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The Mechanism of Frost Action in Concrete - Theory and Practical Implications

by G.G. Litvan

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Résumé

Les expériences révèlent que la séquence de faits menant à la détérioration du béton lors des cycles de gel et de dégel a pour cause l'incapacité de l'eau absorbée en surface, ou contenue dans les petits pores du béton, de geler en raison de l'interaction du substrat et de l'eau. La pression de vapeur de l'eau non gelée contenue dans les pores, très froide, étant plus élevée que celle de la glace se trouvant aux alentours, cette eau migre vers des endroits, comme les gros pores ou la surface extérieure, où elle peut geler. Ce processus entraîne, outre la formation de lentilles de glace et l'accumulation d'eau en surface, la dessiccation partielle du pore. La fissuration résulte de la fonte et du gel des lentilles de glace ou d'une condition dans laquelle la redistribution de l'eau ne peut se produire.

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THE MECHANISM OF FROST ACTION IN CONCRETE –THEORY AND PRACTICAL IMPLICATIONS

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SUMMARY

Experiments indicate that the chain of events leading to deterioration of concrete in freezing and thawing cycles originate by the inability of water absorbed on the surface, or held in the smaller pores of concrete, to freeze due to the interaction between the substrate and water. Because the vapor pressure of the supercooled unfrozen water in the pores is greater than that of bulk ice in the surroundings, water migrates from the interior of the concrete to locations, such as large pores or outer surface, where it can freeze. This process results in partial desiccation of the pore in addition to ice lensing and accumulation of water on the surface. Cracking is the result of melting and freezing of the ice lenses or a condition in which redistribution of the water cannot take place.

This theory has been utilized for the development of test methods for the assessment of frost resistance of porous materials.

Based on these findings, it became possible to develop a novel admixture for the protection of concrete from damages of freezing and thawing. In place of current air entraining admixture, particulate matters with well defined pore structure are added to the plastic mix. The proposed method relies on the action of pre-formed air-voids instead of the formation of air-bubbles in the mixing process. By doing so, the principal cause for the limited reliability of air entrainment by conventional admixture is eliminated.

1. INTRODUCTION

Freezing and thawing is still of great concern in spite of dramatic advances in construction practices, and most notably by the introduction of air entrainment about 40 years ago.

The unacceptably high failure rate is to a large extent due to improper mix design or poor workmanship. But there are other problems, of which the most important are perhaps testing of the resistance to freezing and thawing of concrete and aggregates, and protection against the effect of de-icing salts. It seems that to achieve further progress in these areas a good understanding of the mechanism of freezing and thawing in porous materials is necessary.

Some aspects of the mechanism of freezing and thawing in concrete and their implications in practice are discussed in this paper.

2. THEORY

2.1 Characteristic Features of the Freezing and Thawing Phenomenon

1. The severity of the mechanical damage caused by freezing and thawing is directly proportional to the degree of saturation of the concrete or other porous solids.

In Fig. 1 the dimensional changes of fully saturated cement specimens (water/cement (W/C) ratios 0.5 and 0.8; 3.17 mm (0.125 in) thick) during a cooling-warming cycle between +5 and -70°C are shown [1]. The 0.8 W/C ratio specimen expanded 0.7% when fully saturated while a similar specimen contracted 0.12 % if conditioned at 84% RH (Fig 2). In a fully saturated state few systems can endure even a single freezing and thawing cycle without suffering injury.

2. Under comparable conditions the specimen with the largest minimum dimension suffers the greatest damage. It is well known that decreasing the size of aggregates increases their frost resistance.

A comparison of the length changes of the cement specimens of 1.27 mm (Fig. 3) thickness with that of 3.17 mm thickness (Fig. 1) illustrates this point.

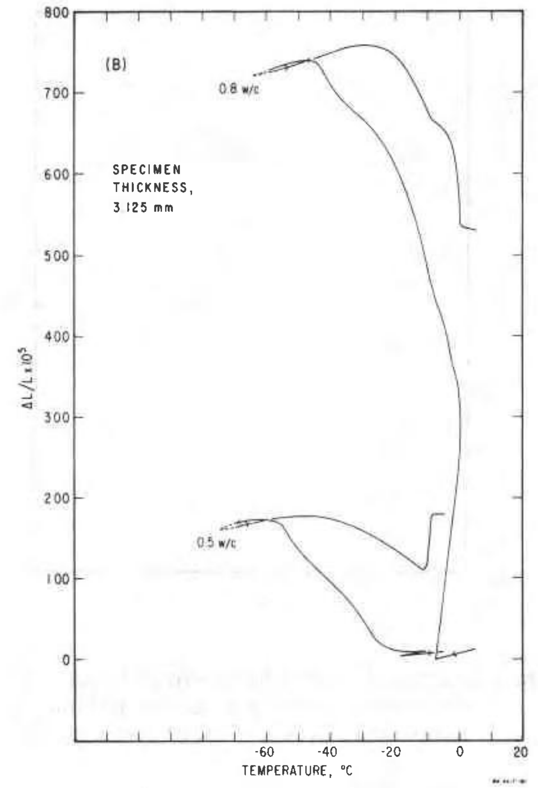

Figure 1 Fractional length changes of vacuum saturated plain cement specimens during temperature cycles. Specimen thickness is 3.17 mm (0.125 in.). The w/c ratio values are indicated on the curves. For sake of ease of presentation curves are shifted along the temperature axis. Starting temperature in each case is +5°C.

