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Litvan, G. G.

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FREEZE-THAW DURABILITY OF POROUS BUILDING MATERIALS

by G.G. Litvan

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SOMMAIRE

L'eau retenue par les pores d'un solide devient instable lorsqu'elle est refroidie à des températures inférieures à $0^{\circ}C$. Dans des conditions propice l'eau quitte les pores et la glace s'accumule à l'extérieur du matériau. Si la vitesse de refroidissement est élevée, que le degré de saturation l'est également et que le parcours de dispersion est long, l'eau ne peut atteindre la surface extérieure et se solidifie dans un état vitreux et informe. Les dommage mécaniques ne se produisent que dans le dernier cas. Cette réaction n'est pas exclusive à chaque type de solide; elle s'applique également au mortier de cimen à la pierre et à la brique et peut être utilisée pour accroître la durabilité des matériaux poreux et pour améliorer les méthodes d'essai.

G. G. Litvan[1]

Freeze-Thaw Durability of Porous Building Materials

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ABSTRACT: Water held in the pores of a solid becomes unstable when cooled to temperatures below 0°C. If the conditions permit, the water leaves the pores and ice accumulates outside the system. In case of high cooling rate, high degree of saturation, and long diffusion path, the water cannot reach the external surface and solidifies in a glassy, amorphous state. Mechanical damage occurs only in the latter case. This mechanism is not indigenous to any single type of solid, thus it is applicable to cement paste, stone, and brick, and could be used for increasing the durability of porous materials and for improving test procedures.

KEY WORDS: freezing and thawing, frost action, freezing, concrete brick, stone, durability, building materials

Destruction of porous bodies caused by freezing and thawing has been of great concern to engineers for more than 200 years [*1*].[2] Under severe freezing climatic conditions, frost action is probably the most important cause of deterioration of exposed porous materials. Most important building materials, that is, concrete, stone, and brick, belong in this class.

Not surprisingly, the pertinent literature dealing with the mechanical breakdown of building materials due to frost action, and with the general problems of phase changes of water adsorbed in the pores of solids, is voluminous.

Great progress has been made in the development of practical means of avoiding damage in certain cases, but these methods were based on experience rather than on understanding of the mechanism.

The purpose of the present paper is to give an account of the studies carried out in the Materials Section of the Division of Building Research. The

[1] Senior research officer, Building Materials Section, Division of Building Research, National Research Council of Canada, Ottawa, Ont., Canada.

[2] The italic numbers in brackets refer to the list of references appended to this paper.

results were published over the years in various papers [*2-8*], and a brief summary of the results together with recent developments now appears to be in order. Because of limitations concerning the length of the paper, a review of the literature cannot be given.

Experimental Observations

A proposed explanation of a phenomenon cannot be accepted as valid unless it is consistent with all the established experimental findings. In order to facilitate testing the theory, the most important observations relating to frost action are:

1. The severity of mechanical damage is directly proportional to the water content of the porous solid. In the fully saturated state, few, if any, systems can endure even a single freezing and thawing cycle without injury.
2. Physical size of the porous solid affects susceptibility; frost resistance improves with reduction in size.
3. Mechanical damage is enhanced with increased cooling rates. Even the most vulnerable system can be taken through freeze-thaw cycles without injury if the freezing rate is very low.
4. Solids with either very high or very low porosity usually have a good service record. Brick and marble, respectively, are examples of such materials. Hydrated cement paste with intermediate porosity is usually vulnerable unless special precautions are taken. This is particularly true in the case of high water-cement ratio pastes.
5. Air entrainment, which consists of the addition of a surface-active agent to the plastic mix resulting in the formation of small air bubbles, around which the paste subsequently hardens, has proved to be an excellent method of increasing the frost resistance of cement and concrete.
6. The main features of frost action appear to be common to all classes of porous solids.
7. The characteristics of frost action with systems containing organic liquids are similar to those observed with water.
8. Repeated freezing and thawing under natural conditions usually results in desiccation and in accumulation of the formerly pore-held liquid outside of the body (lens formation).
9. Mechanical damage is more severe if the porous solid contains a solution instead of a pure liquid. The use of deicing salts is detrimental. Again, the nature or the extent of the damages does not depend on the chemical nature of the solute. The severity of the damage is a function of the solution concentration. The most severe damages occur at relatively low concentrations, in the 2 to 5 percent range.

Adsorption at Temperatures Below the Bulk Freezing Point of the Adsorbate

Because water-containing porous building material must be considered as an adsorption system, the findings of the studies in this field [*4*] are highly relevant to the frost action problem. A summary of the major conclusions follows.

