Critical degrees of saturation at freezing of porous and brittle materials

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CRITICAL DEGREES OF SATURATION AT FREEZING OF POROUS AND BRITTLE MATERIALS

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Rättelselista till

"CRITICAL DEGREES OF SATURATION AT FREEZING OF POROUS AND BRITTLE
MATERIALS". av Göran Fagerlund

I listan tas endast med sådana fel, som kan leda till missförstånd
av innehållet.

u = uppifrån   n = nerifrån

DEGRÉ CRITIQUE DE SATURATION ....etc ....

Sid	Rad/läge	Står	Skall stå
271 Notations	D_{CR}	p 00	p 274
272 "	t_c	t_θ	t_θ -
272 "	k	k	κ
275 "	ekv (10)	K	κ
284 Summary	13 u	fig 9	fig 8

KRITISKA VATTENMÄTTNADSGRADER .... (Rapport 34)

32	översta ekv	Ekv nr saknas	(27)
40	17 n	0,99	0,92
42	ekv (45)	a	ℓ
62	ekv (68)	10^2	10^{-2}
65	ekv (76) o (77)		multipliceras med $\Delta\theta$
69	ekv (83)	28,5	19,6
73	ekv (91)	0,0085 θ	-0,0085·θ
80	16 u	$\frac{150}{0,192}$	$\frac{150}{192}$
80	ekv (102)	+0,25·ΔW_n	-0,75·ΔW_n
94	18 u	Där k_1 är	Där k_2 är
97	17 n	2/1000	2/1000 mm
130	16 n	30x30 cm^2	30x30 mm^2
130	ekv (129)	TOT	x_{TOT}
156	ekv (140)	k·log t	-k·log t
249	fig 48	$K = \frac{W_e}{V_p}$	$K = \frac{W_e}{P}$

SIGNIFICANCE OF CRITICAL DEGREES ....etc ....

12	18 u	"slow air"	"slow water"
18	ekv (21)	$\sqrt{P(1-K)}$	P(1-K)
21	ekv (25)	1000 $\ell o/_C$	1000 $\ell o/C$)
22	under ekv (32)	curved	cured
22	ekv (33)	28,5	19,6

forts SIGNIFICANCE OF CRITICAL DEGREES .... etc ....

Sid	Rad/läge	Står	Skall stå
22	ekv (33)	$\ln(\frac{To-T}{To})$	$\ln(\frac{To-\Delta T}{To})$
23	ekv (34)	$(To-T)$	$(To-\Delta T)$

METHODS OF CHARACTERIZATION .... etc ....

Avsnittet "suction porosimetry"

17	ekv (34)	$\Sigma\, B_i \cdot$	$\Sigma\,(B_i-B_{i-1})\cdot$
20	ekv (40)	$\sum_i B_i$	$\sum_i (B_{i+1}-B_i)$

Avsnittet "freezing point depression"

5	ekv (11)	$(1+1{,}84\cdot10^{-3}- \\ -0{,}40\cdot10^{-6})$	$(1+1{,}84\cdot10^{-3}\Delta T- \\ -0{,}40\cdot10^{-6}\Delta T^2)$
6	ekv (16)	$-\frac{\Delta T}{To} \simeq \\ \simeq \ln\frac{To-\Delta T}{To} =$	$\frac{\Delta T}{To} \simeq - \ln\frac{To-\Delta T}{To} = \\ -$
10	ekv (29)	5	1,63
10	ekv (30)	28,5	19,6

Avsnittet "BET-method"

8	10 n	10^{-4}	10^2
8	9 n	10^{-5}	10^{-7}

GF/ABW 10.5.73

This thesis comprises the following reports under the general heading "Critical Degrees of Saturation at Freezing of Porous and Brittle Materials":

1. G Fagerlund: "Degré critique de saturation - Un outil pour
                      l'éstimation de la résistance au gel des matériaux
                      de construction".
                      Materiaux et Constructions n° 23, volume 4,
                      Sept-Oct 1971. pp 271-285.