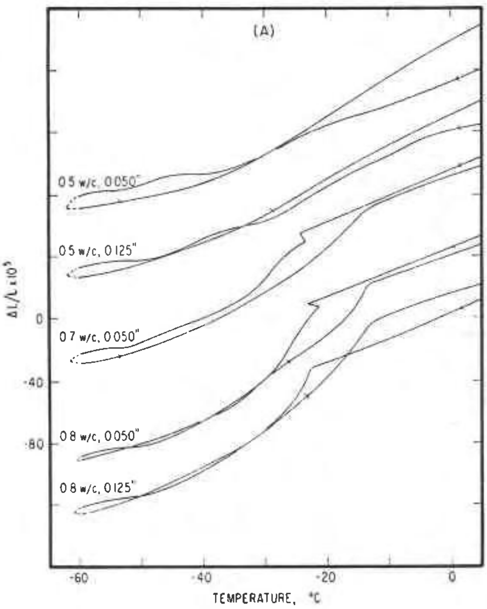

Figure 2 Fractional length changes of plain cement specimens equilibrated at 84% RH during temperature cycles. Rate of cooling is 20°C/h.

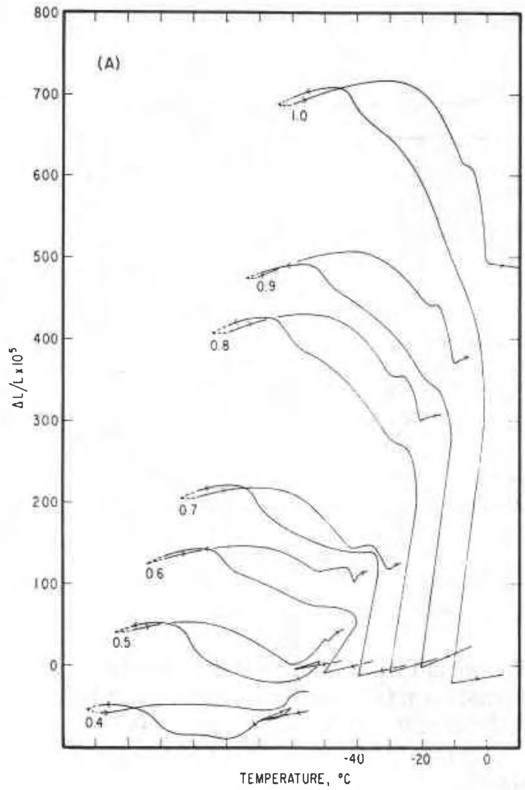

Figure 3 Fractional length changes of vacuum saturated plain cement specimens during temperature cycles. Specimen thickness 1.27 mm (0.050 in.). The w/c ratios are indicated on the curves. For sake of ease of presentation the curves are shifted along the temperature axis. Starting temperature, in each case, was +5°C.

3. Increasing cooling and warming rates result in increased mechanical damage. If the rate is low even very vulnerable systems can go through freezing and thawing cycle without suffering damages. This is shown in Fig. 4 in which the dimensional changes of a cement specimen (W/C = 0.7) indicate no lasting effect by the temperature cycle at 2.5°C/h rate while a similar specimen shows considerable residual expansion at 20°C/h rate (Fig. 3).

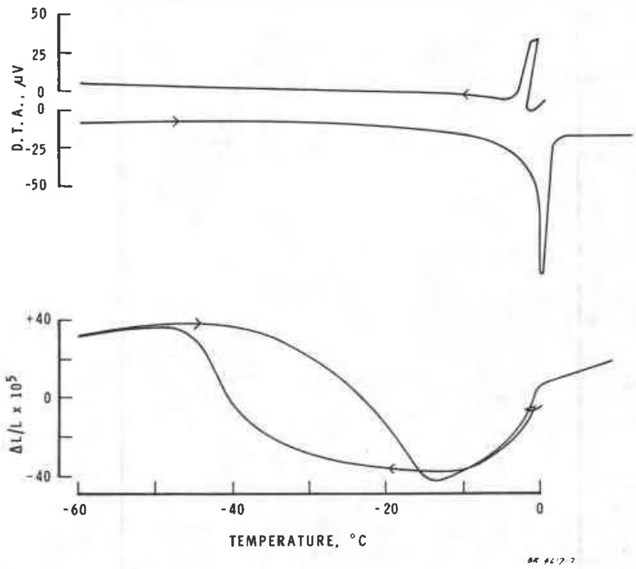

Figure 4 Fractional length changes (bottom) and thermogram (top) of a 3.17 mm (0.125 in.) thick cement specimen (w/c ratio = 0.7) during a temperature cycle at a slow rate (0.0417°C/min).

