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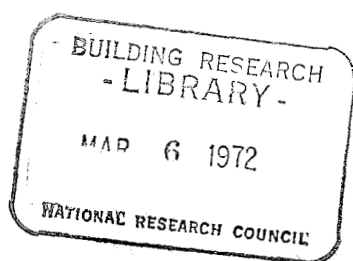
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PHASE TRANSITIONS OF ADSORBATES
IV. MECHANISM OF FROST ACTION IN
HARDENED CEMENT PASTE

BY
G. G. LITVAN

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TRANSITION DANS LES PHASES DES PRODUITS ABSORBES
IV. MECANISMES DU GEL DANS LA PATE DE
CIMENT DURCIE

SOMMAIRE



Les changements de dimension et les thermogrammes de spécimens de ciment ont été déterminés au cours de cycles de température ($+5$ à -60°C , $0.33^{\circ}\text{C}/\text{min.}$). Dans chaque cas, deux processus de congélation (à -8 et à -40°C) et deux processus de fusion (à -11 et à 0°C) ont été observés. Il est possible d'expliquer les résultats par la théorie formulée au sujet du système d'eau—verre poreux. Ainsi, à la température plus élevée, la congélation se produit à la surface extérieure des spécimens et, à la température moins élevée, dans les pores après l'absorption de l'eau. Le rapport eau/ciment, le degré de saturation, la taille des pores et la forme de l'échantillon et le taux de refroidissement sont en accord avec la théorie.

Phase Transitions of Adsorbates: IV, Mechanism of Frost Action in Hardened Cement Paste*

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The dimensional changes and the thermograms of cement specimens were determined during temperature cycles ($+5^{\circ}$ to -60°C , $0.33^{\circ}\text{C}/\text{min}$). In each case, freezing processes at -8° and -40°C and melting processes at -11° and 0°C were observed. The results could be explained by a theory previously developed for the porous-glass-water system. At the higher temperature, freezing occurs on the outer surface of the specimen; at the lower temperature, it occurs in the pores after redistribution of the water. Because water does not freeze in pores filled on adsorption, it migrates out of these pores when the relative humidity (expressed in terms of the vapor pressure of undercooled water), unavoidably decreases on cooling. Expansion is deleterious when the water content of the paste is significantly greater than the equilibrium value at the prevailing relative humidity. The effects of the water/cement ratio, degree of saturation, air entrainment, sample dimensions, and cooling rate were consistent with the theory.

I. Introduction

FROST damage of concrete has been greatly reduced by the widespread use of air-entraining agents and by general compliance with empirical rules for the production of durable concrete. Certain problems, however, such as salt scaling, rapid deterioration of bridge decks, lack of a test method for quantitative measurement of damages from frost action, and inability to assess frost resistance, remain unsolved. Further study of the freezing phenomenon, therefore, is warranted.

The disintegration of concrete at $<0^{\circ}\text{C}$ was first attributed solely to the 9% volume increase of the pore water on freezing.¹ It was argued that, if the cement paste cannot accommodate the increased volume of the ice and exude the excess, destructive internal pressure is generated. This theory also accounted for the observed migration of the water. When it was learned that frost-resistant concrete contracts on freezing, the concepts of osmosis and the transport of water from the gel pores to the capillary cavities via the adsorbed state were incorporated.²

The freezing phenomenon of adsorbates has been extensively studied in porous 96% SiO_2 glass, a substrate better defined and more amenable to investigations than cement paste. A theory developed³ to account for the freezing characteristics of various liquids adsorbed in porous glass contains no element specific to porous glass and is believed to be valid for hydrated cement. The present study was undertaken to verify this assumption.

II. Experimental Procedure

Length changes and heat effects during temperature cycles were determined. The apparatus has been described previously.³

Cylinders 6 in. long and $1\frac{1}{4}$ in. in diameter were fabricated, with air and CO_2 excluded, by the method of Sereda and Swenson.⁴ At the time of the experiments, the cylinders were ≥ 4 years old. The ends of the cylinders were discarded and

wafers 0.050 and 0.125 in. thick were cut; rectangular specimens 1.16 by 0.25 in. were cut from the wafers. The specimens were kept wet at all times. The value of the spacing factor for the air-entrained samples was 0.020 in. and the air content was 3.45%.

