

Theory of Volume Changes in Hardened Portland-Cement Paste During Freezing

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NEW experimental data are presented on the freezing of hardened portland-cement pastes with and without entrained air. They are explained in terms of two mechanisms: 1) the generation of hydraulic pressure as water freezes in capillary cavities and 2) the growth of the bodies of ice in the capillary cavities or air voids by diffusion of water from the gel. Air voids limit the hydraulic pressure and shorten the period during which the ice in the cavities can increase. The closer the air voids are to each other the more effective they are in controlling either mechanism.

● IN two previous papers (1, 2) a hypothesis was advanced to explain the mechanism by which freezing may damage hardened cement paste in concrete and by which air voids may prevent that damage. The hypothesis was based on the assumption that damage is due to hydraulic pressure generated during the process of freezing. Work done in the laboratories of the Portland Cement Association during the last 2 yr. has, we think, advanced the basic assumption of that hypothesis to the status of established fact. At the same time we have learned that hydraulic pressure does not account for all the phenomena produced by freezing. Part of the effect of freezing is apparently due to the tendency of microscopic bodies of ice to grow by drawing water from the gel.

This paper is not intended to be a complete report of the laboratory research on which it is based. Additional details will be given in other papers as soon as the work is finished. The present paper will deal with the salient features of the experimental results and give our interpretation of them.

VOLUME CHANGES DUE TO FREEZING

Several-hundred experiments were made in which the length changes of cement-paste specimens were measured simultaneously with measurements of temperature. Arrangements were such that the temperature could be held constant or could be caused to change at any desired rate through a range extending from +25 to -25 C. Changes in length as small as 1 micron per in. could be detected.

The temperature measurement was sensitive to about 0.1 C. Length change, temperature change, and elapsed time were recorded automatically.

The specimens were composed of neat cement paste, some made with and some without entrained air. They were tubular, about 2 in. long; outside diameter, 1 in.; inside diameter, $\frac{1}{2}$ in. Most of them contained a Type I cement. Various water-cement ratios were used ranging from 0.45 to 0.70 by weight. The specimens were cured so as to maintain the highest possible degree of saturation throughout the curing period. Ages at test ranged from 3 weeks to about 3 mo. for most of the work. Some specimens, however, were about 2-yr. old when tested.

The results of a test on a specimen containing no air voids¹ is shown in Figure 1. The left-hand scale of ordinates gives the change in length and the right-hand scale, the change in temperature. The scale of abscissas gives the elapsed time after the beginning of the experiment. In most respects the features shown are typical of all relatively porous pastes made without entrained air.

Beginning at room temperature, the specimen was cooled about 0.25 deg. per min. In this case the specimen contracted linearly (the contraction is usually not linear) until the temperature was -6.6 C. At the time when this temperature was reached, freezing oc-

¹ Air voids are not considered to be a part of the paste; the paste is the substance surrounding the air voids. The paste is porous (see later) and its pores may contain either air or water. In this paper, we deal only with water-saturated paste, but in no case would we speak of an empty pore in the paste as an air void.

curred, as shown by the sudden rise in temperature. At the instant that freezing began, the specimen began to expand rapidly and with continued cooling it continued to expand.

The particular specimen represented by Figure 1 supercooled about 6 deg. before freezing began. Usually the degree of supercooling is less, often negligible. For specimens of the same kind, the greater the degree of supercooling, the greater the initial expansion. Without supercooling, expansion begins gradually, and apparently in such a case, too, it begins at the same time that freezing begins.

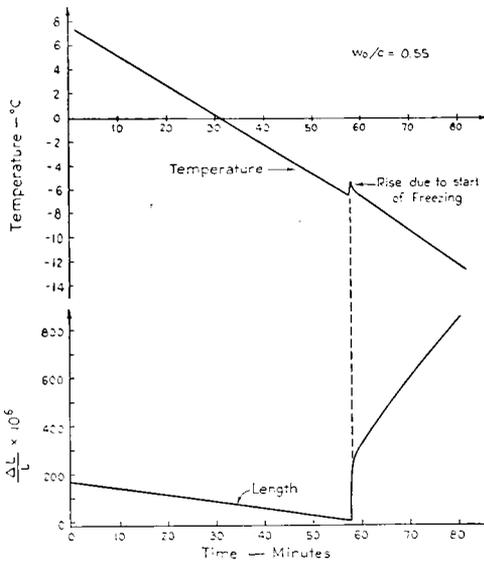


Figure 1. Coincidence of initial expansion with freezing; paste porosity, 0.46.

For a specimen containing no entrained air and for rates of cooling 0.25 deg. per min. or higher, the expansion that occurs during freezing is smaller the smaller the porosity of the sample. The porosity of the sample also influences the temperature at which pronounced expansion begins.

Similar data for a specimen containing entrained air are shown in Figure 2, lowest curve. In this case freezing began at about -1 C. and it was accompanied by a small expansion (about 30 microinches). Then as the temperature continued to fall at a nearly constant rate the specimen contracted. When

the temperature reached -8.3 C, the cooling was stopped and the temperature held practically constant for about 22 min. During this period of constant temperature the specimen containing entrained air (bottom curve) continued to contract for about 12 min. of the 22-min. constant-temperature period. When cooling was resumed, the specimen resumed contracting.

