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FREEZING OF WATER IN HYDRATED CEMENT PASTE

BY
G. G. LITVAN

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Freezing of Water in Hydrated Cement Paste

Le Gel de l'Eau Contenue dans la Pâte de Ciment Hydraté

Summary

Present theory of frost action in cement is re-examined in the light of the results of recent experiments (dimensional changes, adsorption characteristics, calorimetry, DTA). It is found that hydrostatic pressure in cement is not generated by the 9 per cent difference between the specific volume of water and ice but by the changed interaction between the cement and the adsorbed water on its solidification. The proposed mechanism raises the possibility that new methods for frost protection may be developed. Similarly, frost susceptibility may be tested in a more reliable way.

Résumé

L'auteur examine la théorie acceptée de l'action du gel dans le ciment à la lumière des résultats d'expériences récentes, par détermination des changements dimensionnelles et des caractéristiques d'adsorption, par calorimétrie et par analyse thermique différentielle. Il a trouvé que la pression hydrostatique créée à l'intérieur du ciment n'est pas due à la différence de 9 pour cent entre les volumes spécifiques de l'eau et de la glace, mais à la modification des interactions entre le ciment et l'eau adsorbée en cours de solidification. Ce mécanisme entrevu ouvre des possibilités d'élaboration de nouvelles méthodes de protection du ciment contre le gel. On pourrait de même réaliser des essais plus fiables de sensibilité au gel.

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There still exists a need to improve frost resistance of concrete in spite of the advancement achieved by the air-entrainment technique. It would be of great benefit to:

- a) improve the reliability of, and shorten the time required to complete, the accelerated test for frost susceptibility;
- b) extend the capabilities of present engineering practice by developing methods of manufacturing concrete with even better frost resistance in a simpler and more economical way.

Because of the climatic conditions prevailing in Canada the Division of Building Research of the National Research Council of Canada has a particular interest in the study of the freezing of water in porous building materials such as cement, stone, brick, mortar, etc. Freezing of water in concrete is a special case of phase transition of adsorbates in porous solids. Because this phenomenon is still insufficiently understood, experiments to elucidate the general problem were included in the work.

Porous 96 per cent silica glass adsorbent has been extensively studied. Like cement, it is porous and siliceous, but has the advantage of being uniform and stable in chemical composition and geometry. Owing to the complexity of the phenomenon it was necessary to employ a number of experimental methods. The measurement of dimensional changes, isotherms and isosteres in an adsorption apparatus was complemented by calorimetry, differential thermal analysis, and infrared spectroscopy.

The main findings of early work (1, 2) may be summarized as follows:

- a) No freezing will take place if the amount of water present in a porous body is less than that required to form two complete layers on the surface.
- b) If freezing does take place, it will occur at temperatures below the normal freezing point. As in so many other aspects, water behaves differently from all the other liquids investigated. The freezing point of normal liquids in the adsorbed state is a function of concentration, approaching the normal freezing point at saturation; water may have several freezing ranges, some concentration-dependent, others not.
- c) Melting, and probably freezing too, can be classified as an anomalous first order phase change, i.e., it extends over a wide range of temperature.

- d) The values of the latent heat of fusion per gram of adsorbed water in porous glass varied between 49.7 and 55.5 cal/g, depending on the concentration, or approximately two-thirds of the normal value of 79 cal/g.

These results indicate that water adsorbed in a porous solid has characteristics very different from those of bulk water, a fact brought about by the interaction of the water molecules with the surface of the solid. The solid itself is also perturbed as is demonstrated by the anomalous changes of dimensions during adsorption or freezing.

Following this understanding of the freezing phenomenon in the model system, the cement-water system was examined. This paper gives some of the results; a detailed report will be given elsewhere.

Experimental

Apparatus

The specific heat and dimensional changes were determined in an adiabatic calorimeter incorporating an extensometer (3).

Measurements were made of dimensional changes and the amount of water adsorbed in cement specimens as the function of temperature. Companion samples were examined simultaneously in a hermetically sealed apparatus. This included an optical extensometer (4) and a quartz spiral for measuring weight changes. The major and essential part of the apparatus was enclosed in a well cooled by a compressor. With the aid of a controller-governed heater, the temperature could be maintained constant to $\pm 0.05^{\circ}\text{C}$ in the range between $+20^{\circ}\text{C}$ and -45°C .

