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Cement and Concrete Research 35 (2005) 1407–1411

Cement and Concrete Research

A new process by which cyclic freezing can damage concrete—the Erlin/mather effect a concept

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Received 25 May 2004; accepted 31 August 2004

His Final Effort (Coauthor Dr. Bryant Mather died on December 4, 2002).

It was about ten years ago that I mentioned the general concept of this paper to Bryant Mather. He agreed that it was worth pursuing. Since then, we slowly developed details of the concept, which resulted in this paper.

We each felt that there has been little developed during the past several decades about factors, mechanisms, and new theories related to distress caused by cyclic freezing. We discussed the hope that our concept would encourage others to reopen efforts to find some more answers to unanswered questions. Last year, a paper [1] was published on stress and strain in concrete during cyclic freezing. In that paper, comments are made about the differential thermal coefficient of expansion and contraction of ice and concrete, and the following comment is made, "The present theory based on thermodynamics does not take this kind of a situation into consideration." Our paper solely accommodates that consideration!

The paper received one harsh review. I felt obligated to mention that to Bryant several weeks before he died. He insisted on seeing it and, as a consequence, a number of changes to the paper were made.

To the near-end of his career in our industry, to the time when doing most anything created a preponderance of effort (so he told me), he contributed however he could, whenever he could, to be helpful, as best he could. I believe he gave a large part of himself to the writings of this paper—perhaps more so than to his other writings because of the self-enduring pain and his extraordinary efforts during the last days of his life to reconcile some loose ends of the paper—he would not quit until it was finally forced on him.

It is for all of his efforts in helping to develop this paper, and especially for what he captured and contributed at the very end of his existence, that this paper is dedicated—***to the memory of Bryant Mather.***

1. Introduction

Today, after many years of progress, damage to concrete due to freezing and thawing still occurs, although we know how to make concrete that will be immune to the effects of freezing and thawing [2]. Based on our current understanding, the damage is usually attributable to improprieties in the concrete.

Different hypotheses eventually led to the current basis for the current conventional wisdom. Early explanations of the mechanism causing damage cited the development of hydraulic pressures created when water is forced ahead of the freezing front—the hydraulic pressure theory [3,4]. Later, it was believed that pressures were created by concentration differences of solutes left in the remaining unfrozen water after initial pore fluids in capillary cavities froze and raised the solute concentration of the remaining unfrozen fluid—the osmotic theory [5–7]. That leads to a variety of unstable conditions that, in turn, lead to additional cracking and crushing of the paste unless air bubbles are nearby. It was thought that a semiamorphous ice solid in addition to crystalline ice was sometimes created resulting in generation of large stresses [8]. The situation is rendered more complicated because of the

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doi:10.1016/j.cemconres.2004.08.023

contributing influence of chemicals that may be dissolved in the pore fluid either from deicing chemicals or from seawater.

These mechanisms by which freezing and thawing can cause damage to hardened concrete have often been discussed. This paper is an attempt to clarify the relationships of factors that may be interacting.

No single explanation seems to be adequate to explain why freezing and thawing may damage concrete. We attempt here to provide a link connecting some of these theories by directing attention to another phenomenon that seems to be important. We feel that it may connect some of the theories or assist in helping explain more fully some of the theories. We also hope to stimulate research on the mechanism of damage to concrete by cyclic freezing.

2. Prologue

On the south bank of Lake Mendota is the main campus of the University of Wisconsin. The lake freezes over during winter; and sometimes during early January, a sharp crack pierces the cold, dry, very low temperature air. The sound is an airborne resonance caused by the ice just offshore as it cracks and releases energy into the atmosphere. That crack is due to tensile stress imposed into the ice by restraint created by its attachment to the shore and the ice mass of the lake. The crack is a result of thermal contraction of the ice as it is cooled to progressively lower temperatures after an initial 9% volume increase when water is converted into ice.

Near Lake Mendota are a dirt road and a high water table. The road is exposed to the same temperature environment as the lake. Every winter, areas of it are disrupted by large blister-like heaves. These heaves are caused by ice lenses that form under the roadway surface and are due to moisture migrating to and freezing in localized areas. Water moves to a cold front, and the heaving is due to the in situ freezing of that water and the accompanying 9% volume increase that occurs when water converts to ice. This process has been called ice accretion.

We propose that both of these mechanisms, thermal contraction of ice after freezing and ice accretion, are involved in a phenomenon that causes damage to concrete when temperatures cycle below the initial freezing point of pore solutions.