4. Highly porous or very dense solids have good service records. Highly porous "no fines" concrete, or brick on one hand and dense marble on the other are examples of such materials. Portland cement concrete normally has intermediate porosity. The low W/C ratio pastes, less than 0.4, are durable under most circumstances but mixes of higher W/C ratio, though of medium porosity, are usually frost susceptible.

5. Air entrainment, i.e. the creation of a pore structure that contains numerous larger pores at close intervals, has proved to be an excellent method to enhance the frost resistance of cement and concrete.

6. The main characteristics of the freezing and thawing phenomenon appear to be common to many types of porous solids. In Figure 5 the dimensional changes of porous 96% silica glass (2) and in Fig. 6 those of marble, limestone and sandstone during a cooling-warming cycle are shown. The essential features, viz. the existence of two freezing ranges both associated with expansion, hysteresis, residual expansion after completion of the cycle, sensitivity to sample thickness and cooling rates, are similar to those observed with cement paste.

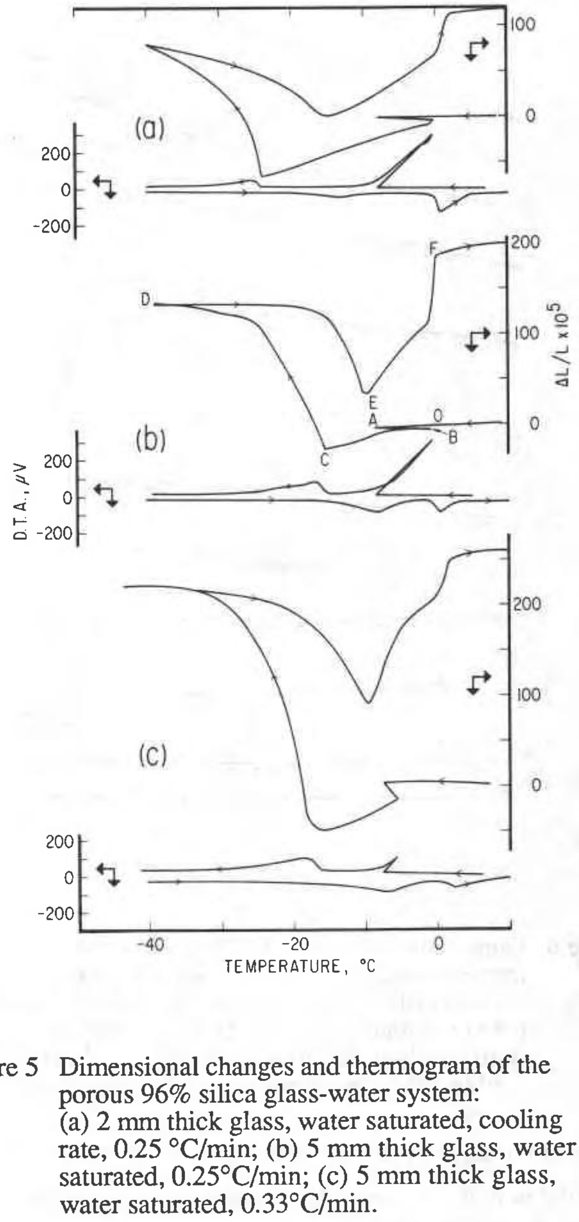

Figure 5 Dimensional changes and thermogram of the porous 96% silica glass-water system: (a) 2 mm thick glass, water saturated, cooling rate, 0.25 °C/min; (b) 5 mm thick glass, water saturated, 0.25°C/min; (c) 5 mm thick glass, water saturated, 0.33°C/min.