2. G Fagerlund   "Kritiska vattenmättnadsgrader i samband med
                      frysning av porösa och spröda material".
                      "Critical Degrees of Saturation at Freezing of
                      Porous and Brittle Materials".
                      Report 34. Division of Building Technology at
                      Lund Institute of Technology, Lund 1972.
                      (In swedish).

3. G Fagerlund   "Significance of Critical Degrees of Saturation
                      at Freezing of Porous and Brittle Materials".
                      Contribution to ACI-symposium Durability of Concrete,
                      Ottawa, oct 1973.
                      Also: Report 40. Division of Building Technology
                      at Lund Institute of Technology. Lund 1973.

4. G Fagerlund   "Determination of Pore-size Distribution from
                      Freezing-Point Depressions".
                      Part of; "Methods of Characterization of Pore
                      Structure - 3 contributions to RILEM committee
                      `Pore Structure and Properties of Materials´".
                      Report 41. Division of Building Technology at
                      Lund Institute of Technology, Lund 1973.

INTRODUCTION

This thesis is based on experimental work carried out during the period 1968-1972. The whole investigation is sponsored by the Swedish Council for Building Research and has been performed at the department of Building Materials at the Lund Institute of Technology.

The thesis treats the problem frost resistance of building materials, a problem which is far from beeing solved despite much scientific work in many countries. According to the author the main reason for this lack of success is, that the problem of frost resistance is not only a function of materials properties but also of properties of the envi-ronment in which the materials are used. Hence, in order to solve the problem it is necessary to investigate separately the effect of mate-rial properties and the effect of environmental properties on the frost resistance of a material.

This distinction between influence of material and influence of environment may seem very logical or even to be a truism. However, very few scientists have made such an approach to the problem. Instead the research has principally been aimed at finding correlations between la-boratory freezing-tests and behaviour of the material of practice. The debate among the scientists has to a big extent consisted in how to choose freezing method for a certain material in a certain situation in order to get the best correlation. Thus, in the normal way of trea-ting the problem frost resistance, material and environment are "mixed together" in a way which obscures the solution of the problem.

In the work presented here a distinction between material and environ-ment is made. Materials properties as well as properties of environment are expressed in terms of "degree of saturation" defined:

$$S_f = \frac{w_f}{w_f + \ell} \tag{1}$$

where S_f is effective degree of saturation, (also written S), w_f is the maximum freezable water content at the lowest temperature used and ℓ is the air-filled pore-volume before freezing.

The materials properties are expressed in a "critical degree of satura-tion", S_{CR}, which corresponds to the maximum water content which can be held in a specimen without risk of frost damage at a freezing.

The properties of environment are expressed in "actual degrees of satu-ration", S_{ACT}, which corresponds to the water contents a certain mate-rial will reach in a certain environment.

S_{CR} is supposed to be a materials constant. Its value may of course pass through a certain change with time since a material may be used for ma-ny decades, why the relevant materials properties may change.

S_{ACT} varies with time since the wetness of the environment is a variable with time.

Of course the separation of materials- and environmental properties are not complete. Above all the hydraulic properties of the material is fun-damental for the value of S_{ACT}. However for an estimation of the frost resistance of a certain material used in different environments the se-paration is logical and helps to clarify the complex problem of frost resistance.

The aim of the thesis is to theoretically and empirically prove the existence of critical degrees of saturation, to advise a new rational method of freeze-testing materials and above all to discuss the signi-ficance and serviceableness of the critical degrees of saturation. The last part also includes theoretical and experimental studies of

mechanisms of destruction by frost, of freezing characteristics of pore water and of connections between materials properties and frost resistance

DIFINITION OF FROST RESISTANCE (Reports 1 and 2)

The frost resistance, F, is defined;

$$F = S_{CR} - S_{ACT} \tag{2}$$

If S_{CR} is considered constant the frost resistance will vary with time according to the way S_{ACT} varies with time. Frost damage will occur when F<0 at subfreezing temperatures.

Hence the problem of frost resistance is of a statistical nature since the occurence of the dangerous combination subfreezing temperature and too high water content depends on statistical factors such as frequency of freezing point passages, of wetness of the environment etc.