The dashed-line curve shows the behavior of a similar specimen without air voids as it followed the same temperature schedule. The behavior is like that shown in Figure 1,

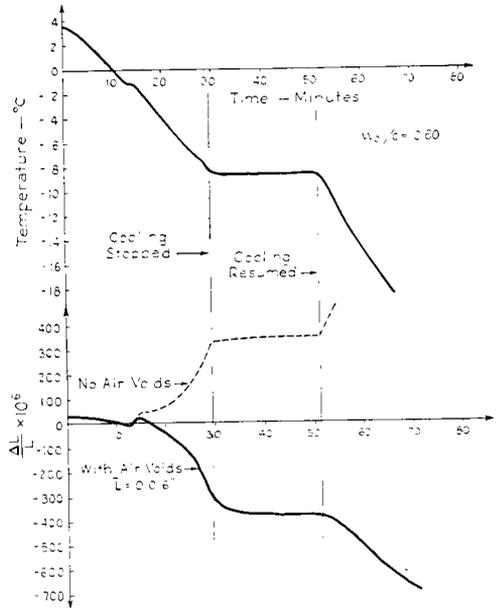


Figure 2. Freezing of pastes with and without air voids; paste porosity, 0.45.

modified by the difference in supercooling. As the temperature fell the specimen expanded at an increasing rate. At the time when cooling was stopped and the constant-temperature period began, the specimen without entrained air continued to expand slightly while the specimen with entrained air was contracting. After a small expansion the specimen without entrained air then remained almost at constant length.

At the start of the second period of cooling, the specimen without entrained air began abruptly to expand, whereas that made with entrained air began gradually to contract.

Figure 3 is presented to show the effect, on a sample containing no air voids, of holding the temperature constant after the freezing process starts. The sample, a relatively dense one, did not begin to expand until the temperature reached -19°C . The graph includes a record of the experiment for a period beginning 30 min. before expansion began and continuing for more than 6 hr. after that time. For the first 40 min. the temperature was decreased at nearly constant rate. When the temperature had reached -21.3°C , cooling was stopped and the temperature was held constant. During the constant-temperature period the specimen continued to expand. Finally, cooling was resumed, whereupon

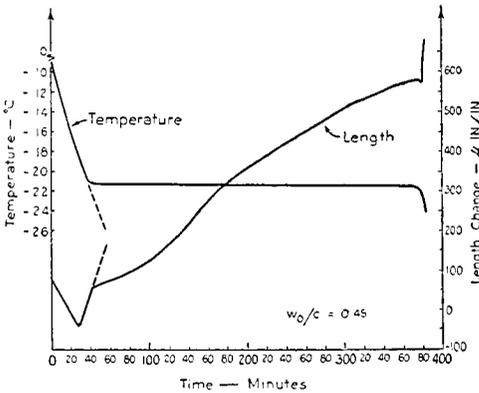


Figure 3. Effect of holding temperature constant after freezing starts in a relatively dense paste.

there was a slight contraction followed by an abrupt increase in the rate of expansion.

The principal point to be noticed in this graph is the expansion during the constant-temperature period. This same tendency is discernible in the dashed line of Figure 2; but for reasons associated with the dimensions and porosity of the sample, the effect was small and of short duration.

Figure 4 shows the relationship between length change and temperature change in the freezing range for pastes containing different amounts of entrained air and, hence, for different void-spacing factors, \bar{L} . The pastes represented by the different curves all had approximately the same porosity. The uppermost curve represents a specimen containing no entrained air. The indicated spacing factor for such a specimen is based on the

geometry of the specimen, i.e., no point in the specimen can be more than 0.1 in. from a boundary. The spacing factors for the specimens containing entrained air were based on the calculated mean distance between voids, the calculations being made by a method previously published (2).

The feature to be noted is that at a given low temperature, say -20°C , the expansion produced by freezing is smaller the smaller the spacing factor. In the low range of spacing factors, the specimens expand slightly and then they contract more than can be ac-

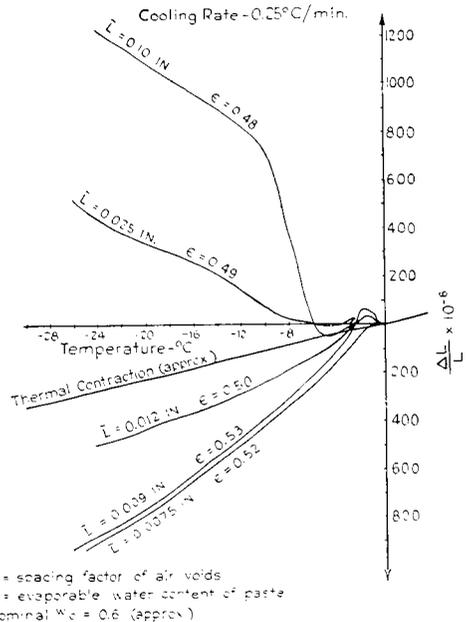


Figure 4. Effect of entrained air.