The samples were vacuum-saturated individually in glass cells. To avoid desiccation, they were de-aired in the presence of water vapor. The partial pressure of air was estimated as $<1 \times 10^{-2}$ torr. Partial saturation to 84% relative humidity was attained by keeping the specimens for 6 weeks over saturated KBr solution in the absence of air in a desiccator kept at constant temperature ($\pm 0.05^{\circ}\text{C}$).

The specimen was quickly mounted in the extensometer and the cell hermetically sealed. The vessel contained a few drops of water to prevent desiccation. The temperature was automatically changed at a constant rate of $0.33^{\circ}\text{C}/\text{min}$ unless otherwise stated.

III. Results and Discussion

The dimensional changes and the thermograms of vacuum-saturated specimens (Fig. 1) show the effect of the water-cement ratio (w/c) and specimen thickness. The influence of air entrainment on the same parameters can be seen in Fig. 2. The results of the experiments with partially saturated specimens, 0.050 and 0.125 in. thick, of various w/c ratios are presented in Fig. 3.

(1) Freezing at -8°C

The anomaly in the length changes occurring near -8°C (Figs. 1 and 2) (Refs. 5-8) is associated with an exothermic heat effect, proving that at least a portion of the water freezes. A similar irregularity in the length plot of porous glass³ was explained by the following theory. Water contained in the pores of a porous body has a lowered freezing point and therefore remains in the liquid state on cooling to $<0^{\circ}\text{C}$. A body fully saturated at 0°C remains in this condition only if 100% rh is maintained, i.e. during cooling, the pressure of the water vapor above the system is equal to the pressure over supercooled bulk water, p_i^0 . This condition, however, does not normally occur.

It should be remembered that the water vapor pressure can exceed the vapor pressure of bulk ice, p_s^0 , only temporarily because condensation in the form of ice restores the value. Thus, at $<0^{\circ}\text{C}$ the maximum attainable pressure is p_i^0 . The value of p_i^0 , however, is greater than p_s^0 and therefore the relative humidity decreases. Furthermore, because the difference between p_i^0 and p_s^0 increases with decreasing temperatures, the specimen, on cooling, is exposed to pressures