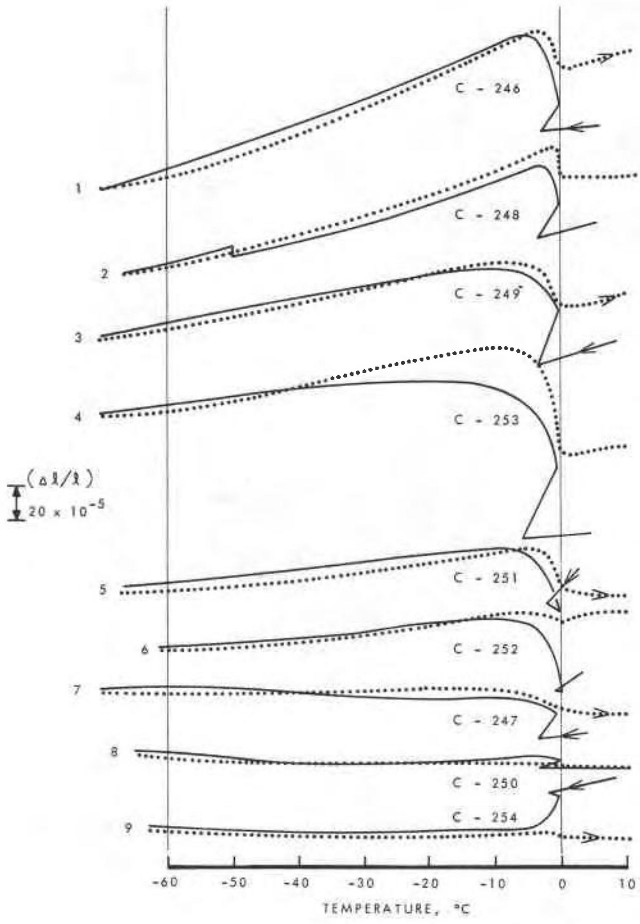

Figure 6 Dimensional changes of stone samples in freeze-thaw cycle. (1) Briar hill sandstone, (2) Colorado marble, (3) crab orchard sandstone, (4) Minnesota limestone, (5) Indiana limestone (buff) (6) Indiana limestone (grey), (7) Missouri marble, (8) Georgia marble, (9) Vermont marble.

7. When the pores of the solid contain organic liquid, the features of the freezing-thawing phenomenon are similar to those observed with water. The length changes during low temperature cycles of porous 96% silica glass saturated with various organic liquids are shown in Figures 7 and 8 (2). Immersed in benzene, porous silica glass manifested 0.3% residual expansion (Fig. 9), indicative of serious permanent damage due to freezing and thawing [2].

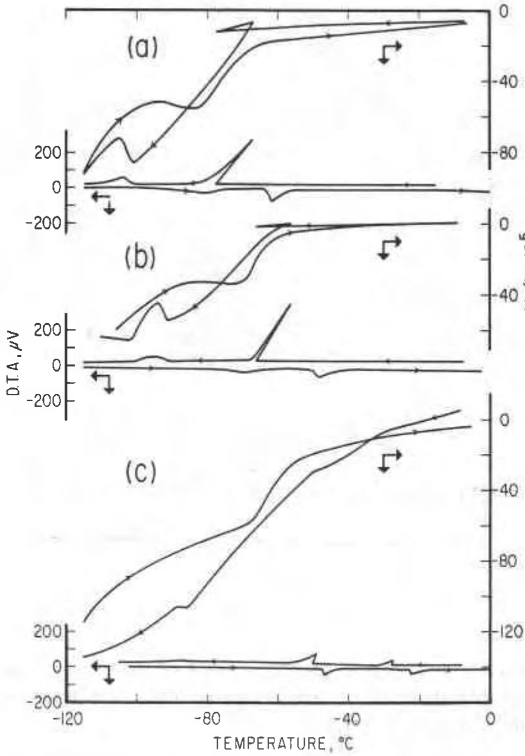

Figure 7 Dimensional changes and thermograms of 5 mm thick porous glass with various adsorbates (a) chloroform, mp-63.5°C; (b) m-xylene, mp-47.9°C; (c) carbon tetrachloride, mp-22.96°C.

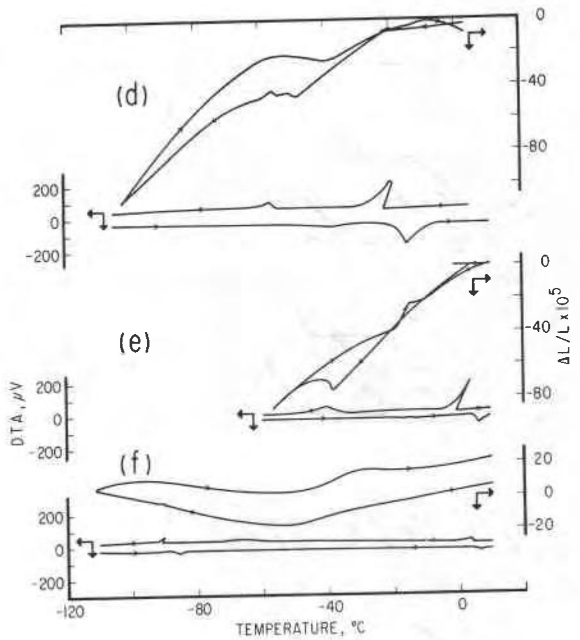

Figure 8 Dimensional changes and thermograms of a 5 mm thick porous glass with various adsorbates: (d) octanol, mp-16.7°C; (e) benzene, mp- +5.5°C; (f) cyclohexane, mp- +6.5°C.