\bar{L} = spacing factor of air voids
 E = evaporable water content of paste
 Nominal $w_0/c = 0.6$ (approx)

counted for by normal thermal contraction alone.

Many variants of these curves were found among the several-hundred obtained. But it is not necessary to deal with those variants here, for they are such as would be expected from the mechanisms that may be deduced from the curves presented above. The data chosen were those that illustrate with a minimum of complication the mechanisms producing the volume changes.

The principal phenomena may be summarized as follows: (1) In all water-soaked pastes not containing air voids expansion

begins at the instant that freezing begins. (2) When air voids are present and closely spaced, initial expansion, if any, begins with freezing and is followed by contraction. (3) When cooling is stopped in the midst of the freezing process and the temperature is held constant, pastes without air voids continue to expand, and those with closely spaced air voids continue to contract, for limited periods. (4) When cooling is resumed after a constant-temperature period, pastes without voids begin abruptly to expand and those with voids begin gradually to contract. (5) On freezing water-soaked pastes of given porosity, expansion is smaller the smaller the spacing factor of the air voids. With spacing factors such as those found in air-entrained concrete, the specimens contract.

INTERPRETATION OF EXPERIMENTS

Knowledge of the submicroscopic structure of hardened portland-cement paste is prerequisite to an understanding of the phenomena under discussion. We shall see that these phenomena can occur only in a material that holds some freezable water in pores so small that the water cannot freeze while it is in those pores, together with some water so situated that it can freeze in place. Experimental evidence has already been published showing that hardened portland cement paste is such a material (3a). Its pores are of two kinds, gel pores and capillary pores. Water cannot freeze in gel pores but can freeze in the capillary pores.

Physical Structure of Paste

In 1947 data were published (3c) showing that the ultimate particles in cement paste (ultimate with respect to water penetration) were exceedingly small, their average diameter being about 140 Å.² The calculation of size was based on measured specific surface of the ultimate particles. A few months ago we obtained data on the low-angle scattering of X rays that confirmed this calculation of average size. More recently, in cooperation with the National Bureau of Standards, we obtained electron photomicrographs showing that the ultimate particles were roughly spherical and ranged in size from 50 to

² 140 angstrom units equal 0.014 micron, or 0.6 micro-inch. On the basis of current work, this figure is being revised downward. The average diameter is now believed to be between 85 and 100 Å.

200 Å, the apparent average being as previously calculated. The Bureau of Standards also obtained low-angle X-ray data confirming the average size. The tiny spheres are evidently linked together to form the cohesive mass we call *cement gel*. Points of contact are believed to be bonded chemically, as if the spheres were spotwelded together.

Other data published in 1947 showed that when the cement gel completely fills the space available to it, the porosity of the specimen is about 25 percent. From this we deduced that the interstitial spaces among the spheres are about 25 percent of the over-all volume, a figure now seen to be consistent with the shape of the particles and their limited size range.

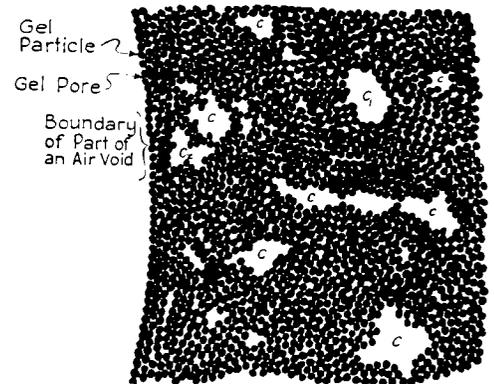


Figure 5. Simplified diagram of paste structure; C indicates capillary cavity.

In most pastes the volume of the gel does not equal the apparent volume of the paste. The unfilled space in the paste occurs as cavities in the otherwise continuous mass of gel. These spaces are called capillary pores or capillary cavities. The gel pores are the interstitial spaces among the massed spheres that surround these cavities.

With this knowledge at hand we are able to construct a diagram on which a discussion of the mechanism of freezing can be based. This is given in Figure 5. The gel particles are indicated by the black spots and the capillary pores by the empty spaces. So as not to obscure the gel pores, we have indicated the dense regions to be much less dense than they really are.³

³ Ca(OH)₂ crystals and residues of unhydrated cement are not represented. These are comparatively few and far between and of no significance here.

The curved boundary at the left is supposed to represent a part of the wall of an air void and is intended to suggest that air voids such as those in air-entrained concrete are extremely large as compared with the capillary cavities and gel pores in the paste. If the air void were drawn to scale and were of average size, the curvature would hardly be discernible.

The capillary cavities are more numerous and larger the higher the original water-cement ratio and the shorter the period of curing. Such cavities are the only places where ice can exist within the boundaries of the paste.

Experimental data show that a very-small amount of water freezes near the normal freezing point, but in most specimens a significant amount of freezing occurs only after the temperature falls well below the normal freezing point. This behavior (as well as other evidence) indicates that most of the capillary cavities are quite small. They are so small that the ice crystals they contain cannot exist except when the temperature is below the normal freezing point. The reason for this is too complex to be dealt with here. A simple explanation is that the surface tension of the bodies of ice in capillary cavities puts them under a pressure that is higher the smaller the body. Hence, the smaller the cavity and, of necessity, the smaller the ice body the higher the pressure and the lower the freezing point.⁴ (The gel pores are so small that freezing cannot occur at any temperature, at least not at any temperature above -78 C.)

