicated above.

Influence of Materials Properties on the Actual Degree of Saturation

This subject will be treated very briefly.

Rate of water uptake and drying--The rate of water uptake as well as the rate of drying increases with increasing pore radius.

For a material with tubular pores of different size the degree of saturation on a critical depth, $D_{CR}/2$ from the surface at a water uptake is (15).

$$(S_e)_{X=D_{CR}/2} = \frac{2}{P \cdot D_{CR}} \cdot \sum_n \left\{ P_n \sqrt{\frac{t \cdot r_n \cdot \sigma_{LG} \cdot \cos \theta}{2 \cdot \mu}} \right\} = \frac{13,0}{D_{CR}} \sqrt{t \cdot \bar{r}} \quad (55)$$

Where P_n is the amount of pores of a certain size. $\bar{r}$ is a mean pore radius.

Hence, at a certain D_{CR} and a certain time, t_{SCR} on the critical depth increases with increasing pore size. The equation is however very simplified since it takes no consideration to bifurcations between different pores which means that $S_e = 1,0$ at long enough time.

The drying can be divided in two parts. The first part corresponds to a saturated water flow from the interior of the material to the surface. The second part is a combination of liquid water and diffusion process when there is no longer a continous water phase in the material. The second part is a considerably slower process than the first.

The first transport has a permeability of type (40). However, the pore properties are of no importance in this stage as long as rate of transport is great enough to keep a free water surface on the materials surface. Then the rate of drying is constant. Of course there is a need of faster water transport within the specimen when the ambient air gets drier or is forced to move along the materials surface.

The diffusion process increases its rate with increasing porosity and pore size. Dependent on the pore size Hagen-Poiseulles law or Knudsen's law is predominant.

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Total water uptake

The total water uptake in the wet part of a specimen when the water front has reached a distance, x , from a free water surface, can be calculated from a combination of the "coefficient of water uptake" k_w and the "coefficient of capillarity" k_c , which in turn can be determined experimentally.

$$k_w = \frac{Q_w}{t k_1} \quad (56)$$

$$k_c = \frac{t}{x k_2} \quad (57)$$

Where k_1 and k_2 are constants. Then it is valid.

$$(S_e)_{MAX} = k_w \cdot k_c^{k_1} \cdot x^{(k_1 \cdot k_2 - 1)} \quad (58)$$

For a single capillary $k_1 \cdot k_2 = 1/2 \cdot 2 = 1$. In this special case $(S_e)_{MAX} = k_w \cdot \sqrt{k_c}$.

For a porous material $k_1 \cdot k_2 \leq 1$ which means that $(S_e)_{MAX}$ as a mean value of the whole wet part of the specimen will decrease with the capillary rise, x . This is an essential result since it means that the surface part of a specimen has a higher $(S_{ACT})_{MAX}$ than the inner parts. cf fig 12.

The constants k_1 and k_2 must be dependent on the pore structure. Perhaps experiments can be designed in order to find out correlations between those constants and the pore properties. Such experiments must be fundamental for the understanding of the second part of the frost resistance problem, viz. the value of S_{ACT} . Many investigators have found correlations between pore size distribution and frost resistance (27, 28). Perhaps this correlation is an effect of the pore size distribution on the constants k_1 and k_2 . viz it seems reasonable to assume that more air is entrapped in a specimen when the pore size distribution is wide than when all pores are of the same size.

In (29) the capillary water uptake of a random pore system with bifurcations is treated. It is shown theoretically, that the coarsest pores are filled at first, but they very soon deliver their water to the smaller pores. Then, they can not be filled again until all the surrounding smaller pores are filled. If the coarse pore has such a shape that it is surrounded only by smaller pores (air pore in cement paste) it cannot be filled again until the air in the pore can penetrate the waterfilled surrounding pores. It is in reality sealed. The air pressure needed is inversely proportional to the surrounding pore radius.

$$p = \frac{2 \cdot \sigma_{LG}}{r} \cdot \cos \theta \quad (59)$$

At a pore radius of 10μ the pressure needed is $\approx 0,15 \text{ kp/cm}^2$. Such a pressure can normally only be obtained by artificial means

Experiments have however shown that even air bubbles in a cement paste may be filled with water if the specimen is stored for a very long time in water. This is possibly an effect of condensation in the pores.

The locking of pores with water according to eq (59) has very important practical significance for light weight aggregate concretes. cf fig 15. Even if the aggregate particles have a bad durability (their $S_{CR} < S_{ACT}$) when they are single they can be used as aggregate in a durable concrete since their pores are blocked by the dense cement paste. Hence they can not be filled again, once they have dried out.

ACKNOWLEDGEMENTS

The author wants to thank professor S. G. Bergström, who initiated this research and who has provided many ideas. Another thank is transmitted to the National Swedish Council for Building Research, which has financed this investigation.

