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Freezing Effects In Concrete*

By
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Synopsis: Theories as to the mechanism of freezing and thawing damage in concrete have been advanced for more than 40 years. The author discusses the evolution of these theories for cement paste, aggregate and the overall concrete. Since the author was prominent in the development of many of the theories his current views of the mechanism of freezing and thawing in concrete are of unique interest.

Keywords: aggregates; air entrainments; bubbles; cement pastes; concretes; cracking (fracturing); deicers; freeze-thaw durability; freezing; lightweight aggregate concrete; plastic shrinkage; scaling, temperature; water-cement ratio.

*Note: This paper is essentially the reply Dr. Powers gave to a letter of inquiry from ACI 201, Durability of Concrete, asking for comments on a committee draft of "freezing and thawing phenomena in concrete."

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INTRODUCTION

Specimens of concrete kept continually wet on all surfaces by spraying or immersion usually become damaged or destroyed when they are cooled well below the normal freezing point of water; if the period of soaking is long, nearly all concretes so exposed, air-entrained or not, cannot withstand freezing. On the other hand, concrete structures having at least one surface exposed to air continually show extremely various behavior, from total failure, usually localized, to apparent immunity to freezing effects. The mechanisms of freezing effects are likewise various; they have been the subject of systematic research for many years and can now be explained; only some matters of detail and certain quantitative aspects remain for conjecture or further research.

Early Hypotheses

Some early attempts to explain damage caused by freezing were based on the fact that water expands 9 percent when it freezes. If a closed vessel is more than 91.7 percent full of water, it will be stressed when the water freezes, perhaps to failure. It was assumed that damage occurs when the pores are more than 51.7 percent full at the time of freezing. On this basis, materials were supposed to have a critical saturation point of 91.7 percent, although experiments indicated that for some materials the critical point was below that level.

In 1945 Powers[1] pointed out that concrete is not a closed vessel, and that even if it were it always contains enough air-filled space to accomodate the increase in water volume caused by freezing. He advanced the hypothesis, which was further amplified in 1949,[2] that the destructive stress is produced by the flow of displaced water away from the region of freezing, the pressure being due to the viscous resistance to such flow through the permeable structure of the concrete; if the water content is above the critical saturation point, such flow will take place. Since the resistance to flow at a given rate is proportional to the length of flow path, it follows that there is a critical length of flow path, or critical thickness of the body being frozen, beyond which the hydraulic pressure exceeds the strength of the material; critical thickness was defined in terms of a state of complete saturation.

Data on the probable rate of ice production at a given rate of cooling, and data on the magnitude of the coefficient of permeability of concrete, gave figures showing that the critical thickness was of the order of 0.01 in., and this seemed to account for the necessity of entrained air in concrete. The air bubbles were thought of as spaces into which the excess water produced by freezing could be expelled and then frozen without generating destructive pressure.

Earlier, a different hypothesis had been advanced by Collins,[3] based on still earlier work by Beskow[4] and by Taylor[5] on frost heaving of soils. By this hypothesis, the stress is not produced by hydraulic pressure but by the segregation of ice into layers, the unfrozen water in the concrete flowing toward the region of freezing, rather than away from it. Powers[1,6] considered this hypothesis, recognized its soundness as applied to certain soils, but believed it to be inapplicable to a cohesive system such as mature concrete, although McHenry and Brewer[6] had demonstrated its applicability to concrete only 4 hr old.

After the development of working hypotheses, there followed a long systematic research which made possible firm conclusions about the nature of frost action in concrete based on experimental observations rather than theory. As is shown in the following discussion, it turned out that in general all the theories mentioned above, with some modifications, are required to account for the nature of freezing effects in concrete.

Freezing Phenomena in Cement Paste

The hydraulic pressure hypotheses described above was based on incomplete studies of the structure of hardened cement paste and quantitative measurements of the amount of water that freezes in it at various temperatures.[7] These studies showed that a considerable fraction of the evaporable water in saturated paste is in the adsorbed state, and we now know from thermodynamic considerations as well as experiment that adsorbed evaporable water is not freezable.[27] The rest of the evaporable water is held in spaces called capillaries or capillary cavities, and it is freezable.

However, there is a wide range of cavity sizes, and there are as many different melting points of ice as there are different sizes of cavity in which the freezing can occur, for all these spaces are so small that the melting point of the ice bodies they can contain are significantly lower than the normal melting point, the lowering of melting point being greater, the smaller the cavity.