Freezing starts at the temperature required by the largest cavity, and as the temperature continues to fall, the water in the smaller cavities progressively becomes frozen. Freezing curves, such as the dashed line in Figure 2, indicate that the water is held in cavities of various sizes.

The foregoing remarks pertain to freezing in a saturated specimen, in which case the free energy of the unfrozen water is at a maximum. Owing to adsorption and capillary forces and to dissolved substances, principally the alkalis, the free energy of the water in hardened paste is a function of its degree of

saturation (3). The same is true of the cement gel considered by itself. The maximum free energy is somewhat below that of pure water in bulk, because of the solute concentration. When water is removed from the paste or the gel, the free energy of the residual water becomes progressively lower. Hence, the highest temperature at which the remaining water can freeze becomes lower as water is extracted from the paste.

Capillary size, limiting as it does the size of the ice crystal, fixes the least amount by which the free energy of ice in a capillary exceeds that of bulk ice. (When the capillary ice is subjected to pressure, its free energy rises above the minimum.) Desiccation of the paste lowers the free energy of the freezable water and fixes the highest temperature at which the freezable water can be in equilibrium with bulk ice. The temperature at which freezing can occur in a given capillary cavity is determined by the free energy of the ice and the free energy of the freezable water; thus, it is controlled both by cavity size and degree of desiccation.

In the following discussion we shall assume, for the sake of simplicity, that the concentration of soluble material is negligible, hence, that the free energy of the water in saturated gel is practically the same as the free energy of pure water in bulk at the same temperature. This condition is not entirely hypothetical; it has been produced in the laboratory.

Freezing in Capillaries and Generation of Hydraulic Pressure

In a water-soaked paste the capillary pores and the gel pores are full, or nearly full, of water. When the temperature falls to the point where freezing can begin, ice crystals should appear, presumably in the largest capillary cavities only. Consider the capillary cavity marked C_1 in Figure 5. When the water it contains begins to change to ice, the volume of water plus ice will exceed the original capacity of the cavity. This comes about, of course, because 1 cc. of water occupies about 1.09 cc. of space after freezing. Therefore, during the time when the water in C_1 is changing to ice, the cavity must dilate or the excess water must be expelled from it.

As indicated by the diagram, cement paste is a permeable material (though the coef-

⁴ The depression of the freezing point should not be confused with the supercooling mentioned earlier. When cavities of a size that should permit freezing at say -0.5 C. are present in a sample and freezing does not begin until -6 C. , the water in those cavities has been supercooled 5.5 deg. In some specimens the water can be cooled to -18 deg. or lower without freezing. But this is not due to supercooling; it is due to the lack of the larger capillary cavities.

ficient of permeability is extremely low). Hence, there is a possibility that the excess water can escape from C_1 during the process of freezing. If we consider Figure 5 to represent half of a layer between two voids, we can see that there is a possibility for the excess in C_1 to escape into the air void at the left. We may think of the growing ice body in C_1 as a sort of pump forcing water through the paste toward the void boundary. Obviously, such a pumping out of water involves the generation of pressure. The factors controlling this pressure have been dealt with in detail in a previous paper (2). The most important factors are: (1) the coefficient of permeability of the material through which the water is forced; (2) the distance from C_1 to the void boundary; and (3) the rate at which freezing occurs.

Let us now consider freezing in the capillary marked C_2 . Clearly, the excess water can escape from C_2 more readily than from C_1 . Therefore, the maximum pressure reached during freezing in C_2 must be less than the maximum reached in C_1 . In general, we can see that during the process of freezing hydraulic pressure will exist throughout the paste, and this pressure will be higher the farther the point in question from the nearest escape boundary. If a point in the paste is sufficiently remote from an escape boundary, the pressure may be high enough to stress the surrounding gel beyond its elastic limit, or beyond its strength, and thus may produce permanent damage.

It becomes clear that every air void enveloped by the paste must be bordered by a zone or shell in which the hydraulic pressure cannot become high enough to cause damage. Theoretically, the pressure increases approximately in proportion to the square of the distance from the void, the pressure being zero at the void boundary. By reducing the distance between voids to the point where the protected shells overlap, we can prevent the generation of disruptive hydraulic pressure during the freezing of water in the capillaries.

The foregoing is the essence of the hydraulic-pressure hypothesis that has been developed in detail previously. Experimental data of the kind already presented advance the hypothesis to the status of established fact. To see how this is so, consider again the capillary cavity represented in C_1 in Figure 5.

Hydraulic pressure must appear in this cavity at the very instant that freezing begins. Therefore, the specimen as a whole (acted on simultaneously by all similar cavities) should begin to expand at the instant that freezing begins. Figure 1 shows that this is exactly what happens. No other mechanism that we can think of can account for this coincidence of events. This evidence alone, when all its implications are evaluated, is enough to confirm the hydraulic-pressure hypothesis. Other evidence will be brought out further on pertaining to responses to changes in rate of cooling.