Water is not in the solid but rather in the liquid state when isothermally adsorbed on porous bodies at temperatures below 0°C. Presumably, this is due to the interaction between the adsorbate and the substrate. Because the vapor pressure of undercooled water is greater than that of ice, the complete isotherm cannot be obtained; when the quantity of the accumulating adsorbate reaches a level at which its vapor pressure becomes equal to that of ice, further addition of water to the system does not result in more adsorption but in formation of ice deposited outside the porous body on the walls of the apparatus. The relative pressure at which the vapor pressure of the adsorbate becomes equal to that of ice depends on the temperature and varies from $p/p^\circ = 1.0$ at 0°C to $p/p^\circ = 0.7$ at −40°C. In other words, while complete saturation can be achieved at 0°C this cannot be realized at colder temperatures. The degree of saturation becomes successively less as lower experimental temperatures are selected.

Moisture Content Affected by Temperature Change

It can be seen that cooling a porous solid, fully saturated at 0°C to below this temperature, creates a nonequilibrium condition. The water in the pores at, say, −2°C is in a liquid-like state and its vapor pressure that of undercooled water, thus higher than the vapor pressure of ice. At the same time the porous solid contains more water than it is possible to adsorb during isothermal saturation at this temperature. This nonequilibrium condition must be eliminated by one of the following processes.

Ideal Case

In the absence of freezing, which would reduce the vapor pressure from that of undercooled water to that of ice, equilibrium can be, and often is, established in nature by a very simple mechanism: part of the water contained in the pores migrates to, and freezes at, locations where the effect of the surface is not felt. Not all the water has to leave the porous solid; only such a quantity that the fraction remaining in the pores is under menisci with the appropriate curvature. Because the free energy of a liquid is less if it has a concave instead of a planar surface, equilibrium can be established between the external ice having relatively low vapor pressure and the unfrozen water in the partially filled pores with reduced vapor pressure.

As a result of this process, the porous body becomes partially desiccated and, consequently, contracts, while ice accumulates in cracks and on external surfaces. Significantly, no mechanical damage occurs.

On further cooling to temperatures lower than −2°C, the previously described sequence of events repeats itself because the difference between the vapor pressures of ice and undercooled water increases with decreasing temperature. Thus, on cooling, the radius of curvature of the menisci decreases, the moisture content of the porous solid decreases, and the amount of external ice increases.

According to the outlined mechanism, cooling of saturated porous bodies produces moisture transfer, but not necessarily mechanical damage.

Practical Case

In nature, and also in laboratory experiments, big step changes are frequently imposed on the system and, although moisture redistribution does take place due to the continuously increasing demand for mass transfer, the system moves through a succession of nonequilibrium states.

In the terminology of thermodynamics, the changes do not take place reversibly. Reversibility is approached if (*a*) the amount of water that has to be redistributed is small (that is, the porosity or degree of saturation, or both, are low), (*b*) the cooling rate is low, (*c*) the permeability of the system is high, (*d*) the migratory path is short, and (*e*) the mobility of the water is high, that is, the viscosity is low or the temperature is high.

It is known from field experience and laboratory studies that these conditions are, indeed, beneficial from a frost action point of view.

In contrast, when one or several of these parameters have unfavorable values, mass transfer does not take place at the required rate and mechanical damage ensues.

Mechanical Damage

Solids can suffer mechanical damage in nonequilibrium freeze-thaw cycles by one or several of the following mechanisms:

(*a*) It follows from the described theory that while on cooling the porous body loses water to the environment, on warming the reverse process takes place: water from the external surface and cracks migrates back to the interior. Whether all the water can be readsorbed before the next cooling period depends on various factors. Usually the resaturation process is incomplete, and because of the reduced water content in the interior the effect of frost action is less severe. The water accumulated in the fine cracks, however, freezes in the next cooling phase and the accompanying 9 percent volume increase may lead to propagation of the crack. The so-enlarged space attracts more water from the interior in the subsequent cycle and further damages occur. This mechanism can account for the destructive effect of repeated freeze-thaw cycling.

(*b*) The volume of porous solids that contain adsorbed water is affected by environmental changes. For example, cooling causes shrinkage as determined by the coefficient of thermal expansion and, in addition, results in an altered moisture content that also affects the dimensions of the porous body.

If cooling is rapid, significant temperature and moisture gradients are created, causing considerable stress.