Measurements were taken under both equilibrium and non-equilibrium conditions. In the former case the temperature was changed by 2 to 3°C and then kept constant until constant weight (± 0.01 per cent) and dimensions (± 0.001 per cent) had been achieved. The time required varied from 3 to 8 days and the completion of a run took 5 months. The results, the final equilibrium values, are shown in Figures 1 and 2. Under non-equilibrium conditions the temperature was changed continuously at a rate of approximately $0.25^{\circ}\text{C}/\text{minute}$. The temperature was measured with a thermocouple attached to the sample. The values so obtained are shown in Figure 1 (curve c).

The differential thermal curve shown in Figure 3 was obtained in a non-commercial apparatus, which consisted of a hermetically sealed cell containing cement and glass reference samples, a 1-mv full-span recorder, and a temperature programmer. The rate of the temperature change was $5^{\circ}\text{C}/\text{minute}$.

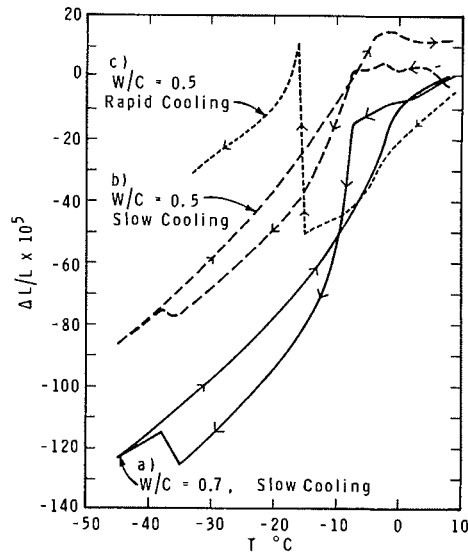


Figure 1 Dimensional changes as a function of temperature

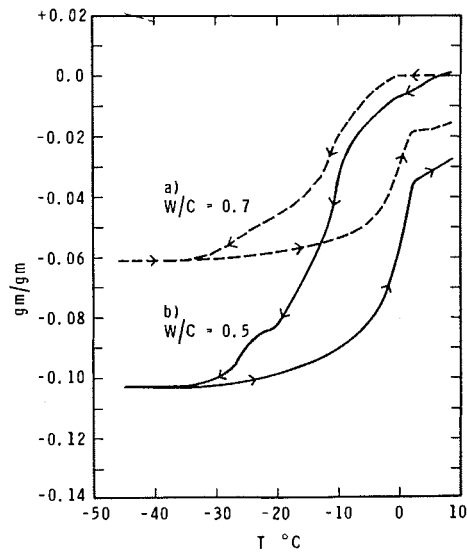


Figure 2 Weight change as a function of temperature.

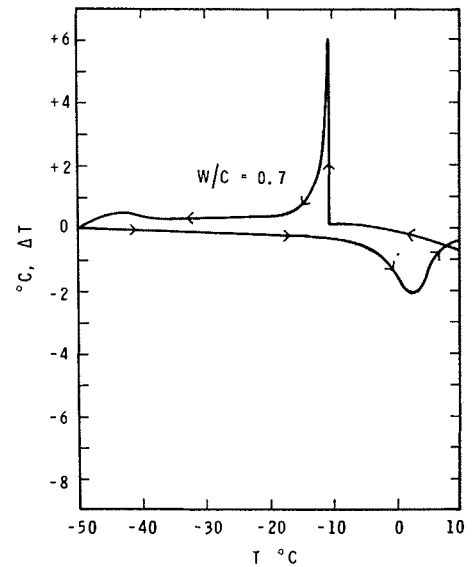


Figure 3 Differential thermal curve.

Materials

Porous 96 per cent silica glass was obtained from Corning Glass Works in the form of plates with various thicknesses. Cement samples with uniform porosity and exclusion of CO_2 and air were prepared by the method of Sereda and Swenson (5). After a minimum hydration period of one year 1.3-mm thick specimens were cut with a circular saw having a diamond blade. The samples were kept in 100 per cent RH at all times.

Discussion

The Existence of Hydraulic Pressure

The curves in Figure 1 represent the length changes of the samples on slow equilibrium cooling (curves a and b) and on rapid non-equilibrium cooling (curve c). It may be seen that whereas curve c is similar in shape to those reported in the literature (6) curves a and b indicate contraction which has previously been observed only for air-entrained cement. It may be noted again that curves a and b represent the final values which the samples attained at a given temperature. Initially, the samples expanded after the temperature was altered, but during the constant temperature period they continued to change and finally contracted.