However, generation of hydraulic pressure through the mechanism just described does not account for all phenomena illustrated in Figures 1 to 4. In particular, it does not account for shrinkage that accompanies freezing when air voids are present nor for certain responses to change in rate of cooling. To account for these phenomena, we must consider what may happen after the water in a given capillary cavity becomes frozen.

Diffusion and Freezing of Gel Water

With the water in cavity C_1 turned to ice, we have to consider the relationship of that ice to the unfrozen water in the surrounding gel. (Remember that water cannot freeze in the gel.) If the gel is saturated, the gel water has the same free energy as that of ordinary water in bulk. Therefore, it can be in thermodynamic equilibrium with the ice in C_1 at 0 C if both the ice and the gel water are under a pressure of 1 atmosphere and if C_1 is so large as to have negligible surface energy. If now the temperature drops below the temperature at which the water in C_1 became frozen (we here assume it to be 0 C), the gel water is no longer in thermodynamic equilibrium with the ice; its free energy is higher than that of the ice. We know this because we know that the water that can be extracted from a saturated gel has a higher entropy than that of ice (3b). When such a difference in entropy exists, it is a direct thermodynamic consequence that lowering the temperature will cause the water to gain free energy faster than does the ice. As a consequence, the gel water acquires an energy potential enabling it to move into the cavity and cause the ice crystal to grow and enlarge the cavity. Our

conclusions regarding the mechanism by which this growth takes place will now be described.

As indicated in Figure 5, the walls of the capillary cavities are made up of gel particles. Each gel particle carries its adsorbed water "film" and the water film separates the gel particles from the ice, the degree of separation being submicroscopic, only a few molecular diameters. We attempt to show this boundary region between ice and cavity wall in Figure 6. The body of ice is shown to be separated from the cavity wall by an unfrozen film, the adsorbed layer, which film is continuous with the adsorbed layers within the gel.

The water molecules in the film tend to have the orientation demanded by the force field of gel particles. The same molecules are also

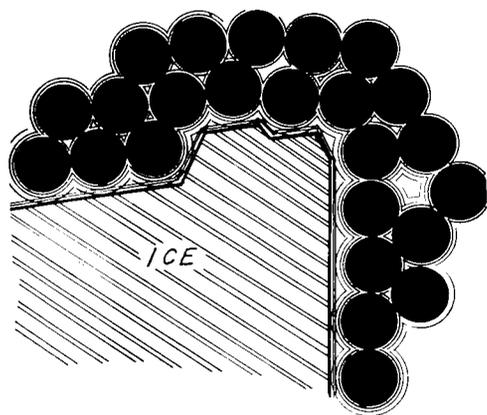


Figure 6. Disposition of water films.

subject to the force fields of the ice crystal which tend to produce the molecular orientation characteristic of the crystal. Thus, the water in the film is subject to competitive forces. At a given temperature below 0 C, the ice crystal is able to capture some of the film water and reduce the thickness of the film below what it would be if no ice were present. As the temperature becomes still lower, more of the molecules in the film are captured by the ice and the film becomes thinner. Since the films are identical with the adsorbed layers on the gel particles in the interior of the gel (the gel water), the depletion of the film in the capillary cavity by the ice in the capillary cavity produces a free-energy difference between the film in the cavity and the gel water. Consequently, water creeps along

the surfaces of the gel particles into the film in the ice-bearing cavity as required to reduce the free-energy potential created by depletion of the film in the cavity. The process is called surface diffusion.

Whenever the gel loses water it tends to shrink, no matter whether the water is lost by evaporation or by freezing. The tendency of the gel to shrink as water is extracted from it, by freezing and the growth of the ice body, places the ice in the capillary cavities and the film around the ice under pressure. Such pressure increases the free energy of the ice and of the water in the film between the ice crystal and the gel particles and tends to prevent the replenishment of that film by diffusion of water from the gel. However, the swelling pressure in the film is enough to produce dilation. For example, if the gel were saturated and if the capillary cavities contained ice at -5 C, the pressures in the film between the ice and the solid could be as much as 1,200 psi. This amount of pressure would surely cause the paste to dilate appreciably. Thus, expansion can be caused by diffusion of water from the gel to the capillary cavities.

Diffusion to Air Voids

Up to this point we have spoken mostly of the diffusion of gel water to capillary cavities. From the same considerations of thermodynamics, we can see that while gel water is diffusing to capillary cavities it is diffusing also to the ice in the air voids.

The amount of ice in the air voids is not equal to the capacity of the voids.⁵ Consequently, as the ice grows and the gel shrinks, the ice in the air void may be under no significant pressure. Such would be the case when the ice exists as discrete crystals or as a thin shell lining the void, the shell having negligible rigidity. If the shell becomes thick enough, it might offer resistance to the contraction of the void. But it could not offer as much resistance as the ice in the completely filled capillary cavities. The point is that the pressures on the capillary ice may be much higher than the pressures on the air-void ice.

⁵ Under some circumstances the air voids in cement paste or in concrete can become filled, or partly filled, with water prior to freezing. In practice, such circumstances are rare, as attested by the successful use of air-entrained concrete. In the present discussion we assume that the air voids contain no water except that received during the process of freezing. However, they could contain a considerable additional amount of water without appreciable alteration of their protective effect.