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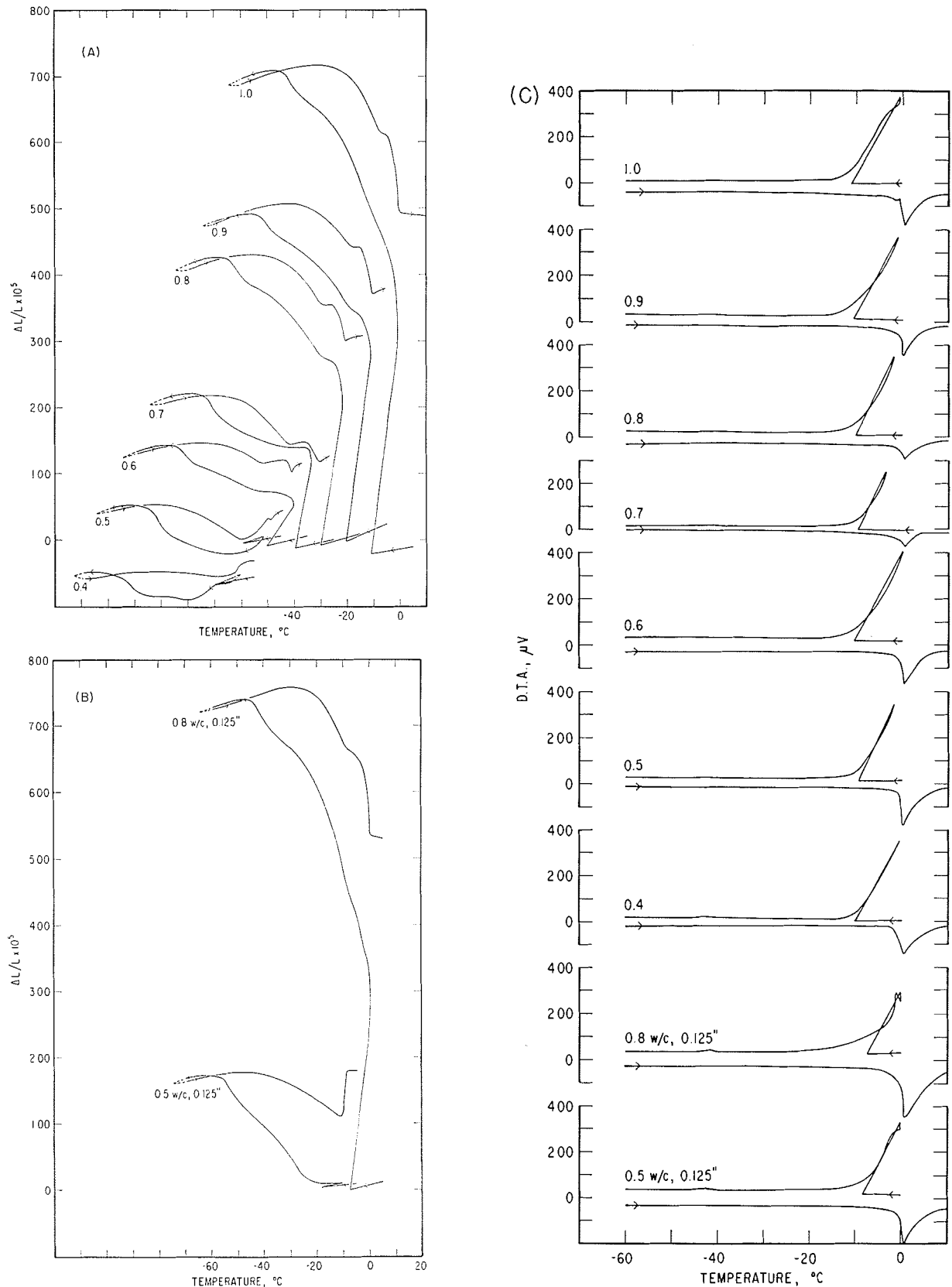


Fig. 1. (A) and (B) Fractional length changes and (C) thermograms of vacuum-saturated plain cement specimens determined simultaneously during temperature cycles. Specimen thickness (A) 0.050 in. and (B) 0.125 in. The w/c values are indicated on the curves. For sake of clarity the curves are shifted along the temperature axis. Starting temperature in each case is +5°C.

of smaller and smaller fractions of p_i^0 , i.e. diminishing relative humidity that causes continuous desiccation. The desorbed water migrates to the outer surface where it freezes.

This explanation is consistent with the observed behavior. The heat is released abruptly due to undercooling of the water on the surface; migration begins at 0°C and the accumulated

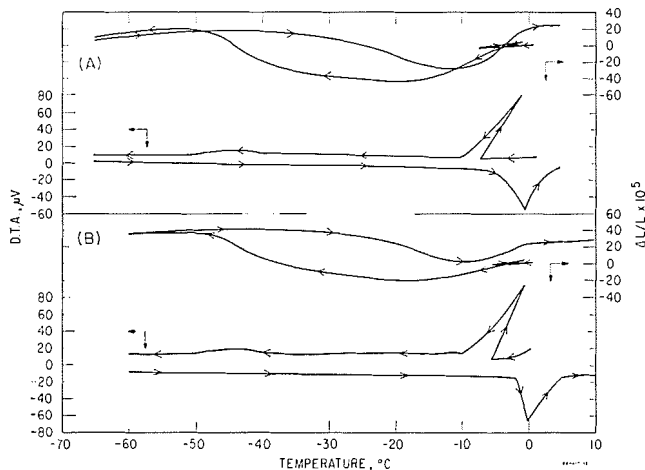


Fig. 2. Fractional length changes and thermograms of air-entrained specimens vacuum-saturated with water. (A) 0.050 in. and (B) 0.125 in. thick; $w/c=0.5$, spacing factor =0.020 in., and air content=3.45%.