The melting point of ice in cement paste is lowered also by dissolved alkali, but the effect, although significant, is not as great as that due to small dimensions.

The import of the findings just mentioned is that after cooling to a temperature in the freezing range, all the freezable water in spaces smaller than a certain size corresponding to that temperature must remain unfrozen, the lower the temperature the smaller the amount remaining unfrozen. Some of the water in the larger spaces will be frozen, but not all of it; owing to the dissolved alkalis, each cavity containing ice will contain also a relatively concentrated unfrozen alkali solution having a solute concentration determined by the requirements for thermodynamic equilibrium with the ice in the cavity. Also, as discovered by Helmuth,[8] if the temperature was reached by cooling, the actual quantity of ice is generally much smaller than the quantity that is thermodynamically freezable at the given temperature. This phenomenon is a consequence of the fact that water will generally supercool rather than freeze unless it is seeded by an ice crystal; freezing in paste is propagated from a starting point by rapid growth of dendritic ice crystals; the ends of these dendrites are presumably larger (blunter) the higher the temperature, and vice versa; hence an isolated cavity cannot begin to freeze until the temperature is low enough to produce a crystal slender enough to penetrate an opening into that cavity. The methods used by Powers and Brownyard[7] revealed the amounts of ice in a specimen that had been cooled to 78 C, and gave data on progressive melting as a function of rising temperature; thus they gave the maximum amounts of ice that might exist, but not the actual amounts produced during cooling. Helmuth's experiments, showing the relatively small fractions that freeze on cooling, are supported by data of Vuorinen[12] which show that at 15 C, for example, approximately one-half of the water in pores large enough to be frozen at 15C remains unfrozen. These data show that early attempts to quantify hypotheses were based on overestimates of the rates of ice production.

In 1953, Powers and Helmuth[10] reported studies of the effects on specimen volume of freezing in cement paste, with special reference to the hydraulic pressure hypothesis of 1945-1949, referred to above. Although in some experiments there seemed to be clear evidence of effects due to hydraulic pressure, especially with pastes of relatively high porosity, fully saturated, there were other important observations that could not be explained on that basis; specifically, with non-air-entrained paste the hydraulic pressure hypothesis could not account for continued dilatation while the temperature was held constant, and it could not explain the shrinkage of air-entrained paste; moreover, the expected effects of changes in rate of freezing were not observed consistently. Later sutdies by Helmuth[9] showed also that a slightly desiccated non-air-entrained paste will shrink during cooling after the beginning of freezing, but will expand sharply after some low temperature had been passed; this too is incompatible with the theory that expansion is caused by hydraulic pressure generated by flow away from the freezing sites.

It became evident that most of the effects of freezing in cement pastes were due to the movement of unfrozen water to the freezing sites; indeed, the reaching of thermodynamic equilibrium between the ice and the unfrozen solution, and between the concentrated solution at the freezing site and the more dilute solution in the unfrozen capillaries, required such a transfer of water.[14] The initial production of ice in cavities produces a relatively concentrated alkali solution in those cavities, and therefore the movement (diffusion) of unfrozen water to these cavities is like osmosis, and the generated pressure, if any, is osmotic pressure. It is easy to show that osmotic pressure can be sufficient to account for disintegration.

It was shown[14] that the process of generating pressure by diffusion of water to an ice containing cavity will operate at any solute concentration including zero, i.e., pure water. In the latter case a cavity becomes filled with ice (and a layer of adsorbed water) rather than with ice and concentrated solution, and the pressure developed from the in diffusing water could aptly be called crystal pressure due to the growth of the body of ice in the cavity. However, there is no fundamental difference between the two cases, and the discussion becomes simpler by speaking of osmotic pressure regardless of the magnitude of the solute concentration.

Whether or not osmotic pressure is generated in a cavity where freezing has occurred depends on whether or not the cavity is full of solution and ice. If the supply of unfrozen capillary water is relatively abundant, an unfilled cavity becomes expansive after diffusion has filled the cavity; before the expansive stage is reached, the paste tends to shrink as water is drawn from the unfrozen cavities to the cavities containing ice: the observed change is a resultant of the two effects.