In Fig. 1, the changes of the relative dynamic modulus of elasticity of neat cement ($W/C = 0.40$) prism (2.5 by 2.5 by 15 cm) are shown during drying at room temperature when exposed to (*a*) 50 percent RH, and (*b*) to 84 and

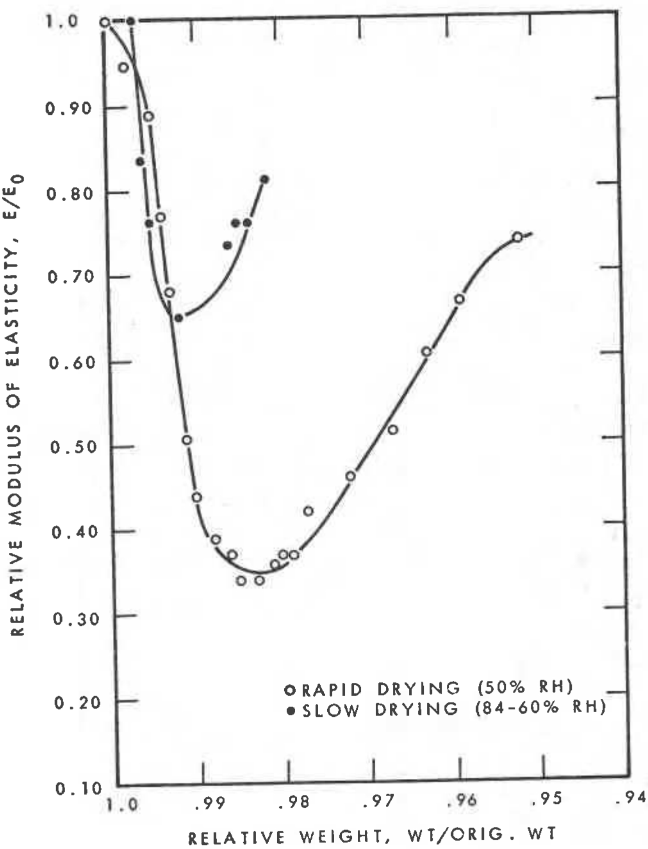

FIG. 1—*Relative dynamic Young's modulus of elasticity of a hydrated neat cement paste bar (water-cement ratio 0.4) during first drying. Solid circles ● indicate slow and open circles ○ rapid drying.*

subsequently to 66 percent relative humidity. The modulus was determined according to ASTM Test for Fundamental Transverse, Longitudinal and Torsional Frequencies of Concrete Specimens (C 215 - 60(76)).

It can be seen that on rapid drying the dynamic modulus of elasticity undergoes a transient decrease to a minimum of 33 percent of its original value, while on slow drying the minimum value of the modulus is 65 percent of that of the initial value. This transient decrease of the modulus of elasticity then depends on the drying rate, a characteristic feature consistent with the process of frost action.

The change in the modulus cannot be attributed to shrinkage or loss of water because similar transient reduction occurs also during wetting when the system expands.

That inhomogeneity created by rapid wetting or drying can create stresses that result in cracking is, of course, well known [*9, 10*]. Still, the question has to be asked, "Why do porous materials break up so much more frequently at low temperatures than above 0°C, at which temperatures wetting and drying often take place?". The answer to this query lies in the fact that it is extremely difficult, if at all possible, to create by other means rates of drying of the magnitude produced during cooling in the range below 0°C.

It is fair to assume that the transient modulus decrease shown in the drying or wetting process is an indication of distress to the material with possible undesirable consequences if the transient is too great and a more serious distress would occur during the freezing process. At this time, these observations are given without any attempt at complete explanation.

(*c*) Another process also leads to damage. If on cooling, the amount of water to be transferred is produced at a higher rate than the rate of moisture migration out of the pores, an excess of water is created. Because the ultimate adsorbed water content continuously decreases with decreasing temperature below 0°C, and in this range the migration rate decreases as cooling progresses, the quantity of nonequilibrium water continuously increases. At some stage, due to the greatly increased viscosity, mass transfer comes to a complete halt and the excess water forms a noncrystalline, amorphous solid.

The dimensional changes of the porous system due to changes of temperature and moisture content are affected by the presence of a glassy solid in the porous body. This is manifested by the abrupt and significant changes in the extension curves of porous adsorbent-adsorbate systems on cooling below a certain temperature at which presumably the glass formation occurred. As a rule, the dimensional changes, or the coefficients of thermal expansion, are very small in the temperature region in which amorphous ice is present in the pores. While in this state the mechanical properties of the system improve, due to the stiffening effect of the solidified water, warming to above thawing temperatures usually reveals the occurrence of mechanical damages manifested by permanent volume increase of the system. In practice, too, damages caused by freezing and thawing in roads become apparent only in the springtime when the ice has melted.