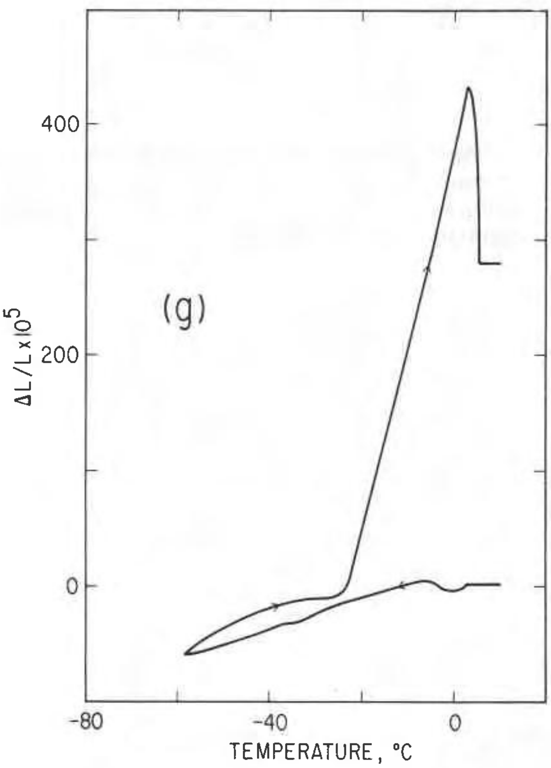

Figure 9 Dimensional changes of 5 mm thick porous glass immersed in benzene.

8. Repeated freezing and thawing under field conditions leads to desiccation and accumulation of the liquid outside of the body (lens formation) emanating from the pores.

9. When a solution is contained in the pores the damage from freezing and thawing is much more severe compared to that found with systems saturated with a pure liquid such as water. For example, the residual expansion found with a 0.5 w/c ratio cement paste in a 5% sodium chloride solution was 1% (Fig. 10) [3] more than five times larger than in water, 0.18% (Fig. 3).

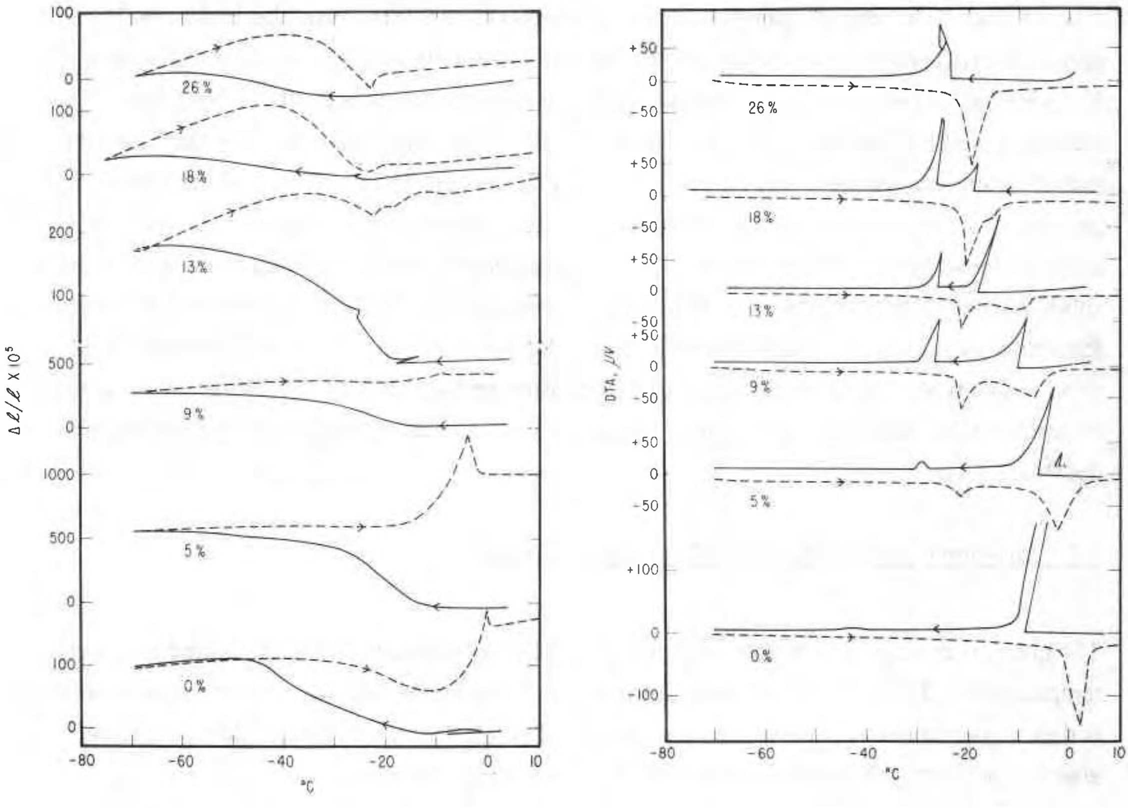

Figure 10 Fractional length changes and thermograms of 0.5 w/c ratio cement pastes impregnated with NaCl solutions (concentrations as indicated) during temperature cycles.