3. Ice volume changes

The density of bubble-free ice is 0.91650 at a pressure of one atmosphere (101 kPa) [9]. In Ref. [9], there is provided the following formula for calculating the density of ice at any temperature in the range of 0 to −30 °C:

$V_{\mathrm{it}}=0.91650[1-10^{-6}t(157.556+0.2779t+0.008854t^2+0.0001778t^3)]$ where t is in negative Celsius values. The change in relative volume of ice can also be calculated using an average value for the linear coefficient of thermal expansion of ice of 50×10^{-6}/°C. Based upon the above formula and relative volume, the changes in density of water and ice are shown in the Table 1. The progressive increase in density with decreasing temperatures was calculated, for example, as volume changes relative to the density of ice at 0 °C. These values are given in the Table 1 along with values for relative volume of ice expressed as a percentage of the volume of ice at 0 °C.

It, therefore, follows that:

(A) As the temperature decreases, ice formed by water freezing in a capillary cavity in concrete will occupy a progressively smaller volume due to thermal contraction resulting from cooling. Other material present will also get smaller as it gets colder. If the capillary cavity is full, or more than 91% full of pore fluid, the initial volume increment of ice that forms is sufficient to overfill the cavity. That puts the remaining unfrozen liquid under hydraulic or hydrostatic pressure. That liquid will have a lower freezing point because it is under pressure and also contains solutes in solution, the concentration of which will increase as more ice is formed so the freezing point is progressively lowered.

As the temperature continues to drop, some of that solution now becomes ice. Because the unfrozen fluid stays fluid until the freezing point drops to its reduced freezing point, it will be able to move into and occupy any increment of space made available by the reduction in volume of the ice as the temperature drops. Detailed information of ice formation is given in Ref. [10]. The linear coefficient of thermal expansion of ice ranges from 35.5 to 73.6×10^{-6}/°C for the range of temperatures 0 to −35 °C [11]. The linear coefficient of thermal expansion of cement paste ranges from 5.5 to 12.0×10^{-6}/°F [12], which converts to 9.9 to 21.6 10^{-6}/°C [13]. This process can continue as the isotherms that pass through the capillary cavity get lower and lower until the temperature in the cavity is as low as it is going to get. At that time, freezable water that can freeze at that composition, temperature, and pressure freezes.

Table 1
Density and volume change of ice with decreasing temperatures

Temperature (°C)	Density of water and ice (mg/m^3)	Density of ice as percent of ice ensity at 0 °C	Relative volume of ice as percent of ice volume at 0 °C[a]
0[b]	1.00000	–	–
0[a]	0.91650	100.00	100.00
−5	0.91722	100.08	99.92
−10	0.91793	100.16	99.84
−15	0.91863	100.23	99.77
−20	0.91932	100.31	99.69
−25	0.92001	100.38	99.62
−30	0.92069	100.46	99.54

Calculated from Bader [9].

[a] Frozen (i.e., ice).

[b] Unfrozen (i.e., water).

Because all of the ice that forms is essentially pure water in solid form, its melting point at atmospheric pressure is 0 °C (32 °F) regardless of the temperature at which it formed. Therefore, as the temperature increases in the subfreezing range and the ice volume increases, there will be fluid that was squeezed into entrained air voids that will not come back at the same temperature that it went over at because the ice that formed to push it formed at a relatively low temperature but thaws at a higher temperature.

Two bits of information that may assist in clarifying the geometry of the arena in which these phenomena are happening and differentiating them from somewhat similar but different ones are:

(1) The geometry: Philleo [14] noted the presence of three size ranges of pores:

Type of pore	Diameter
Gel	Less than 3.2 nm
Capillary	3.2 to 3000 nm
Entrained	Greater than 3000 nm

(2) Because the capillary cavities in which all freezable fluids located in cement paste range in sizes from 3.2 to 3000 nm, it is pertinent to recall that the freezing point of the pore fluid is lower as these voids get smaller. It is also relevant that, as Powers [4] pointed out, when the range of freezing points depends on capillary cavity size, the temperature at which ice melts is the same as that at which it froze rather than the situation where the freezing point depends on the concentration of dissolved material in the pore fluid—as is the case with regard to the phenomena dealt with in this paper. Helmuth [12] provides detailed discussions on this subject.

(B) Additionally, by combining the changes in ice volume with temperature change and the accretion theory, the following is proposed as a contributory mechanism for the creation of stresses sufficient to cause concrete distress:

(1) A cold front (frontal zone) moves into the concrete and a 0 °C (32 °F) isotherm subparallel to the concrete surface results. At some lower temperature, depending on the amount of material in solution in the pore fluid and pore sizes, some fluid within the capillary cavities freezes. If any capillary cavity is completely filled with fluid when the isotherm is at its freezing point, some of the fluid will freeze, increase in volume, and subject the unfrozen fluid to hydraulic pressure, however small. If the rate of cooling is high and the permeability of the concrete surrounding the pore is low, the ability of the unfrozen fluid to escape and reduce any pressure created may be inadequate, and strain, ultimately resulting in cracks, occurs in the concrete. This is the basis for the hydraulic pressure theory of frost damage to concrete. Based upon the hydraulic pressure theory, if the concrete is provided with an adequate air-void system, the probability of such damage can be reduced to a negligible level. Assuming concrete of normal permeability, the air-void system will be one in which the distance to an air void from any point within the paste is not over 0.20 mm (0.008 in.). The hydraulic pressure hypothesis is now considered to be obsolete and was replaced by the ice accretion theory (ACI Committee 201.2R report).

