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SUBJECT

Some Fundamental Aspects Relative to the Destruction of Concrete by Freezing and Thawing

NOTE

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SOME FUNDAMENTAL ASPECTS RELATIVE TO THE DESTRUCTION OF CONCRETE BY FREEZING AND THAWING

by E.G. Swenson

The two theories advanced to explain the mechanism of the destruction of concrete by cycles of freezing and thawing are the ice-segregation hypothesis of A.R. Collins and the hydraulic pressure hypothesis of T.C. Powers. A survey of the literature would indicate that certain factors other than crystal pressure due to ice formation may contribute materially to deterioration of concrete. Much pertinent information can be obtained from research on soils, building stone and other materials. Fundamental studies of the behaviour of water in porous solids insure better recognition of the factors which are responsible.

A review is being prepared which is intended to bring into focus the various changes which may occur during the testing of concrete for durability to freezing and thawing. It consists of the following topics:

1. The physical structure of concrete
   - character of the cement paste
   - pore structure of cement paste and of aggregate.

2. The effect of moisture change in concrete
   - how the water is physically "held"
   - effects of changes in moisture distribution
   - thermal actuation of moisture movement.

3. Destruction of concrete by freezing and thawing
   - evaluation of durability
   - factors which influence durability
   - theories.

4. Discussion of related phenomena.

The present report is a brief summary of the more significant aspects of this review.

The physical structure of both cement paste and aggregate is extremely complex and variable. From available information it is possible to assess the factors which influence the durability of concrete to freezing and thawing.

Hardened portland cement paste is essentially a rigid gel which, like all hydrophilic colloids, tends to shrink on drying and expand on wetting. The void system is roughly classified into three types: the very small gel pores of about 30 Angstrom units in diameter, the capillaries which vary from about 200 to 800 Angstrom units in diameter, and the larger Macro pores.

The gel pores are characteristic of the hydrating cement and change only in quantity as hardening progresses. The Macro pores are too large to be affected appreciably by the deposition of hydration products. They can also be considered as remaining unchanged in character. The capillary system, however, may vary greatly both in character and extent due to the following factors:

1. The original water-cement ratio. Excessive mixing water tends to increase the capillary system.

2. Compaction. Excessive vibration or tamping of a wet mix accentuates capillary formation.

3. Initial curing. Drying out of fresh concrete retards hydration and thereby leaves interconnecting channels which do not become filled by hydration products. This is true particularly of exposed surfaces which become more vulnerable to frost action.

4. Continued curing and aging permits the filling and plugging of capillaries with hydration products.

5. Crystallization of dissolved salts during drying and "self-desiccation" tends to choke off capillaries.

6. Restrained shrinkage in the cement paste caused by the presence of aggregate may tend to produce micro-cracking which will form new capillary systems in the paste. The process of autogenous healing tends to offset this effect to some extent.

The aggregate pore system varies with the type of aggregate but, in general, is not unlike that of cement paste. The capillary system, however, remains essentially unchanged.

The changing nature of the pore system in the cement paste and the factors which influence these changes emphasize the necessity of great care in fabrication and conditioning of samples to be subjected to freezing and thawing tests. They also emphasize the possibility of variable results which would complicate interpretation.

The moisture retaining potential of a hygroscopic material such as concrete is related to the internal surface area as determined by the pore system. It has been estimated that the specific surface of hardened portland cement paste is in the order of two million square centimeters per gram of cement, most of which is due to the gel pores.

The adsorption or absorption of water by concrete, as in other hygroscopic, porous solids, is a surface phenomenon similar in mechanism to certain surface catalytic reactions. It is determined basically by forces resulting from an unbalanced electron distribution at any surface. This is the result of polarization phenomena exhibited by certain ions and atoms. The polar nature of the water molecule is conducive to surface adsorption and very strong forces are therefore involved.

Adsorbed water is different from ordinary water just as ice is different. It is much denser and has a much lower vapour pressure. It therefore does not freeze until the temperature is considerably below the normal freezing point of water and will freeze progressively from the less strongly adsorbed layers which are considerably removed from the surface to the nearer layers.

The first monomolecular layer, treated theoretically by Langmuir, is bound very strongly, probably more firmly than hydrated water. Succeeding layers are adsorbed less and less strongly as postulated in the multimolecular concept of the B.E.T. theory. When these adsorbed layers reach a thickness that permits contact in the smaller capillaries menisci are formed which correspond to capillary water. In hardened cement paste the formation of capillary water occurs at a moisture content which corresponds to a relative humidity of about 45%.