3. MECHANISM

Frost action also occurs with organic liquids that normally contract on freezing, clearly indicating that the 9% increase in volume associated with the freezing of bulk water cannot by itself explain all the phenomena.

3.1 Absence of Crystallization of Water in Pores

It was found in isothermal adsorption studies that water is unable to crystallize in the confined spaces of small pores, a fact responsible for the chain of events leading to mechanical failure [2]. If a porous solid contains liquid water instead of ice at temperatures below 0°C, complete saturation would take place only if the vapour pressure above the solid were to become equal to that of supercooled water. This cannot be realized in practice, however, because the vapour pressure of supercooled water is greater than that of ice; any attempt to elevate the vapour pressure above the level of that of ice will result in ice deposition outside the pore system of the solid. As a consequence, complete saturation of porous solids with water cannot be achieved at temperatures below 0°C. Furthermore, because the difference in the vapour pressures of supercooled water and of ice increases with decreasing temperature, the equilibrium water content of porous bodies falls short of complete saturation by an increasing margin as the temperature decreases.

3.2 Moisture Content Affected by Temperature Change

The question arises: what happens if a porous solid, fully saturated at 0°C, is cooled to lower temperatures? The water in the pores at, say, -2°C is in a liquid-like state and its vapour pressure is thus higher than that of ice in the environment. This non-equilibrium condition can, in the absence of freezing, be eliminated by one of the following processes:

a. Ideal case

In the absence of freezing (which would reduce the vapour 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, ie. in larger pores. Only enough liquid leaves the pores to put the fraction remaining in the pores under menisci having vapour pressure equal to that of ice. 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 and the unfrozen water, the vapour pressure of which is reduced by menisus effect.

As a result of this process, the porous body becomes partially desiccated and consequently contracts; ice accumulates in the large pores and on external surfaces. Significantly, no mechanical damage occurs. On further cooling to temperatures lower than -2°C, this sequence of events has to repeat itself because the difference between the vapour 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.

b. Practical case

In nature and in laboratory experiments large cyclic changes are frequently imposed on the system and, although moisture redistribution takes place under the continuously increasing demand for mass transfer, the system is unable to change rapidly enough to maintain equilibrium. In the terminology of thermodynamics, the changes are not reversible.

Reversibility, or coping with the demand, is possible if (a) the amount of water to be redistributed is small (that is, the porosity or the 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 under these conditions damage is, indeed, minimal. In contrast, if one or several of the parameters are unfavorable, mass transfer does not take place at the required rate and mechanical damage ensues.

4. MECHANICAL DAMAGE

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

a. It follows from the described theory that if, on cooling, the porous body loses water to the environment, the reverse process will take place on warming: water migrates back to the interior from the external surface and cracks. Whether all the water can be re-absorbed before the next cooling period depends on various factors, but usually the re-saturation process is incomplete. The water accumulated and remaining in the cracks freezes in the next cooling phase and the accompanying 9% volume increase. The space so enlarged will attract more water from the interior in subsequent cycles inflicting further damage. This mechanism can account for the destructive effect of repeated freeze-thaw cycling.

b. The volume of porous solids containing adsorbed water is affected by environmental changes. For example, cooling causes shrinkage of the solid as well as reduction of the moisture content. If cooling is rapid significant temperature and moisture gradients are created that create considerable stress.

In Fig. 11 the changes in the relative dynamic modulus of elasticity of a water saturated cement prism (2.5 by 2.5 by 2.5 cm, w/c ratio 0.4) on exposure at room temperature to (a) 50% RH or to (b) 84 and subsequently 66% RH are shown. The modulus was determined according to ASTM C215-60(76), Test for Fundamental Transverse, Longitudinal and Torsional Frequencies of Concrete Specimens.

It can be seen that during rapid drying the dynamic modulus of elasticity falls to 33% of its original value; on slow drying the minimum value of the modulus is higher, 65% that of the initial value as is transient decrease of the modulus of elasticity. It should be noted that one of the characteristic features of the freezing-thawing phenomenon is the dependency of the severity on the cooling rate. According to the described theory cooling results in desiccation and the significant effect of drying rate on the impairment of mechanical properties is consistent with the theory. 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.