The main function of entrained air bubbles in cement paste is to prevent the development of osmotic pressure. Moisture in an air bubble freezes as soon as any freezing in capillary cavities occurs. The unfrozen capillary water may diffuse either to the ice and solution in the air bubble or to that in the capillary cavity. If it moves to a cavity already full of ice and alkali solution, osmotic pressure develops, but if it moves into an air bubble, no osmotic pressure develops there because the air bubble is far from being full; therefore the ice and solution in the air bubble wins the competition for the unfrozen capillary water, and withdrawal of water from the cement paste produces shrinkage--a freeze-drying effect; the shrinkages per degree of cooling is about two times the normal thermal contraction per deg of cooling. If the air bubbles are close enough together, the elimination of osmotic pressure is practically total. Experience indicates that the required bubble-spacing factor[15,28] is about 0.006 in., which corresponds to an actual spacing somewhat less than that.

An important finding of these studies is that any paste of normal composition, i.e., of any practically acceptable water-cement ratio, and made with any type of portland cement, can be made completely immune to damage by the freezing of the water it contains by means of entrained air. On the other hand, any paste made with any type of cement without entrained air will fail the first time it is frozen in a saturated state. Therefore, where exposure conditions require it, entrained air to protect the cement paste is prerequisite to building a durable concrete structure. However, as is shown below, air-entrainment alone does not preclude the possibility of damage of concrete due to freezing; freezing phenomena in rock particles must be taken into consideration.

Freezing Phenomena in Rock Particles

Studies of the freezing of various rocks by Thomas[13] and others revealed the same kinds of phenomena as those observed with cement paste; therefore, results of the extensive studies of freezing in cement pastes can be applied to rocks.

The rocks commonly used for concrete aggregates contain interconnected capillaries as shown by their ability to absorb water. When saturated, a rock contains unfreezable adsorbed water, and there is a wide range of small capillary sizes, giving rise to a range of melting points when the system is frozen. However, in an ordinary rock of good quality, the amount of adsorbed water is negligible, the average capillary size is much larger than that in a typical hardened cement paste, and a relatively large fraction of the evaporable water in a saturated specimen can freeze in a narrow range of temperatures not far below the normal melting point. For this reason, most saturated rocks tend to expel water during freezing,[17] and stress in rock and matrix is produced by hydraulic pressure; in other words, the hydraulic pressure hypothesis is applicable.

A given kind of rock, frozen by itself, will show a critical size below which it can be frozen without being damaged, as was demonstrated by Verbeck and Landgren.[11,16] The critical sizes* of rock quality range upwards from perhaps a quarter of an inch, whereas the critical size or thickness of cement paste is less than 0.006 in., an observation that reflects the great structural difference between cement paste and rock quality.

When in air-entrained concrete, each particle of an aggregate is isolated by a matrix composed of cement paste and air voids. When freezing occurs, the excess water in rock particle produced by freezing tends to be forced into the matrix. If for example the porosity of the rock is 2 percent by volume, all the efflux must try to enter the matrix through only about 2 percent of the interfacial area between the rock particle and the matrix; this consideration, together with the

*Note: for warnings about oversimplifying the concept of critical size and critical saturation, see Reference 16.

lowness of the coefficient of permeability of hardened cement paste, explains the fact that an ordinary good quality aggregate is able to destroy air-entrained concrete if some of the rock particles became saturated before freezing occurs. The results of standard freezing and thawing tests prove the point: the nature of the test is such that the aggregate particles must eventually become saturated and produce failure.

On the other hand, there are some comparatively rare aggregates having capacities for freezable water so near to zero that they do not produce stress when freezing occurs, and air-entrained concrete made with such aggregate has been found to withstand more than a thousand standard cycles while suffering only superficial damage.

With ordinary aggregates, the destructive effect of freezing in air-entrained concrete is larger, the larger the particle, assuming that large and small particles have the same structure. This has been observed experimentally, and it is to be expected from consideration of the volume of water to be expelled per unit of interfacial area, as well as from the effect of critical size; a rock that would fail if frozen alone could be doubly destructive if frozen in concrete.

The role of entrained air in alleviating the effect of freezing in rock particles is minimal. There is some evidence that the air bubbles in the matrix are able to relieve the pressure from water forced out of sand particles, but not so for the larger particles.