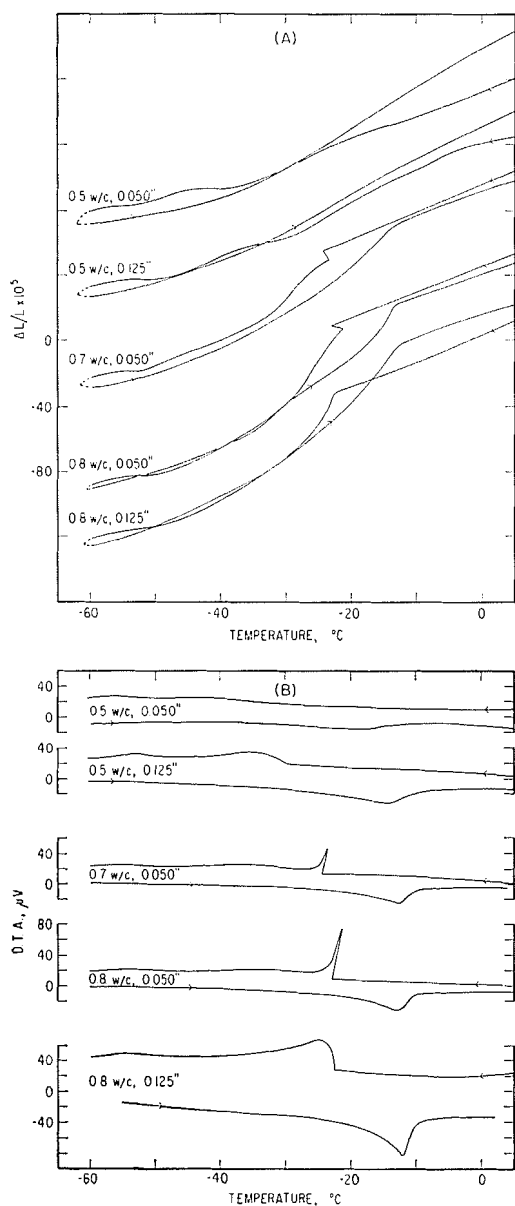


Fig. 3. (A) Fractional length changes and (B) thermograms of plain cement specimens equilibrated at 84% rh.

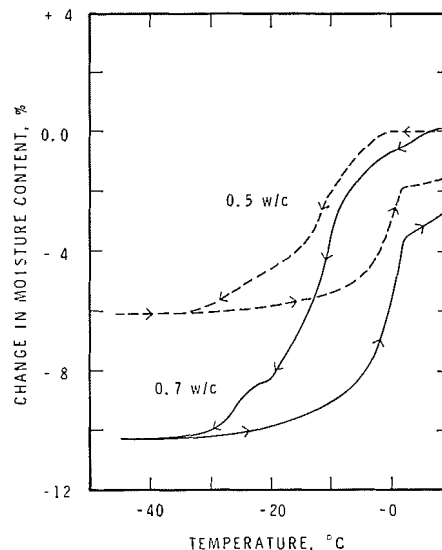


Fig. 4. Weight change of cement specimens vacuum-saturated with water during a temperature cycle. Results were obtained in gravimetric adsorption experiments and represent equilibrium values.

water freezes at -8°C . That such desiccation occurs can be seen in the plots of weight change vs temperature (Fig. 4) obtained in equilibrium adsorption experiments. At $<0^{\circ}\text{C}$ the weight decreases rapidly. As expected, this ice, being on the outer surface, melted at 0°C in temperature cycles between $+5^{\circ}$ and -10°C (Fig. 5).