CHOICE OF MATERIALS AS REGARDS FROST RESISTANCE (Reports 1 and 2)

According to eq (2) the frost resistance of an arbitrary material can be quantified. This makes rational choices of material as regards frost resistance possible.

The way of choosing material can be directly compared to a normal choice or design of a structural component as regards strength /1/.

FREEZE-TEST METHOD (Report 2)

A freeze test method will be divided in two parts of quite different character:

- Part 1: Determination of critical degrees of saturation. 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.

Part 1 is principally dependent only on materials properties and part 2, for each material, principally dependent only on properties of the environment.

In /2/ are given comprehensive descriptions and discussion of methods of determination of S_{CR}. This can be done by multi-cycle experiments followed by measurements of damage after termined freezing cycles or by one-cycle experiments accompanied by simultanous measurements of for instance length change of the specimen.

Critical degrees of saturation have been measured for 41 different porous materials, normally by multi-cycle experiments. The results are shown and discussed in /2/.

S_{ACT} can from a theoretical point of view only be determined by experiments exactly reproducing the actual environment which demands knowledge of climate-data and of moisture measurement methods. Another way of solving this part of the frost resistance problem is to use moisture mechanics in an analytical calculation. Both those methods are however inapplicable for the present day since almost all information needed is lacking.

As a substitute simple water absorption tests can be used. Comparisons found in literature /2/ between water contents of different materials in practice and water absorption of the same materials in laboratory have shown,that the in-situ-values often corresponds to many days of capillary water absorption.

Hence each material ought to get a lower value of S_{ACT} at many days water uptake then its S_{CR} if the material is to be frost resistant.

In /2/ is shown in which way a water absorption test can be performed. It is also discussed the influence on frost resistance of rate of water absorption, of rate of drying, of the so called critical thickness and of specimen size.

Practical experiments have been performed with all the materials for which S_{CR} have been determined. The results are shown and discussed in /2/.

By use of eq (2) for frost resistance it is experimentally shown that the frost resistance on a critical depth from the wet surface of a material will be a function of time of water absorption of type;

$$F = F_1 - k \cdot \log t \tag{3}$$

where k is a constant, t is time of water absorption, F_1 is the frost resistance at time one of the time unit chosen

By determination of the constants k and F_1 and by taking consideration to the rate of drying and the critical thickness eq (3) can be used for comparisons between frost resistance of different materials.

CONNECTIONS BETWEEN FROST RESISTANCE AND MATERIALS PROPERTIES
(Reports 3 and 4)

The definition of frost resistance in eq (2) gives good possibilities of analyzing connections between materials structure and frost resistance. This problem can evidently be limited to an investigation of the influence of the relevant structural characteristics on S_{CR} and on S_{ACT}.

The value of S_{ACT} is mainly dependent on the pore structure. Connections between pore structure and water absorption is in turn treated by the "classical" moisture mechanics. Hence, verly little is mentioned in the thesis about this part of the problem, /2, 3/.

In order to know about connections between materials structure and S_{CR} it is necessary to know which freezing mechanism is predominant at freezing of different materials.

Freezing experiments have been performed where amount of·ice formed, rate of ice formation and length change of specimen has been measured simultanously during a freezing cycle, /3/. By such experiments it seems as if the major freezing mechanism,for both coarse-porous and fine-porous materials,is· hydraulic pressure occuring when unfrozen water is expelled from the freezing site. In order to arrive to this conclusion certain considerations pertaining permeability of the materials at freezing temperature must be made. Coarse-porous materials have high permeabilities at ordinary temperatures but on the other hand they have small amounts of non-freezable water,/4/,which makes the permeability very much reduced at freezing temperatures. This explains why the same freezing mechanism can be valid for two so different materials as cement-paste and clay brick,/3/.

The hydraulic pressure theory predicts the existence of critical water-saturated volumes inside a material /3/. Such·critical volumes (cri-

tical thicknesses of saturated slices) have been measured experimentally which also confirms the destruction by hydraulic pressure,/3/.