Because of capillary size effects, and perhaps the presence of solutes, some of the water in a rock remains unfrozen at a given sub-freezing temperature. Therefore, secondary effects due to diffusion of unfrozen water to the ice are probably present but are not ordinarily observable. However, Thomas[13] did observe some rocks to expand while the temperature was held constant, and other to shrink. Some argillaceous rocks hold considerable amounts of free capillary water in very small spaces and show freezing behavior similar to that of cement paste not protected with entrained air; some of these rocks are even worse for they can be disintegrated by water without freezing.[27]

Dunn and Hudec[27] advanced the hypothesis that the principal cause of disintegration of rocks is not freezing but the expansion of adsorbed water during cooling; specific cases of failure without freezing seemed to support their more general conclusion. However, extensive studies of adsorbed water by Helmuth[9] and others gives no support to the assumption that adsorbed water expands when cooled. It is true that the cooling of a system that contains both adsorbed and capillary water will cause the relative proportion of adsorbed water to increase, but this increase produces no expansion of the system beyond its original dimensions. It now seems clear that the Dunn and Hudec experiments on certain clay-bearing rocks either involved the osmotic pressure mechanism explained above for cement paste,[18] or swelling produced by the disjoining action of adsorbed water in the unbonded-clay constituent of the rock.[19]

Overall Effects in Concrete

A general discussion of results of experimental investigations of frost action in concrete was given by Powers in 1955[25] and again in 1965.[26] It is now clear that the paste and the aggregate should be considered separately not only when explaining frost action, but also when making concrete for severe exposure.

If the matrix of the aggregate in concrete is composed of hardened cement paste and a sufficient concentration of air bubbles, (spacing factor not more than about 0.006 in.)[28] freezing the capillary water in the paste does not produce destructive stress, but without entrained air, the matrix fails as soon as the paste becomes saturated.

With ordinary "sound" aggregates, the saturated particles must expel water when freezing occurs. Consequently, air-entrained concrete is ordinarily not able to withstand stresses due to freezing when the concrete is subjected to a perpetually wet environment. This is shown by the fact that nearly all air-entrained concretes disintegrate in a standard freezing and thawing test; they disintegrate at once if the aggregate particles are saturated at the start, an unusual condition because of the effects of self desiccation during early hydration; otherwise, they disintegrate gradually as the aggregate absorbs water in the course of the test. Such failure reflects the inability of entrained air to control stress originating in the aggregate, particularly the coarse aggregate; it does not necessarily signify that the paste is inadequately protected, although such can be the case in air-entrained concrete if the void size distribution is abnormal. For extensive discussion of the air content, see Reference 23, Chapters 7 and 8.

Pressure originating in an aggregate particle may rupture the particle and the matrix, or it may cause a separation between the matrix and the particle; if the particle is near the surface of a pavement, a popout may be produced.

There are a few rocks that can contain practically no freezable water. Air-entrained concrete made with an aggregate composed entirely of such rock will withstand freezing under continually wet conditions for a long time, but it cannot do so for an unlimited time because the air bubbles eventually become filled with water, and the leaching of lime from the paste eventually destroys it even if freezing does not. Moreover, fluctuation of temperature without freezing can produce gradual swelling and eventually failure,[21,22] at least with some materials.

Because of the rarity of "unfreezable" rock, durable structures must in general be built with intrinsically vulnerable concrete, the absorbtive aggregate being the uncontrollably vulnerable constituent. The durability of most structure, made of air-entrained concrete is to be attributed, generally, to circumstances that keep the aggregate particles from becoming critically saturated. The most obvious factor is the alternation of drying and wetting periods; the rock pores cannot become critically saturated until after the paste becomes saturated; the process is slow, and is slower the lower the coefficient of permeability of the paste. Therefore, under severe conditions rich air-entrained concrete lasts longer than lean; it may even last indefinitely as far as freezing is concerned.

An equally important factor is the phenomenon called transpiration, which in the present context is the diffusion of water away from a wet region in the concrete toward an exposed dry surface, first discussed in 1965,[16] if an air-entrained concrete structure standing in water or wet soil presents one or more exposed surfaces, transpiration will usually keep the moisture content of the aggregate under the critical point at levels in the structure well below the water or ground line.

Besides being subject to the intrinsic limitations of most aggregates, concrete structures may be also vulnerable because of structural flaws that may develop spontaneously during the bleeding period because of shape of form, or horizontal bars, or faulty curing and finishing procedures. For a discussion of the nature of these phenomena, see Reference 23, Chapter 11.