(2) As the freezing isotherms move inward, unfrozen pore fluid deeper in the concrete moves towards the frozen concrete in an effort to bring the temperatures of the two pore fluids to a compromise balance (thermo-osmosis).

(3) As the solution concentration of the remaining unfrozen pore fluid increases, pore fluid of lower solution concentration elsewhere in the concrete may move toward the now more concentrated solution (chemo-osmosis).

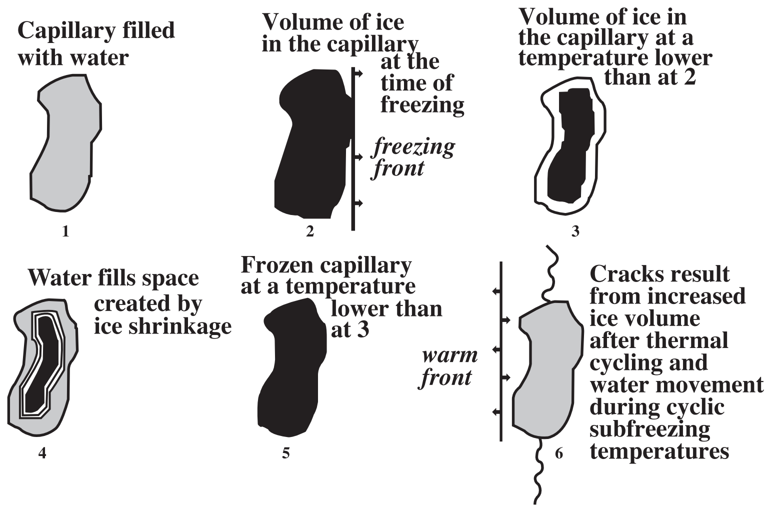


Fig. 1. Response of water and ice in a capillary pore in cement paste as the freezing temperature decreases—The Erlin/Mather Effect.

(4) As the temperature drops, the ice that formed in the cavity contracts; and the peripheral space created by the contraction fills with unfrozen pore fluid that has migrated to the freezing front (Fig. 1—for non-air-entrained paste).

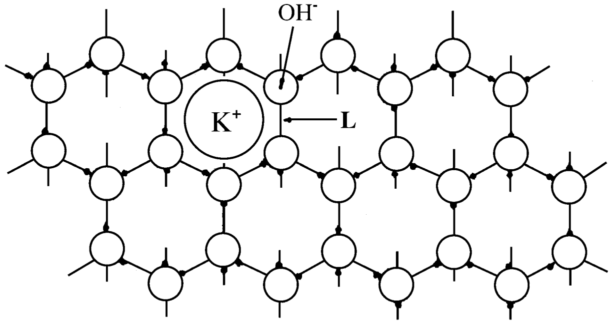
(5) When the increment of pore fluid freezes, there is a volume increase of the small increment of such fluid, which produces greater internal pressure on the pore structure, which can lead to cracking if the pressure cannot be relieved.

(6) Subsequent exposure to cyclic subfreezing temperatures causes ice in the capillary cavity to expand and contract attended by a small incremental volume change each time the temperature cycles.

(7) Temperature cycling within the subfreezing range will cause; expansion and contraction of the ice, cyclic increase and decrease of stress on the paste and ice along a plane subparallel to the concrete surface, attendant cracking and surface scaling, and distress deeper into the concrete. A simplified but exaggerated version of the above sequence for non-air-entrained paste is depicted in Fig. 1.