As stated earlier, mechanical damage is caused by a condition in which moisture transfer cannot take place in an orderly fashion, that is, reversibly. It is not unreasonable to assume that in this irreversible catastrophe the system can suffer damages by one or more of several mechanisms.

Implications of the Theory

Testing

Labeling a specimen frost-resistant, in the case of concrete, brick, or stone, is undoubtedly incorrect because under certain conditions any porous material can be destroyed by freezing and thawing. It follows from the dynamic character of frost action that a statement concerning the durability of a material is meaningful only in the context of specified geographical areas and a particular application, for example, concrete for road pavement in Montreal or bricks for high-rise building in Southern Ontario. At present specimens are subjected to repeated freezing and thawing under severe, and not necessarily representative, conditions. It would be clearly most desirable to assess the suitability of a material for a given application by evaluating the relevant material properties with reference to the anticipated severity of the environment expressed by well-defined factors. Unfortunately, these have not been identified for any of the cases.

The most important factor is the moisture content. Remarkably little effort has been made to collect information on the water content of common building materials in representative settings. It is not known whether the average and extreme values of moisture content of, say, a concrete parapet wall are 60 or 95 percent of complete saturation at the time of the onset of frost action. Furthermore, the water content of the specimens in the standard freeze-thaw test is neither known or specified. Frequently, the specimens are frozen and thawed with a low water content (short saturation period), declared frost resistant and the material then put in service under conditions in which it will collect a lot of water. While, in this case, failure occurs, no estimate can be made of the instances in which materials have been rejected on the basis of too severe tests.

Material's Characteristics to Enhance Frost Resistance

Good service of materials can be expected if the porosity is low, because the amount of water in the pores is thus reduced. In the case of concrete, low porosity can be effected by selecting low values for the water-cement ratio.

On the other end of the spectrum, very high porosity can be beneficial because large pores become filled only when the relative humidity is almost

100 percent, a condition which seldom occurs. In addition, the water can escape easily from systems having large pores.

It is perhaps useful to mention that any condition that reduces permeability without decreasing drastically the porosity is detrimental and should be avoided. All surface coverings, be it glazing on bricks, or paint or even silicone treatment, are potentially detrimental because, while they do not prevent the accumulation through condensation of moisture in the pores, they hinder egress of water.

Air entrainment is a highly successful method for improving the frost resistance of concrete by the formation of air voids in the paste at regular and frequent intervals. The protective effect can be ascribed to the provision of a refuge for the excess water thus eliminating the need for the moisture to migrate to the external surfaces or, conversely, avoiding the accumulation of excess water in the pores. It is obviously very important for the voids to be distributed evenly and be present in large numbers.

The more serious damages in the presence of deicing salts are, according to laboratory experiments, due to the higher degree of saturation brought about by the presence of a solution, instead of pure water, in the pores.

Design Principles To Improve Freeze-Thaw Durability

In order to avoid mechanical damage due to frost action the moisture content should be such that the amount of excess water generated in unit time is less than the quantity lost by the porous solid to the exterior in the same period. This condition will exist if the total moisture content of the body is low, in which case no excess water is produced, or failing that, the permeability is high and the cooling rate low, or permeability low but thickness of elements small (spacing between air voids). The means to achieve the latter condition were discussed in the preceding paragraph. The requirements to realize low water content shall now be considered.

Sources of water in porous building materials are precipitation, driving rain and melting snow. There are various ways to minimize the ingress of water by careful design. Vertical walls can be protected with roof overhangs, eaves-troughs, and cladding. Horizontal surfaces always should be provided with a slope, crown, or camber to promote drainage and avoid the formation of water pools.

Another, often overlooked, source of water is condensation from the vapor phase. In wintertime, walls of enclosures are usually the coldest region of the interior space and unless effective vapor and air barriers are installed water vapor condenses in the walls.

As a rule, no reasonable effort to avoid high water content during service should be spared in the design stage. With relatively modest expenditure the occurrence of serious and costly problems usually can be prevented.

Conclusion

All the observations listed under "Experimental Observations" are explicable with the described theory. The significance of water content, cooling rate, porosity, and physical dimensions of the body are readily understandable. The mechanism is not specific to water or to a single type of solid. The theory is applicable also to cases in which deicing salts are present.

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