Since the pressure on the capillary ice may be higher than that on the air-void ice, its free energy may be correspondingly higher. Also, as we have already seen, the bodies of capillary ice are very small, and as a consequence, the free energy of the capillary ice is higher than that of the bulk ice in the air voids at the same temperature and pressure. Hence, at a given temperature the free energy of the capillary ice will be higher than that of the air-void ice, because of the smallness of the particles of capillary ice and, at times, because of higher pressure on the capillary ice.

The consequences of these differences in free energy can best be understood with the aid of Figure 5. Consider again capillary C_2 . Let us suppose as before that a temperature has been reached at which the water

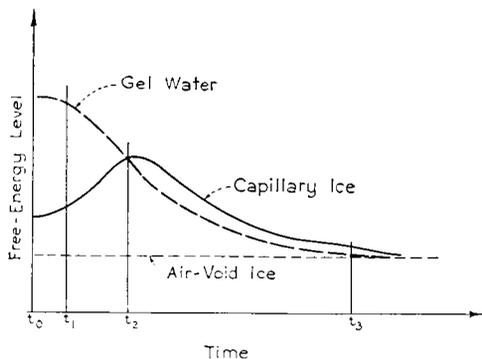


Figure 7. Free-energy changes in reaching equilibrium.

in this cavity becomes frozen. Because of the nearby air void, we may now assume that the excess water produced in this cavity has been forced into the air void where, along with the excess water from other cavities, it has produced a thin coating of ice on the void boundary. We shall suppose further that the hydraulic pressure has been relieved so that the ice in the air void, the water in the gel, and the ice in the cavity are under equal pressure. Now let us cool this region quickly to a lower temperature and then hold the temperature constant.⁶ The effect of this change is illustrated in Figure 7.

This diagram shows the changes in free energy of the gel water, the capillary ice, and the air-void ice that will take place while the

⁶ Lowering the temperature should cause other, smaller cavities to freeze, but we are considering only the small region indicated.

temperature is held constant. The upper curve represents the free energy of the gel water at a particular point within the gel, which we shall call Point A. This point is assumed to be nearer to C_2 than it is to the air void. The time, t_0 , corresponds to the time at which the diffusion is assumed to begin. At this time the capillary ice and the air-void ice are assumed to be under the same pressure, but the free energy of the capillary ice is shown to be higher than that of the air-void ice, because the body of capillary ice is assumed to be very small. The free energy of the gel water is shown to be higher than either of the ice bodies, because in dropping from the first to the second temperature, it gained more free energy than did the bodies of ice.

The starting point of the curve for capillary ice relative to the other two points will depend upon the size of capillary void in question. The smaller the ice body, the smaller will be the initial difference between its free energy and that of the gel water and the greater will its free energy exceed that of the air-void ice. Figure 7, therefore, represents conditions pertaining to a particular size of capillary cavity.

Since at the start the free energy of the gel water exceeds that of the two ice bodies and since the gel separates the two, gel water will begin to diffuse in both directions, that is, to the air void and to the capillary cavity. As diffusion proceeds, the gel water at Point A is not immediately affected. After a certain time interval, t_0 to t_1 , the amount of gel water at Point A begins to diminish and the free energy begins to decrease.

During the interval t_0 to t_1 , the capillary ice increases and, through the mechanism already discussed, produces pressure on the walls of the cavity. As a consequence, the free energy of the capillary ice increases during this interval.

The air-void ice also receives water during this period; but, being at constant temperature and under negligible pressure, its free energy remains constant.

During the interval t_1 to t_2 the free energy of the gel water continues to decrease, because of continued desiccation of the gel. At the same time the free energy of the capillary ice rises until it equals the free energy of the residual gel water. At this time diffusion through Point A to the capillary cavity

ceases. Thereafter, the gel water moves toward the air void only.

During the interval t_2 to t_3 the system comes close to equilibrium. In this period the free energy of the capillary ice is at all times higher than that of the residual gel water. Hence, the capillary ice loses water to the gel and eventually to the air-void ice. At equilibrium the gel has reached the required degree of desiccation, and the ice in the capillary cavities has been depleted enough to relieve the pressure.

During the interval t_0 to t_2 , the capillary ice increases by approximately 1.09 times the volume of water it receives. The parts of the gel from which this water is received tend to shrink, but even when unrestrained the shrinkage is much less than the volume of water lost. Hence, the net effect is a tendency to expand.

The concomitant volume increase of the air-void ice either results in no expansive force at all or else in only a feeble one, as we have already pointed out. Consequently, the net effect of water lost from the gel to the air void is a tendency to shrink. Both tendencies coexist during the interval t_0 to t_2 , that being the period of diffusion in both directions; but in the following interval gel water diffuses toward the air void only, and the net effect is shrinkage throughout the gel. Over-all expansion due to diffusion is possible while the capillary ice is still receiving gel water, though it may cease while diffusion to some capillary cavities is still going on.