The results of runs with partially saturated systems (Fig. 3) can be explained as follows: The capillaries of a porous body are filled in the order of their increasing diameters as the relative humidity is rising, and, conversely, they empty in the order of their decreasing diameters as the relative humidity decreases. It follows then that the largest pores of the samples equilibrated at 84% rh were empty even at 0°C , and, on cooling, migration of water began only after the relative humidity decreased to a value at which the largest filled pore must be emptied. The 84% rh is attained at -18°C [$(p/p_0) \times 100 = 0.939/1.117 \times 100 = 84\%$]. Accordingly, above this temperature no anomaly occurred, and at -21°C the desorbed water solidified. Significantly, none of the specimens expanded regardless of the w/c ratio or thickness, the reason for which will be discussed later.

(2) Freezing at -40°C

When the sample temperature reached approximately -40°C on cooling, there was gradual expansion extending over a temperature range of $\approx 15^{\circ}$ to 20° with a simultaneous release of heat (Fig. 1). The magnitude of the expansion does not appear to be a function of the w/c ratio nor is it affected by air entrainment (Fig. 2) or degree of saturation (Fig. 3). The effect of sample thickness is assumed to be insignificant although assessment is hindered, particularly at high w/c ratios, by the overlapping of the two freezing ranges.

These anomalies are related to that occurring at -20°C in the porous-glass-water system and were attributed to freezing of the water in the larger pores to which it drained from the small capillaries at this temperature. Because the maximum attainable relative humidity is reduced at -20°C , pores with large diameters are not full at this temperature, regardless of the initial degree of saturation at 0°C .

The anomaly of the extension plot observed on warming at $\approx -10^{\circ}$ (Fig. 1) is, presumably, associated with the melting of ice formed at -40°C . Detection of the endothermic heat effect is hampered by the slow heating rate and the proximity of the 0°C peak.

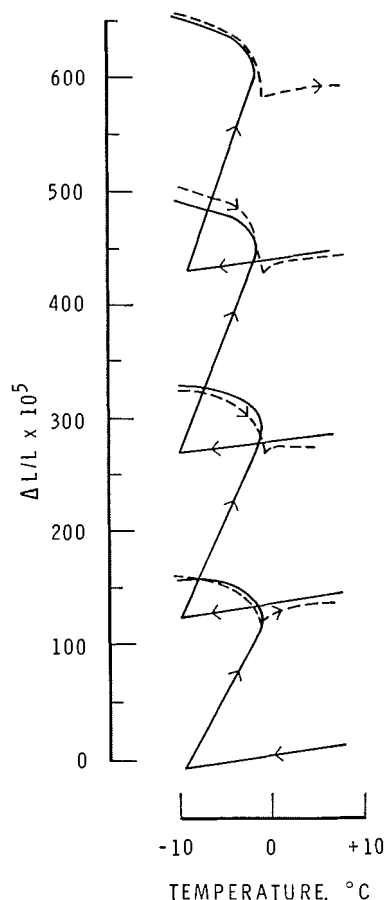


Fig. 5. Fractional length changes during repeated temperature cycles. Full saturation was maintained.

(3) Assessment of Frost Damage

Concrete is considered frost-resistant if, when exposed to winter conditions in the field, it suffers no inelastic volume changes. Thus, the residual, not the transient, expansion is of principal interest. Residual expansion is defined as the irreversible increment in length and is obtained by comparing the values, at 0°C, before and after a temperature cycle.

According to the results shown in Figs. 1(A), 1(B), and 3(A) the residual change increases with increasing w/c ratio, sample thickness, and degree of saturation. Since frost susceptibility is similarly related to these parameters, it seems probable that the value of the residual expansion is a measure of frost susceptibility, a possibility that had been considered and rejected because of poor correlation.⁵ The poor correlation, however, may have been due to the incomplete restoration of the water concentration after the cycle (Fig. 4) and to the different states of sorption (desorption on cooling and adsorption on warming).⁹ Both water content and nature of the adsorption state greatly affect the dimensions of the system and can obscure the effect of mechanical damage.