These observations are consistent with the assumption of the present theory (6) that hydraulic pressure was generated on cooling. The pressure was subsequently relieved gradually because uncompensated large internal pressure cannot be maintained in equilibrium.

Confirmation of the existence of the hydraulic pressure seems to be valuable because it was proved only in an indirect way. It was considered as evidence that samples cooled at the rate of $0.25^\circ\text{C}/\text{min}$ continued to expand when kept at constant temperature. It was argued that there is no mechanism other than the hydrostatic pressure hypothesis to explain the phenomenon and that therefore it must be true. This reasoning is not quite justified, however, because the experimental results indicate only that the temperature change initiated a process that is slow to reach completion. The nature of the process is undefined and may be, besides a generation of pressure, a rearrangement of the molecules in the adsorbed layer, changes in the area accessible to the water molecules, and so on.

Origin of the Hydraulic Pressure

According to the theory the well known 9 per cent volume increase of water on freezing generates hydrostatic pressure in cement: Since the cement is completely saturated, i.e., all the pores are completely filled, the internal volume cannot accommodate the larger volume of ice and the pressure increases. As a result the cavity must dilate or the excess water be expelled from it.

According to Figures 1 and 2 the samples have contracted and lost water with slow cooling, indicating that not dilation but the expulsion mechanism was operative. If the theory is correct and the pressure is caused by the volume increase of water, the maximum amount of water to be expelled from the system can not be more than 9 per cent of the total water present. The water actually expelled is, however, several times greater.

Figure 2 shows that the two samples have lost 0.061 g water per 0.814 g cement and 0.102 g water per 0.7460 g cement, respectively, representing 33 and 40 per cent of the total water present, as determined by the D-drying method. These values are inconsistent with the theory and warrant re-examination.

Interpretation of the Present Results

The findings of the present work may be explained in the following way:

When water freezes, the molecules, which are in a relative disarray in the liquid state, have to order themselves as required by the crystal structure of ice. The mobility of the adsorbed molecules, however, is limited owing to the surface forces. In the first two layers where the attraction to the surface is the strongest, no rearrangement can occur even at low temperatures, and in the subsequent layers it may take place only below 0°C. On formation of an adsorbed layer with ice-like structure, the interaction between the cement surface and the water molecules decreases. As a direct consequence, the maximum amount of water held in the surface is reduced. Thus part of the water required for saturation before freezing becomes excess after ice formation. As all the pores were completely filled at saturation, this excess water cannot be accommodated and pressure is generated. In an open system pressure differences cannot be maintained, so that the water has to leave the void system by diffusion.

This explanation is consistent with the experimental results and with field experience. Expansion was observed only on rapid cooling. If sufficient time was allowed for equilibration to be reached, the water did migrate out of the void system and an overall contraction took place. The amount of diffused water exceeded 9 per cent of the total water content primarily because of decreased adsorption capacity and not volume increase, as experienced with bulk water. It has to be emphasized that the 9 per cent increase in volume is specific to a situation where the water changes from the disordered state, characteristic of bulk water, to the ordered state of bulk ice I. This transition is connected with a heat effect of 79 cal/g. The latent heat of fusion of adsorbed water was found to be reduced by 30 percent, indicating that transition takes place between states, any or both of which are different from the respective states

in the bulk.

Air entrainment, the provision of empty voids, is expected to protect the concrete by accommodating the excess water and reducing the pressure. The very significant differences in behaviour of the two samples, as shown in Figures 1 and 2, can be explained by the large surface areas of the sample with $w/c = 0.7$.

Conclusion

The above explanation of the mechanism of freezing in cement attributes the generation of hydraulic pressure and migration to causes different from those postulated in the present theory. The current study indicates that a portion of the water in cement will always freeze and result in disruption unless empty reservoirs are provided in sufficient numbers and spacing. Air voids weaken the cement and there is a limit beyond which their number cannot be increased. If the explanation put forward in this paper is correct, then air entrainment is not the only method of protecting cement. A second possibility exists, at least theoretically, namely, surface modification. As the change in the interaction between water and cement on freezing is held responsible for the damage, modification of the chemistry or geometry of the surface will affect the freezing characteristics.

Furthermore, by measuring the adsorptive properties of cement samples it may be possible to assess their frost susceptibility more reliably and more quickly than by the present accelerated tests.

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