Whatever the mechanism which causes adsorption, the pressure of held water is always less than that of the atmosphere, the magnitude of this pressure deficiency being referred to as moisture suction. For comparatively dry, porous materials the suction pressures may exceed 10,000 p.s.i. Saturation corresponds to a suction pressure of zero. For two porous, hygroscopic solids in contact, equilibrium is reached when the suction pressures are equal. This state does not mean that moisture contents are equalized; equilibrium moisture contents may differ widely depending on the materials.

The importance of recognizing the relative suction properties of aggregate and cement paste in durability testing is evident. A very dry aggregate would tend to extract a large quantity of water from the paste, particularly at early ages. A saturated aggregate would tend to lose water to the paste as aging progresses. The moisture movement resulting from this redistribution would accentuate the capillarity in the paste at the aggregate-paste interface and thereby weaken the bond. The low resistance to freezing and thawing of concrete with these combinations is well known. The most durable concrete is one in which the aggregate is atmosphere-dry but immersed in water before use.

The weakening of the aggregate-paste bond is further affected by the bleeding characteristics of the paste. Internal bleeding at the aggregate-paste interface is accentuated by high water-cement ratio, excessive compaction, and the excessive bleeding tendencies of some cements. The increase in capillarity and the weakening of the bond are real factors in the lowering of resistance to frost action. Although the value of air-entrainment lies primarily in reduction of mortar saturation, a very important function is the reduction in internal bleeding which accompanies its use.

In any hygroscopic, porous material the water lost in drying is always less than the water gained on wetting for any given temperature and relative humidity. The resulting hysteresis in the adsorption-desorption curves can be explained on theoretical grounds. The vapour does not completely wet the solid during adsorption but desorption corresponds to complete wetting. That part of shrinkage and expansion which is reversible is associated with the compression effect in the adsorbed water and tension in the capillary water. Irreversible expansion is ascribed to the strong liquid-solid attraction which forces apart the narrow crevices in the solid which are too narrow to accommodate layers of adsorbed water. This exposes new surface for further adsorption and the crevice walls are spread too far apart to recover their original positions by forces of attraction in the solid. This corresponds to the irreversible portion of expansion accompanying continued wetting. The desorption-adsorption cycles occurring in freezing and thawing may to some extent be responsible for volume changes.

Temperature changes by themselves may decrease strength and modulus of elasticity in concrete, particularly under certain moisture conditions. The difference in coefficients of thermal expansion of cement paste and aggregate may be a primary cause of deterioration in some instances. Recent papers in the Journal of the A.C.I. indicate considerable lack of agreement as to the degree to which this factor may contribute to loss in durability. The work of S.L. Meyers appears to be very significant in this regard. He found that the "apparent" coefficient of thermal expansion is at a minimum for saturated concrete or neat cement paste, and also for a "bone dry" condition. This probably corresponds to the true kinetic coefficient. But at moisture contents corresponding to relative humidities of 60-70% the coefficient is at a maximum. The variation in the coefficient is much greater in neat cement paste than in concrete which suggests that in the case of fairly high moisture contents serious stresses are set up between the aggregate and the paste during cycles of temperature change. The rapid deterioration of samples of concrete subjected to freezing and thawing in water may to a large extent be caused by this factor. This is borne out by the results reported by Reagel who found that a mere cycling of concrete to a temperature range above the normal freezing point of water will cause a reduction in strength. Air-entrained concrete which shows an appreciable reduction in dynamic modulus only after some three hundred cycles may be destroyed by this process rather than the freezing of water. The wetting and drying test of C.H. Scholer which involves temperature changes, may produce deterioration by this process also.

Cycles of freezing and thawing of concrete set up temperature gradients which may actuate moisture transmission from warm regions to cold regions. In actual concrete walls and pavements the quantity of moisture thus transmitted may be considerable and would thereby affect the durability of the material as well as producing efflorescence and condensation. The accumulation of water at the cold face followed by freezing would result in spalling of concrete.

The theories of thermally actuated moisture transmission, or thermo-osmosis, have been summarized by Winterkorn. Although they are largely based on soil research, they are fundamentally applicable to concrete, and will be considered briefly. In a porous solid moisture may be transmitted by:

1. Diffusion of water vapour through the pore space under the potential of partial pressure.

2. Diffusion of water in solid solution as for hydrophilic membranes separating chambers of different water vapour pressures.

3. Movement as capillary water due to difference in surface tension at different temperatures.

4. Flow of moisture in the film phase along the internal surfaces of the porous system due to changes in water affinity with changes in temperature.