(4) Mechanism of Frost Damage

The volume change at -40°C, a temperature to which concrete structures are seldom, if ever, exposed, is small and of little practical importance. On the other hand, at least two observations suggest that the residual expansion originates from the dilation at -8°C and leads to the destruction of cement paste: (1) this dilation can be very large (0.7% for 0.7 w/c and 0.125 in. thickness, Fig. 1(B)) and (2) its magnitude is related to the degree of frost susceptibility as established by field experience (w/c ratio, dimensions of specimen, etc.). The severe damage resulting from repeated cycling

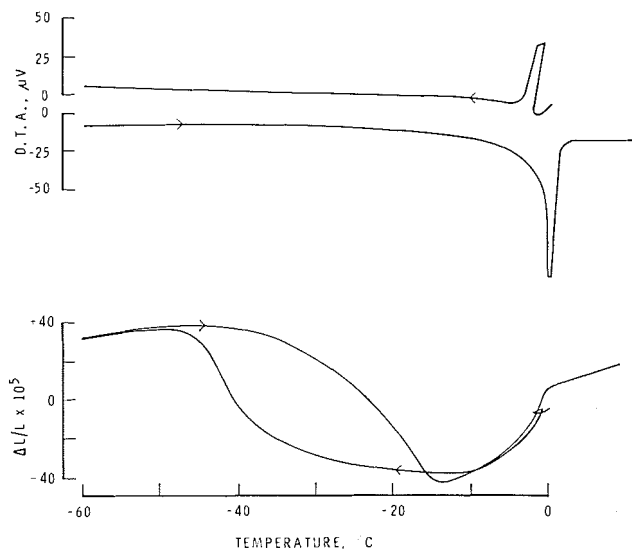


Fig. 6. Fractional length changes (bottom) and thermograms (top) of cement specimen 0.125 in. thick ($w/c = 0.7$) during a temperature cycle with slow cooling and heating rate (0.0417°C/min).

between +5° and -10°C, while full saturation was maintained, provided direct proof of the relation (Fig. 5).

The assumption that the expansion at -8°C is caused by the 9% increase of the water volume on freezing cannot be accepted because, in two slowly cooled samples, 33 and 40%, respectively, of the total water present was expelled (Fig. 4); this amount is equivalent to >3 and 4 times the specific volume increase. Furthermore, similar freezing characteristics were found with adsorbates other than water, which on freezing decrease in volume.²

The length changes of a vacuum-saturated cement sample ($w/c = 0.7$) during very slow cooling are plotted in Fig. 6. Although the thermogram indicates that freezing did occur at -4°C, there was no expansion above -40°C, suggesting that the rate of the process causing dilation is the controlling factor. On this basis, the process must be the desorption or expulsion of water resulting from the reduction of the relative humidity.

The implication is that expansion occurs if the water concentration is much higher than the equilibrium value at the prevailing relative humidity. This conclusion is supported by the observation that, on freezing, the length of a specimen 0.125 in. thick increases more than that of a specimen 0.050 in. thick (Figs. 1(A) and (B)). Since most of the water reaches the outer surface by migration along the shortest path (in this case the thickness), an increase of this distance understandably reduces the amount of water leaving the specimen and dilation occurs. In addition, the relaxation effect observed after freezing at constant temperature (Fig. 7) is proof of the existence of nonequilibrium conditions, a state consistent with the mechanism.

It must be emphasized that the absolute value of the permeability of the solid does not determine frost resistance but rather its adequacy for the given conditions. The quantity of water to be exuded in unit time is determined by the cooling rate (the rate of the relative humidity decrease), the shape of the desorption isotherm (the number of pores to be emptied for a given relative humidity change), and the initial degree of saturation at 0°C. A solid having many pores with large diameters and fully saturated at 0°C may be severely damaged at moderately fast cooling rates, whereas a solid with only small pores is invulnerable under the same conditions. If the specimens are partially saturated, desorption begins only

at low temperatures when the water flows into the essentially empty large pores where it freezes without causing expansion (Fig. 3(A)).