In a paste of given characteristics, the amount of gel water that can enter a capillary cavity by diffusion and freezing will be a maximum if the paste contains no air voids and if the boundaries of the specimen are at a practically infinite distance from the cavity.⁷ In this case, the capillary ice can grow for as long as necessary to reach equilibrium with the gel. If the stresses, whether from hydraulic pressure or from subsequent growth of capillary ice, rupture the gel and thus release the pressure on the ice, the growth will be limited only by the amount of water in the system freezable at the given temperature.

On the other hand, if the paste contains air voids and if the capillary cavity is adjacent to a void, the free energy of the gel water between

the cavity and the void must decrease rapidly. The period of diffusion to the capillary cavity will be correspondingly brief (see C_2 of Fig. 5). If the cavity is remote from the void, depletion of the gel water in the vicinity of the cavity by diffusion to an air void will be correspondingly delayed and diffusion to the capillary cavity prolonged (see C_1 of Fig. 5). In terms of the relationships shown in Figure 7, this means that the farther the capillary cavity is from the nearest air void, the longer the interval t_0 to t_2 and the greater the proportion of total freezable water received by the capillary cavity.

Application to Test Data

Let us now apply this theory to the data presented in Figures 1 to 4. First, the evidence of expansion due to hydraulic pressure:

As already mentioned, the instantaneous expansion shown in Figure 1 seems to be explainable only in terms of the hydraulic pressure generated during the freezing of capillary water, that is, by water freezing in place. Because of the relatively high porosity of the sample and because of supercooling, a relatively large amount of water was able to freeze at one time. (The only escape for the excess water was the outer boundaries of the specimen.) The continued expansion accompanying further cooling was also due mostly to hydraulic pressure, but the evidence for this conclusion does not appear in Figure 1 (see discussion of Fig. 4).

In Figure 2 the first rising part of the dashed-line curve represents expansion due to hydraulic pressure, though again the proof does not appear in this diagram. This part of the curve is mentioned, however, as an illustration of the fact that expansion due to hydraulic pressure is not always greatest at the start of the freezing process, though the start of expansion is always coincident with the start of freezing. The clearest indication of freezing in place is shown at the end of the constant-temperature period: when the temperature began to drop, expansion at a relatively high rate began abruptly.

In Figure 3, resumption of cooling at the end of the 6-hr. constant-temperature period gave evidence of freezing in place and expansion due to hydraulic pressure. Notice that the sample showed a momentary contraction,

⁷ An ice coating on a specimen is like the ice in the air voids within the specimen. It can receive water from the gel as its temperature falls below 0 C, and it can produce a tendency for the specimen to shrink.

probably thermal, followed by abrupt expansion, when cooling started.

In Figure 4 the topmost curve representing an air-free paste represents expansion primarily due to the generation of hydraulic pressure, as already mentioned. Various experiments show that if at any time during the production of such a curve the rate of cooling is suddenly increased, the rate of expansion is also suddenly increased. This response to a change in rate is characteristic of the hydraulic pressure mechanism; expansion due to diffusion to a capillary cavity responds in the opposite way.

Now we shall examine evidence of expansion due to diffusion and freezing of gel water:

The clearest example is that shown in Figure 3. These data were from a relatively dense specimen in which an appreciable amount of freezing did not begin until the temperature reached -19°C . After freezing started, the specimen was allowed to expand for 10 min., during which time cooling was continued. This expansion is characteristic of that due to hydraulic pressure. At the end of the 10-min. period, cooling was stopped and the temperature held constant for 6 hr., as described before. At the start of this constant-temperature period we have a limited amount of ice in capillary cavities in contact with saturated gel at a temperature of -21°C . This corresponds to time t_0 of Figure 7. The capillary ice is probably under pressure, but it is not under enough pressure to raise its free energy to that in the saturated gel. In this case the "air-void ice" is represented by whatever ice may be on the exterior surfaces of the specimen. This ice is too far away from the interior parts to have any discernible effect in a specimen as impermeable as this one. As the capillary ice grows, the pressure on it increases and it undergoes corresponding increases in free energy. Thus we see that the expansion during the 6-hr. constant-temperature period corresponds in Figure 7 to the rising part of the energy curve for capillary ice.

The process of diffusion is relatively slow. Hence, when the temperature is falling $\frac{1}{4}$ deg. or so per min., an experiment such as that shown in Figure 1 can be completed before an appreciable amount of diffusion takes place. Diffusion phenomena are apparent only when the temperature is kept constant

for a considerable length of time or when closely spaced air voids are present. They should be apparent, too, when the cooling is very slow.