Vapour diffusion alone is considered too slow to account for the appreciable transfer of moisture exhibited by soils at moderate to high moisture contents. Where adsorbed water alone is present, as in the case of concrete with moisture contents corresponding to relative humidities below 45%, vapour diffusion may be entirely responsible for moisture transfer. At higher moisture contents capillary transfer is postulated by some hypotheses. In one theory it is believed that vapour diffusion serves as a trigger to start the coalescing of adjacent globules of capillary water, thus producing a net movement in the direction of the colder regions.

Johansson considers vapour diffusion as operating alone at low moisture contents but at higher moisture contents, where capillary water is present, transfer is much more rapid. This he attributes to evaporation at the warm end of a water globule and condensation at the cold end, producing a movement towards the cold end. This is termed localized capillarity. Since the moisture ratio in the cold region becomes greater than that in the warm region, a reversal occurs in moisture transfer whereby water is drawn back towards the warm side by what is termed moisture equalizing capillarity. This effect is negligible at low moisture contents but increases with increasing moisture content. If these conclusions are valid the accumulation of moisture in cold regions is to some extent limited by moisture equalizing capillarity and the deterioration processes retarded.

Winterkorn considers that moisture transfer is achieved by flow in the film phase and advances good arguments for his claim. He has also demonstrated the electrical character of thermo-osmosis and notes that liquids like water, with little or no electrical conductivity, possess the greatest transfer efficiency in soils. The dissolved ions, Na^+, K^+ and Ca^{++}, are the most efficient retarders. Since these are the ions also present in the water in concrete, it is possible that moisture transmission may be of a lesser order here than in the case of soils.

Whatever the mechanism of thermo-osmosis in concrete, it is important to know its magnitude. Besides the possibility that it may be an important factor in durability, it may also be responsible for efflorescence and other phenomena in masonry materials. In a preliminary experiment in our laboratories a measurable flow was obtained through concrete under a thermal gradient. Further studies are being carried out.

According to A.R. Collins the freezing of water in concrete occurs in definite planes as in the case of some soils. Cooling progresses into the concrete until the water begins to freeze. During the formation of ice the latent heat released maintains the temperature until all the freezable water has been converted to ice. During this time further cooling does not progress inward. The ice crystals grow by drawing moisture from the inner regions. If sufficient water was present originally, the pressure exerted by the ice crystals will disrupt the concrete at this plane. When all the freezable water has been used up at this point, the temperature drops and cooling progresses inward again. Further ice formation will not take place until a plane is reached where the larger pores still contain water. Ice lenses are therefore formed at intervals, the spacing being determined by the moisture content and the rate of cooling.

This theory presumes that moisture migration occurs and that destruction is achieved by direct crystal pressure. There appears to be considerable evidence to support this claim.

The Powers' hypothesis is based on the concept that freezing and thawing destruction is caused by hydraulic pressures set up by expansion due to ice formation. These hydraulic pressures are created by the resistance to flow offered by the small pores. The pressures increase with increasing rate of freezing, increasing degree of saturation, and decreasing size of pores. Destruction occurs when these pressures exceed the tensile strength of the material. The hydraulic pressure hypothesis appears to distinguish between the spalling of lean, porous concrete and the slower but more penetrating destruction of denser and stronger concrete. Powers' calculations appear to make this theory satisfy practically all the phenomena associated with deterioration of concrete by freezing and thawing. He has also supplemented this with mathematical considerations of the role that air-entrainment plays in increasing the frost resistance of concrete.

The extensive investigations of Thomas into the frost destruction of building stone suggests that the extrusion of ice from pockets in the material is a factor in relieving pressures caused by ice formation. This may be important in slow freezing but offers no relief in rapid freezing. He found that a stone may show entirely different degrees of durability under different rates of freezing.

Beskow, on frost action in soils, has found evidence that ice may form, not as the conventional glass-like material, but in needle-like conglomerates very much like hoar frost. He points out that enormous pressures can be exerted in this manner. It is possible that in concrete, where the moisture content is well below the critical saturation value, deterioration may occur as a result of this phenomenon.

Bollen has reported results of testing concrete by what he terms "primary directional freezing" followed by thawing. This method is claimed to produce more rapid destruction than the conventional methods. Whether or not moisture movement plays a part in this case would be important to know.

In conclusion it may be pointed out again that the testing of concrete for durability to freezing and thawing may involve a number of factors, a knowledge of which is required to interpret properly the results obtained. Furthermore a basic knowledge of the physical structure of the material and the behaviour of water is essential in the preparation of specimens and the control of testing conditions.