In solids with larger external dimensions, the path of diffusion to the outer surface is too long to achieve the required degree of desiccation unless the rate of cooling is very slow. Under normal conditions and a high degree of saturation on freezing, a great deal of expansion occurs causing cracks. These fissures are the sites to which water migrates on further cooling and, therefore, are soon filled. The water in the crevices expands on freezing, propagating the break and creating new voids. Thus the expansive force associated with ice formation is concentrated at the weakest area of the solid (the reason the fissure formed there) and on repeated cycling leads to its destruction.

(5) Practical Considerations

The proposed mechanism explains the observations made under field conditions.

It has been shown that freezing is destructive when concrete, both air-entrained and non-air-entrained, is fully saturated (Figs. 1(A) and (B) and 2). On the other hand, when the degree of saturation is low, little damage occurs (Fig. 3(A)). Air entrainment is beneficial because the uniformly and closely spaced voids 10 μm to 2 mm in size become filled with water only on prolonged exposure to 100% rh; therefore under normal field conditions proportionately fewer voids are filled with water in air-entrained concrete than in non-air-entrained concrete.

Freshly placed concrete is vulnerable to frost damage because of the high water content. Concrete placed late in the autumn has insufficient time to desiccate before freezing occurs. Air entrainment is beneficial in this case also. Incorporation of air bubbles provides reservoirs into which the water can flow from neighboring smaller capillaries when the temperature falls below 0°C.

Probably bridge decks are exposed to the most severe conditions. The relative humidity over the water is often near 100%, and the bridge deck is exposed on all sides to the atmosphere so that its temperature closely follows the ambient temperature. Not surprisingly, satisfactory protection of bridge decks from frost damage has not been achieved.

The properties that enable porous solids to withstand frost (low porosity (low water uptake) and high permeability) unfortunately mutually exclude one another. Because it is impossible to significantly increase permeability without increasing porosity, the best compromise for achieving frost resistance is a low w/c ratio. Although permeability is low in this case, so is porosity; very little water has to be expelled from the paste and that only at low temperatures. This low w/c ratio is much safer than having a high-permeability and high-porosity paste, which is probably just as resistant at partial saturation but is certain to be destroyed if it becomes fully saturated.

(6) Testing

Despite numerous prolonged efforts, a satisfactory test for assessing frost susceptibility has not been developed. The difficulties are (1) lack of a good method for quantitative measurement of the damage suffered and (2) limited relevance of the conditions imposed by the accelerated test to field conditions.

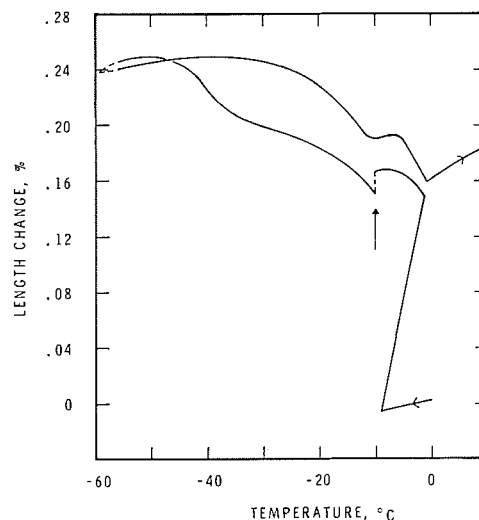


Fig. 7. Fractional length changes of a vacuum-saturated cement specimen ($w/c=0.7$). Arrow indicates temperature at which isothermal conditions were maintained; broken line represents changes in length during this period.

If the proposed mechanism is correct, it may be possible to assess frost susceptibility by determining parameters such as permeability, adsorption capacity, and pore-size distribution; then, with the knowledge of the maximum cooling rate and degree of saturation to be expected in the field, durability can be predicted.

Acknowledgment

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