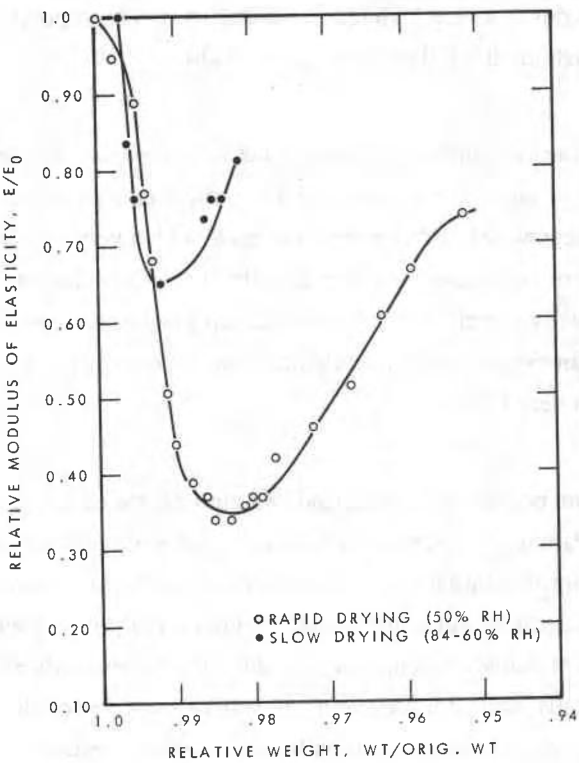

Figure 11 Relative dynamic Young's modulus of elasticity of a hydrated cement paste bar (w/c ratio 0.4) during first drying.

Inhomogeneity created by rapid wetting and drying is known to create stresses that result in cracking. In frost action the damage is more severe by the very high rate of drying during cooling to temperatures below 0°C.

c. In a frost-susceptible porous solid the rate of water movement out of the pores declines with decreasing temperature to a level much less than that required to maintain equilibrium. As the temperature is lowered the amount and viscosity of the excess water increase to the point where the movement of water ceases and as a consequence a non-crystalline, amorphous solid forms.

5. FACTORS AFFECTING FROST RESISTANCE

The theory makes it possible to recommend measures to achieve good resistance to freezing and thawing. The single most important factor is to keep the water content low. Moisture content in a porous solid will be low if either porosity is very low, or very high. In the former case there is no space for water to accumulate, and in the latter case water will accumulate in the pores only on exposure for extended periods to a very high relative humidity and most pores will empty immediately as the relative humidity falls slightly below 100%.

Low porosity in concrete can be achieved by keeping the w/c ratio low. Concrete with a 0.4 w/c ratio has such good frost resistance that the need for air entrainment is questioned by some experts. Unfortunately, it cannot be said that concrete made with a very high w/c ratio is also durable; although the porosity increases very significantly, it does not reach a sufficiently high value. In fact, 0.6 or 0.7 w/c concrete is highly frost susceptible because considerable amounts of water can be contained in the pore system while the average pore diameter is still quite small and the permeability is not very high.

Reduced moisture loss from porous bodies can lead to a high degree of saturation and, because of this, to frost damage. Painting a concrete or brick wall with a "non-breathing" oil paint can transform a well functioning structure to one with a durability problem. Special mention has to be made of waterproofers, sealers, and impregnants. Reduction of porosity and a ingress of water is very beneficial in principle. Often, however, these agents also reduce the rate of evaporation very substantially while not preventing all water from entering the network. Silicone application, for example, prevents rain penetration but not moisture condensation resulting in a drastically reduced water loss and elevated water content and, thus, frost damage.

Architects, engineers and designers should recognize that frost damage can be minimized by providing means to avoid accumulation of water in roads, building walls, and bridge decks. Ponding on horizontal surfaces should be avoided by appropriate detailing such as slopes, camber or flashing, drains, etc.

Permeability is also important since it affects the accumulation of water before freezing, the rate of its expulsion during freezing, and therefore, frost resistance itself. Material properties affecting diffusion rate also influence frost action. Among these, the length of the diffusion path or size of the porous solid is of great significance.

6. SALT SCALING

Apart from exceptional cases, de-icing salts do not attack concrete through chemical action. The aggravating effect of de-icing salts on frost action results from the fact that solutions have lower vapour pressure than pure liquids; at a given relative humidity, therefore, saturation of the concrete is more closely approached than without solutes. Conversely, if concrete or another porous body is saturated with a solution rather than pure water, desiccation or evaporation will commence at lower relative humidity than would be the case with pure water in the pores. For example, a porous solid containing a 26% NaCl solution will not lose any liquid, remaining saturated until after the relative humidity falls below 77%. The importance of the degree of saturation in frost action has already been emphasized. High moisture content can thus account for the aggravating effect of de-icing salts.

7. AIR ENTRAINMENT

The method of improving frost resistance of concrete by entrained voids in the paste has been used with great success for many decades. The protective effect can be attributed to the provision of a reservoir for the excess water, eliminating the need for the water to migrate to the external surfaces or, conversely, avoiding the accumulation of excess water in the pores. The voids obviously have to be distributed evenly and to be present in large numbers.