Scaling Due to Deicers

The use of deicers on non-air-entrained concrete slabs usually results in localized failures near the surface, described as scaling. Experimental evidence indicates that the localized effects are severe because of the dissolved sodium chloride or calcium chloride becoming concentrated in the larger capillary pores of the paste near the surface of the slab. This augmented concentration tends to increase the magnitude of osmotic pressure that develops after or during freezing, and thus makes the destructive effect more severe. Entrained air has the same effect explained above: it prevents the build-up of osmotic pressure in the capillary cavities.

Field experience indicates that with entrained air of normal characteristics, and in the absence of improper finishing procedures, entrained air prevents scaling; however, in laboratory tests, where the concrete is denied the benefit of occasional drying, it does not always appear to be fully effective, and this is probably due to the aggregate particles near the surface becoming critically saturated. For a more complete discussion, see Reference 16.

REFERENCES

1. Powers, T. C., "A Working Hypothesis for Further Studies of Frost Resistance of Concrete," ACI JOURNAL, Proceedings V. 41, No. 3, Feb. 1945, pp. 245-272.

2. Powers, T. C., "The Air-Requirement of Frost Resistant Concrete," Proceedings, Highway Research Board, V. 29, 1949, 184-211.

3. Collins, A. R., "The Destruction of Concrete by Frost," Journal, Institution of Civil Engineers (London), 1944, pp. 29-41.

4. Beskow, Gunnar, "Soil Freezing and Frost Heaving with Special Application to Roads and Railroads," The Swedish Geological Society, (Series C, No. 375), 1935. (Published in English by the Technological Institute, Northwestern University, Evanston, Illinois, 1947.)

5. Taber, Stephen, "The Mechanics of Frost Heaving," The Journal of Geology, V. 38, No. 4, 1930, pp. 303-317.

6. Discussion of Reference 1, ACI JOURNAL, Proceedings V. 41, No. 5, Nov. 1945, pp. 272-1 to 272-20.

7. Powers, T. C., and Brownyard, T. L., "Studies of the Physical Properties of Hardened Portland Cement Paste," ACI JOURNAL, Proceedings V. 43, Oct. 1946 - Apr. 1947.

8. Helmuth, R. A., "Capillary Size Restrictions on Ice Formation in Hardened Cement Pastes," Proceedings, Fourth International Symposium on the Chemistry of Cement, Washington, D. C., V. 2, 1960, pp. 855-869, (National Bureau of Standards, Monograph 43, Sept. 1962).

9. Helmuth, R. A., "Dimensional Changes of Hardened Cement Pastes Caused by Temperature Changes," Proceedings, Highway Research Board, V. 40, 1961, pp. 315-336.

10. Powers, T. C., and R. A. Helmuth, "Theory of Volume Changes in Hardened Portland Cement Paste During Freezing," Proceedings, Highway Research Board, V. 32, 1953, pp. 285-297.

11. Verbeck, George, and Robert Landgren, "Influence of Physical Characteristics of Aggregates on the Frost Resistance of Concrete." Proceedings, ASTM, V. 60, 1960, pp. 1063-1079.

12. Vuorinen, Jukka, "On Use of Dilation Factor and Degree of Saturation in Testing Concrete for Frost Resistance," Nordisk Betong (Stockholm), No. 1, 1970, pp. 37-64.

13. Thomas, W. N., "Experiments on the Freezing of Certain Building Materials," Building Research Technical Paper No. 17, Department of Scientific and Industrial Research, London, 1938.

14. Powers, T. C., "Resistance of Concrete to Frost at Early Ages," Proceedings, RILEM Symposium on Winter Concreting, (Copenhagen, 1956), Danish National Institute of Building Research, Copenhagen, 1956, pp. C1 - C47. Also, Research Bulletin No. 71, Portland Cement Association.

15. Powers, T. C., "Void Spacing as a Basis for Producing Air-Entrained Concrete," ACI JOURNAL, Proceedings V. 50, No. 9, May 1954, pp. 741-760.

16. Powers, T. C., "The Mechanism of Frost Action in Concrete," Stanton Walker Lecture No. 3, National Sand and Gravel Association, Silver Spring, Maryland, 1965, 35 pp.