The critical volume is,at fairly constant temperature conditions,only dependent on materials properties as strength, permeability, pore-size (influences the freezable water content,/4/),specific heat (influences the rate of ice formation) etc. A property like strength or specific heat is in turn a function of more basic structural parameters like porosity and pore-size.
Hence it is quite possible to evaluate connections between materials structure and critical distance,/3/.

The existence of a critical degree of saturation is only a geometrical consequence of the existence of critical volumes.

The problem of finding a critical degree of saturation is therefore reduced to the problem of finding a geometrical connection between volume of air-filled pores, size of those pores and size of the water-filled critical volumes.

Such geometrical connections are found in literature. The final expression for S_{CR} is /1, 3/.

$$S_{CR} = 1 - \frac{1}{(1 + \alpha \cdot f(V_{CR})) \cdot P(1 - K)} \tag{4}$$

where α is the mean specific surface of air-filled pores (inversely proportional to their size), $f(V_{CR})$ is a simple function of the critical water saturated volume, P is total porosity and K is non-freezable water as fraction of total porosity.

Consequently all parameters determining the value of S_{CR} can be expressed in structural characteristics of the material. This has been done in /3/.

FREEZING CHARACTERISTICS OF PORE WATER (Report 4)

The definition, eq (1), of degree of saturation demands that the freezable water content is known. Besides, a complete description of the connections between materials structure and frost resistance demands knowledge of the connections between pore structure and freezing characteristics of the pore-water. cf eq (4) where the freezable water is expressed implicitly in V_{CR} and explicitly in K.

On basis of theoretical expressions for the freezing-point of a crystal in its own melt an expression is derived for the freezing point of pore-water as function of the pore-size,/4/;

$$r \simeq - \frac{2 \cdot \sigma_{LG} \cdot M}{\rho_L \cdot \Delta H} \cdot \frac{1}{\ln(\frac{T_o - \Delta T}{T_o})} + 19.6 \cdot 10^{-10} \cdot \sqrt[3]{\frac{1}{\Delta T}} \tag{5}$$

where r is the pore radius in meters, σ_{LG} is surface tension water-air, ρ_L is density of the water, ΔH is the molar heat of fusion, T_o is the freezing point of bulk water and ΔT is the freezing point depression of pore-water. The second term is the thickness of the adsorbed layer on the pore-walls.

This equation has with good result been compared with semiempirical expressions found in literature.

Eq (5) gives possibilities of a calculation of pore-size distributions from determinations of non-freezable water contents. In /4/ is given the formulas for such calculations. This is a method of pore structure analysis that is completely unexploited as far as the author know of, despite it gives many advantages.

The pore radius is also coupled to the pore-water pressure in a way which is normally expressed by Kelvin's law (or Laplace equation).

By combination of Kelvin's law and eq (5) it is possible to give a connection between freezing point depression, ΔT, and the relative humidity, p/p_s, with which the material is in equilibrium;

$$\Delta T = - \frac{R \cdot T_o (T_o - \Delta T)}{\Delta H} \ln p/p_s \tag{6}$$

where R is the gas constant.

This equation has been used for comparison between experimentally determined non-freezable water contents at different temperatures and non-freezable water contents calculated from adsorption and desorption water-vapour isotherms for the same materials,/2/.

The non-freezable water contents are determined by melting experiments in adiabatic calorimeter. The calorimeter construction and results are accounted of in /2/.

Only comparisons with adsorption isotherms give satisfactory agreement, which confirms theoretical considerations that melting of ice is a process of adsorption.

Hence, on basis of experiments and theory, it has been proved that information on non-freezable water contents at different temperatures can be gained from the adsorption isotherm in the high pressure range (eq (6)) or from the pore-size distribution for pores with radii <1000 Å (eq (5)).

LITERATURE

The most essential theoretical background to this work is the following reports;

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T C Powers: The air-requirement of frost resistant concrete. Highway Res Board Proc 29 (1949) pp 184-211.

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pp 1-46. Proc RILEM Symposium "Winter Concreting",
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resistance of concrete. Part B.Hypothesis and
Freezing Experiments. Swed Cem and Concr Res Inst
Proc Nr 36. Stockholm 1964.

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