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SYMBOLS

A	= specimen surface (m^2)
B	= coefficient of permeability (including viscosity of fluid) ($m^3 \cdot s/kg$)
C	= cement content (kg/m^3)
D_{CR}	= critical thickness of <u>saturated</u> slice (m)
E_B	= Young's secant modulus at fracture (N/m^2)
E_n	= Young's modulus after n cycles freezing (N/m^2)
K	= non freezable water content at lowest temp as fraction of pore-volume, cf eq (10)
K	= bulk modulus (N/m^2)
$\bar{L}_{CR}$	= critical wall thickness of saturated hole-sphere (Powers' spacing factor) (m)
M	= molecular weight of water (kg/k mole)
P	= porosity (m^3/m^3 material)
P_{CR}	= critical porosity where $\sigma_B = 0$
Q_{dry}	= weight of dried specimen (kg/m^3 material)
Q_{we}	= weight of evaporable water (kg/m^3 material)
R	= gas constant ($Nm/^\circ K \cdot k$ mole)
R	= radius of materials sphere (m)
R_{CR}	= critical radius of saturated sphere (m)
S	= degree of saturation, eq (2)
S_a	= coefficient of absorption, eq (1)
S_e	= degree of saturation, eq (3). <u>Note:</u> $S_e \neq S_a$
$(S_e)_x$	= degree of saturation on depth x
S_{ACT}	= actual degree of saturation (cf $(S_e)_{ACT}$; u_{ACT})
S_{CR}	= critical degree of saturation (cf $(S_e)_{CR}$; u_{CR})
T	= "Tortuosity factor" (m/m)
T_o	= ordinary freezing temp ($^\circ K$)
V	= volume in general

V	= specimen volume, eq (36) (m^3)
Y	= specific surface of the <u>waterfilled part</u> of the pore system (m^2/m^3 material). Note: $Y \neq \alpha$
c	= specific heat ($\text{Nm/kg} \cdot ^\circ\text{C}$)
$\frac{d\beta}{dt} w_f$	= rate of ice formation (m^3/m^3 material $\cdot$ s)
k	= constant in general
k	= non freezable water as multiples of non evaporable water content, eqs (25), (26)
k_c	= "coefficient of capillarity"
k_w	= "coefficient of water uptake"
l	= air content before freezing (m^3/m^3 material)
l_{ACT}	= actual air content correspondant to S_{ACT} (m^3/m^3 material)
l_o	= air content at mixing (m^3/m^3 concrete)
n	= exponent eq (27)
p	= pressure (N/m^2)
p/p_s	= relative vapour pressure
q	= constant eq (28)
r	= (Kelvin) radius of capillary (m)
s	= Frost resistance, eq (5) (cf s_u ; s_e)
t	= time (s)
u	= moisture ratio (kg/kg)
u_o	= moisture ratio at complete saturation (kg/kg)
v_{ice}	= rate of propagation of ice front (m/s)
w_a	= max water uptake at capillary water uptake at ordinary pressure and constant temp (m^3/m^3 material)
w_e	= evaporable water content at lowest temp (m^3/m^3 material)
w_f	= freezable water content at lowest temp (m^3/m^3 material)
w_f'	= freezable water content in a completely saturated slice within a materials volume (m^3/m^3 watersaturated material). Note $w_f' \neq w_f$.

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w_{nf}	= non freezable water content at lowest temp (m^3/m^3 material)
w_o/c	= water cement ratio (kg/kg)
x	= distance from materials surface to ice front or water front (m)
x_{us}	= unsaturated depth; depth from surface to a place where expelled water can be taken care of (m)
$(x_{us}-x)_{CR}$	= "critical depth of unsaturation", eq (15) (m)
α	= specific surface of air filled pores, eq (13) (m^2/m^3 pore-volume)
α	= thermal expansion coefficient ($m/m \cdot ^\circ C$)
β	= fraction of w_f actually frozen
β	= degree of hydration = fraction hydrated cement. eqs (25), (26) (kg/kg)
β_o	= fraction of w_f freezing at ceasing of supercooling
γ_p	= density of dried specimen (kg/m^3)
Δh	= heat of fusion (Nm/kg)
ΔH	= molar heat of fusion (Nm/k mole)
Δt	= time needed in order to raise temperature ΔT at ceasing of supercooling (s)
ΔT	= freezing point depression ($^\circ C$)
ΔT_o	= temperature rise at ceasing of supercooling ($^\circ C$)
$\frac{\Delta V}{V}$	= relative volume change
ϵ	= linear strain at hydrostatic tension
ϵ_B	= fracture linear strain at hydrostatic tension
ϵ_o	= fracture strain of solid phase
μ	= viscosity (Ns/m^2)
ν	= poisson's ratio
ω	= shape factor of ice crystal
ρ	= density (kg/m^3)

- σ_o = theoretical strength of solid phase (N/m²)
 σ_B = tensile strength of material (N/m²)
 σ_{LG} = surface tension liquid-gas (N/m)
 θ = temperature (°C)
 θ = wetting angle

Indici

- L = liquid
 LG = liquid-gas
 i = ice
 p = dry specimen
 w = water

TABLE 1 Analysis of data from (9).