4. Discussion

Discussions involving the damaging effects of freezing and thawing in concrete today are commonly based on the 9% increase in volume resulting from the water conversion to ice. As has previously been discussed, that hypothesis has been replaced based upon work largely done by Powers and Helmuth supplemented by Litvan and Bruere. Ice, as a material, still undergoes positive and negative volume changes as it responds to changing temperatures. There is a progressive volume decrease with decreasing temperatures and, conversely, a progressive volume increase with increasing temperatures—therefore, there also is a need to consider the effects of the volume change of ice since the linear coefficients of thermal expansion and contraction of concrete are of a different magnitude than that of ice. We feel that our concept that cyclic positive–negative ice volume changes within the subfreezing range merits further consideration as a contributor to distress.There are many other complicating phenomena that can mitigate or enhance aspects of the development of stress. Those other phenomena include the specific nature of the ions in the capillary fluid, Van der Waals forces, modulus of elasticity, and strength properties of the paste and its permeability, plus the compressibility of ice.An example of the complexity of any analysis is studies that indicate that not all chemical impurities in solution are exsolved when ice forms. It is reported in Ref. [14] that sodium hydroxide (NaOH) and potassium hydroxide (KOH) can be incorporated into the ice structure (Fig. 2).The sodium or potassium atoms are accommodated in the interstices of the unit cell, and the hydroxyl ion (OH^{-}) is directly incorporated into the crystal lattice by replacing its counterpart in a water molecule. Thus, the effects of alkalis from the cement, aggregates, and sources external to the concrete (e.g., deicing chemicals and seawater) may be contributory to concrete performance in a cyclic freezing environment in addition to their osmotic effects. Shumaskii [16] reported several unstable compounds ($NaC1 \cdot 2H_2O$, $MgC1_2 \cdot 8H_2O$) that have melting points around 0 °C (32 °F). Parkhomenko [17] (as reported by Shumaskii) classified this group of minerals as cryophiles (cold lovers). (Perhaps there is some romance to our staid science!) These minerals could be derived from deicing chemicals, and if their formation involves in situ solid-to-solid phase transformations those may be important relative to the resistance of concrete to effects of freezing and thawing.



How KOH dissolved in ice is thought to introduce defects. The K ion is interstitial, the OH ion substitutes for its water counterpart leaving one bond without any proton - an L-defect.

Fig. 2. Hypothesized pattern of KOH impurity incorporated into the structure of ice (Petrenko and Whitworth [15]).

Acknowledgements

The authors thank Richard A. Helmuth, Edward F. O'Neil III, and Dipayan Jana for their reviews of this paper in which they suggested valuable additions and corrections.

References

[1] Vesa Penttala, Fahim Al-Neshawy, Stress and strain state of concrete during freezing and thawing cycles, Cement and Concrete Research 32 (9) (2002) 1407–1420.

[2] Bryant Mather, How to make concrete that will be immune to the effects of freezing and thawing, in: David Whiting (Ed.), Paul Klieger Symposium on Performance of Concrete, American Concrete Institute SP-122, Detroit, MI, 1990, pp. 1–18.

[3] T.C. Powers, A working hypothesis for further studies of frost resistance of concrete, ACI Journal, Proceedings 41 (3) (1945) 245–272.

[4] T.C. Powers, Freezing effects in concrete, Durability of Concrete, American Concrete Institute SP-47, 1975, pp. 1–12.

[5] T.C. Powers, R.A. Helmuth, Theory of volume changes in hardened portland cement paste during freezing, Proceedings of the Highway Research Board 22 (1953).

[6] T.C. Powers, Basic considerations pertaining to freezing and thawing tests, Proceedings of the American Society for Testing Materials 55 (1955).

[7] George Verbeck, Paul Klieger, Studies of salt scaling of concrete, Highway Research Board Bulletin 150 (1956 (January)) 1–13.

[8] G.G. Litvan, Phase transitions of adsorbates: IV. Mechanism of frost action in hardened cement paste, Journal American Ceramic Society 55 (1) (1975) 38–42.

[9] Henri Bader, Density of Ice as a Function of Temperature and Stress, U.S. Army Material Command, CRREL, Special Report 64, Hanover, NH, (August 1964).

[10] R.A. Helmuth, Capillary size restrictions on ice formation in hardened portland cement pastes, Fourth Symposium on the Chemistry of Cement, Washington, DC, 1960.

[11] N. Dorsey, Properties of Ordinary Water-Substance, Reinhold Publishing, New York, 1940, pp. 473–474.

[12] R.A. Helmuth, Dimensional changes of hardened portland cement pastes caused by temperature, Proceedings of the Highway Research Board 40 (1961).

[13] M. Fintel, Handbook of Concrete Engineering, Van Norstrand Reinhold, New York, 1974, pp. 156–157.

[14] Robert E. Philleo, Freezing and thawing resistance of high strength concrete, in: National Cooperative Highway Board Program, Synthesis, vol. 129, Transportation Research Board, Washington, DC, 1986.

[15] Victor F. Petrenko, Robert W. Whitworth, Structure of ordinary ice I_h, Part II: Defects in Ice, Volume 1: Point Defects, Special Report 94-4, U.S. Army Corps of Engineers, CRREL, Hanover, NH, 1994 (April).

[16] P.A. Shumaskii, Principles of Structural Glaciology, Dover Publications, NY, 1964, (translated from the Russian by David Kraus).

[17] S.G. Parkhomenko, Merzoltovedenie kak uchenie o kriofil'nykh gornykh porodakh (Permafrostology as the Science of Cryophilic Rocks1938Akademiia Nauk SSSR, pp. 177–194 Kamitet po Vechnoi Merzloty, Trudy, 6: AB 31187.