The performance of concrete in freezing and thawing containing a high range water reducer admixture raises questions concerning the type and size of voids required for protection. In such concrete a 0.2 mm spacing factor is very difficult to achieve; despite this apparent shortcoming, the freeze-thaw resistance very significantly better than expected on the basis of paste characteristics [4].

Analysis of the pore structure showed the presence of a large number of relatively small pores (0.8 to 2 μm diam) in air-entrained pastes containing high range water reducer (Fig. 12). This finding suggests that for freeze-thaw protection pores of relatively small size if present in large numbers are sufficient. Air voids of large sizes in the 30 to 500 μm range which are conventionally considered as air-entrained may not be essential [4]. In fact because of their large size at a given air content they cannot be as closely spaced as smaller sized pores.

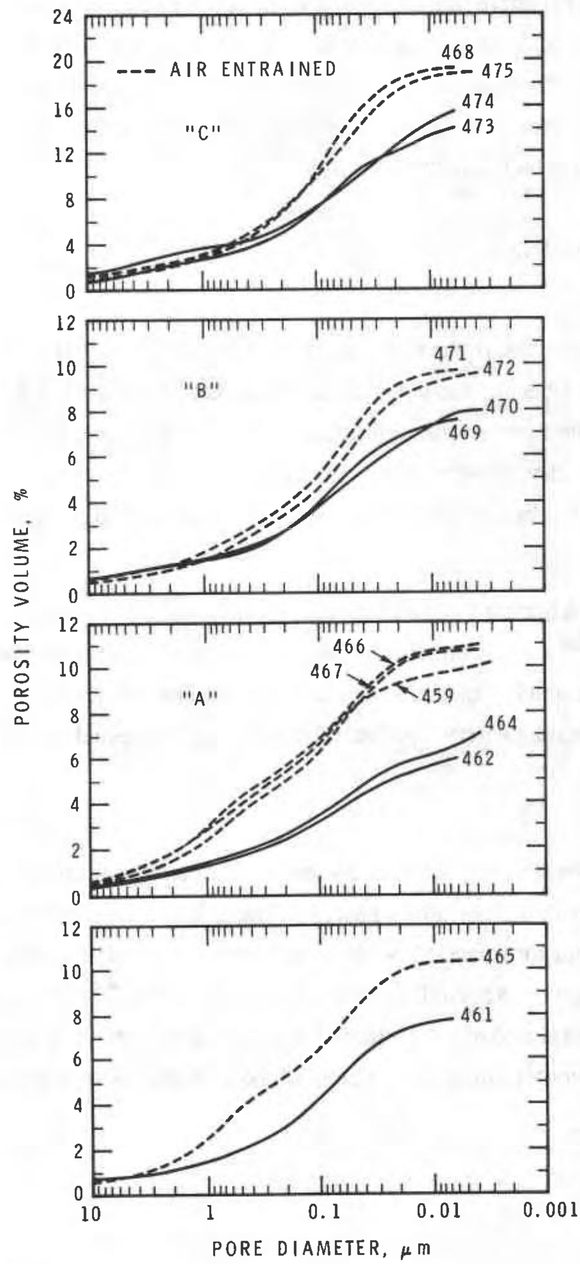

Figure 12 Pore size distribution of specimens determined by mercury porosimetry. Plain mixes are drawn with solid lines, air entrained mixes are represented by broken lines.

8. AIR ENTRAINMENT BY POROUS PARTICULATE ADMIXTURE

Air entrainment is normally effected by the addition of a surface active agent to the plastic mix. The great disadvantage of this method is that the success of the operation depends on many environmental factors such as temperature, length and rate of mixing, impurities in the mix, the shape of sand particles, etc. As the spacing factor of the plastic mix cannot be measured, uncertainty exists concerning of the quality of the concrete at the time of placement in the form. By the time deficiencies can be determined it may be too late for corrective action.

The addition of preformed voids in the form of particles overcomes these difficulties. Porous particulates with at least 30 per cent total porosity and pore diameters mainly between 0.8 and 2 μm have been found to enhance the freeze-thaw resistance of hydrated portland cement and mortar [5,6]. It should be mentioned that the effective particulates had pores with diameters similar to those found in large numbers in air-entrained pastes.

9. TESTING

The performance of a given concrete cannot be predicted unless the characteristics of the environment to which it will be exposed are known. The term "frost resistant concrete" is somewhat misleading because it implies that the concrete will withstand the action of freezing and thawing under any condition. It should only be interpreted to mean that under the anticipated service conditions it will not be damaged by freezing and thawing.

Testing, therefore, requires an estimate of the most important service conditions, particularly the moisture content at the time of freezing. Given its wide variation, the degree of saturation at freezing is the major source of error in the assessment of frost resistance.

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