Method ASTM	Time in un- frozen water (>0°C) per cycle t_w (h)	Time in air per cycle t_a (h)	Time in air of unfrozen speci- men (>-5°C) per cycle t_{aw} (h)	$\frac{t_{aw}}{t_w}$	$\frac{t_a}{t_w}$
C290: Rapid wa- ter	1,2	0	0	0	0
C291: Rapid air	0,7	1,3	0,3	0,43	1,85
C292: Slow wa- ter	29	0	0	0	0
C310: Slow air	7	18	1,5	0,21	2,57

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TABLE 2 The frost-resistance of four types of light weight aggregate concrete

Material, type and density (kg/m ³)	S _{eCR}	Frost resistance, a _u according to eq (7)				
		At knick-point absorption	At absorption for			
			24 h	240 h	720 h	1730 à 1850 h
1	0,46	0,243	0,230	0,194	0,159	0,110
860	0,48	0,258	0,246	0,210	0,182	0,149
2	0,33	0,135	0,120	0,083	0,046	-0,007
785	0,34	0,159	0,145	0,107	0,066	+0,011
3	0,22	0,062	0,036	-0,011	-0,040	-0,060
630		0,066	0,050	-0,002	-0,030	-0,037
4	0,27	0,049	0,030	-0,016	-0,047	-0,070
1240	0,28	0,075	0,054	+0,005	-0,030	-0,047

TABLE 3 Test of the correctness of equations (17), (18) and (19).

Material	S _{eCR} meas.	l _{CR} meas.	a _{CR} calc. (mm ⁻¹)	2·L _{CR} calc. (mm)	D _{CR} calc. (mm)	D _{CR} meas. (mm)
Cellular concrete, type 1, density ≈500 kg/m ³	0,62	0,309	6,45	0,648	0,783	<1,7
Cellular concrete, type 3, density ≈500 kg/m ³	0,48	0,420	3,57	0,774	0,886	<1,7
Underburnt clay brick	0,85	0,061	5,37	5,78	12,20	12
Well burnt clay brick	0,76	0,076	5,90	4,12	7,90	12 à 14

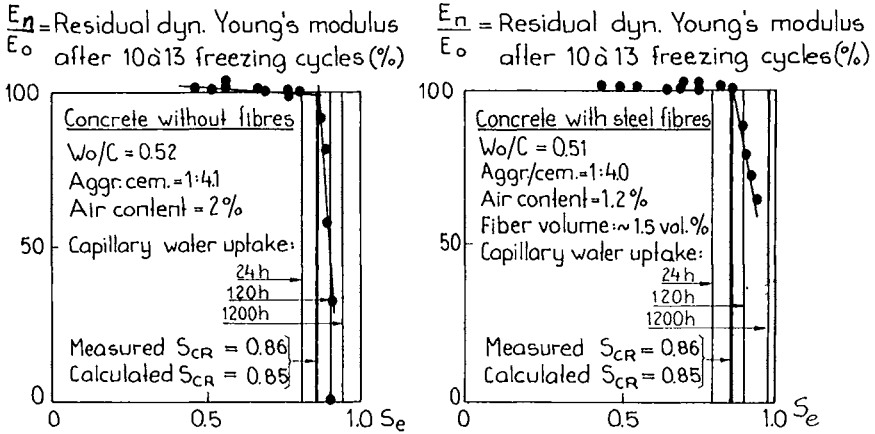


Fig. 1--Experimental and theoretical critical degrees of saturation of a concrete with and without steel fibers. Capillary water uptake indicated in the figure

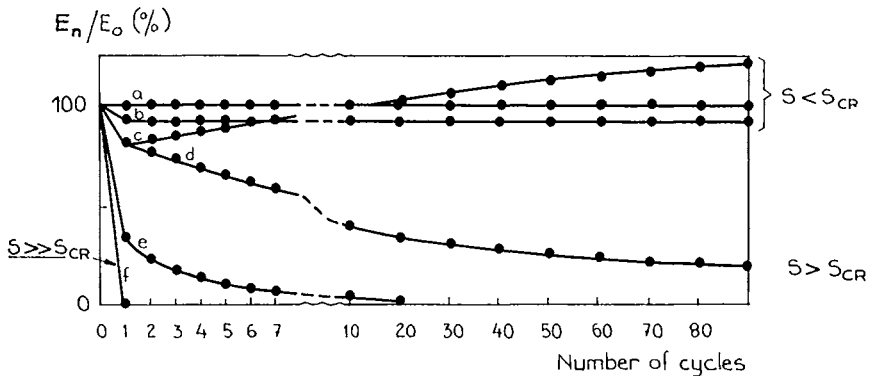


Fig. 2--Principles for variation of dynamic Young's modulus with number of cycles when the degree of saturation is constant