The influence of air voids is shown by the bottom curve of Figure 2. As stated before, the small initial expansion is probably due to hydraulic pressure. As the temperature falls, more capillary cavities freeze and tend to cause expansion while, at the same time, the ice in capillaries already frozen tends to draw water from the gel. With the air voids only a few thousandths of an inch apart and with the ice they contain under no pressure, diffusion from the gel can occur at a relatively high rate. Very soon after freezing starts, the relationship between the capillary ice, air-void ice, and gel water must be as indicated for the time interval t_2 to t_3 of Figure 7 for most of the capillary cavities in the paste surrounding the air voids. Hence, the over-all effect is contraction.⁸

A study of responses to change in rate of cooling was rewarding. The process of diffusion must always lag behind the development of potential causing the diffusion, that is, it lags behind the drop in temperature. Consequently, when the cooling is stopped, the lag is manifested by a continued contraction. This is shown clearly in Figure 2, bottom curve. The rate of contraction decreases in the manner expected. At the end of the constant-temperature period, probably little potential between air-void ice and gel water remained. When cooling was resumed, the potential began to increase, probably linearly with the decrease in temperature. As would be expected, continued shrinkage developed only gradually, the rate of shrinkage increasing with the increase in potential. The gradual beginning of shrinkage on resumption of cooling is to be contrasted with the abrupt expansion that occurred for the paste without air voids (dashed-line curve). This difference in behavior is one of the clearest means of distinguishing between a volume change controlled by diffusion and one controlled by hydraulic pressure.

Under certain conditions the tendency to expand from the freezing of capillary cavities is about equal to the thermal contraction plus the tendency to contract due to diffusion

⁸ Valore (5) observed this previously. Specimens of air-entrained concrete or of plain concrete partially dried showed shrinkage at constant temperature after fast cooling.

to ice bodies. While such conditions exist, the specimen does not change in volume as the temperature falls. Also, if the rate of cooling is varied, the specimen does not respond in a manner distinctive of either mechanism. Among the many experimental curves obtained almost every possible variation has been observed.

In Figure 4 we see the effect of differences in void-spacing factor. The results are as would be expected from the two mechanisms discussed above. However, curves such as these alone do not tell whether hydraulic pressure or diffusion to cavities is the principal factor causing expansion, when expansion occurs. Auxiliary experiments were necessary to observe the effects of changes in cooling rate, as already discussed.

When considering the curves of Figure 4, we must remember that the volume changes shown are those that occur during the course of cooling. When the specimens are returned to their original temperature, some return to approximately their original dimensions, if given enough time; others show residual expansion. Specimens undergoing as much expansion as the two represented by the upper curves will show a considerable residual expansion. For a specimen to show no residual expansion the spacing factor must be small enough to produce over-all contraction throughout practically all the freezing-temperature range.

We noted that with various families of curves, such as that shown in Figure 4, reductions in the spacing below 0.01 in. produced relatively little additional shrinkage. It seems, therefore, that a spacing factor of 0.01 in. is about that required to produce the practical maximum effect of entrained air. This is also about the optimum spacing factor found from freezing-and-thawing tests on air-entrained concrete.

It is of some interest to speculate as to why to protect the paste we must produce a spacing factor that gives a substantial amount of contraction. Why is it that a factor that just prevents expansion is not enough? We have already seen reasons to believe that although freezing may produce no over-all expansion, a tendency to expand may nevertheless be present in some regions. The regions tending to contract offset the regions tending to expand. On repeated freezings the tendency

to expand, opposed by the tendency to contract, may gradually produce mechanical damage. The paste evidently can be fully protected only when the regions tending to expand approach the vanishing point. From these considerations, admittedly speculative, test results on neat cement pastes, like those shown in Figure 4, seem to be in excellent agreement with test results on air-entrained concrete.

GENERAL REMARKS

The two earlier papers dealing with the theory of frost resistance, previously referred to, gave the development of a hypothesis. As such, they aimed to be a logical development of a stated premise. They were not based on experimental data and consequently could be no more valid than the premise on which they were based. In contrast, the present paper is based on experimental data. The data are those obtained not only from freezing experiments on hardened cement paste but also from studies pertaining to the submicroscopic structure of hardened paste and the thermodynamics of the physical interactions between the solids and the evaporable water in the paste. Therefore, the theory presented here is more than a hypothesis; it rests on experimental results and known physical principles. Moreover, it is able to account for the phenomena observed.

It was gratifying to find that the original hydraulic-pressure hypothesis was correct with respect to its major premise and that the principal deductions from that premise are borne out by the experimental results. To make the theory complete, it was necessary to develop further the observation made in 1945 to the effect that diffusion could play a part. Experiments showed that it played a prominent role and could not be regarded simply as an auxiliary phenomenon.

In this paper we devoted much space to developing the theory of diffusion and freezing of gel water and relatively little to the freezing of capillary water and the generation of hydraulic pressure. As already indicated, this does not mean that we hold the diffusion theory to be the more important or to displace the hydraulic-pressure theory. Both are indispensable parts of a general theory, and neither part alone can account for all the observed phenomena. We did not need to

devote much space here to the theory of hydraulic pressure, because that was treated rather exhaustively in the earlier papers.

Although the experimental evidence of hydraulic pressure is easily observed, the basis for the diffusion part of the theory may not be as clear, because the experimental evidence is less direct. The data reported in Reference 3b pertaining to the energy of binding of evaporable water in hardened paste is the starting point. Figures 4 to 9, p. 571 of the paper referred to, give the results of calculations of the change in entropy that water undergoes when it enters a dry paste. The data show that the water first to enter dry paste undergoes more entropy change than the entropy change of freezing, but they show also that as the paste nears saturation the increments of water undergo a negligible change in entropy. It is thus experimentally established that the entropy of the water that might be extracted from the gel by freezing at a given temperature within the range of temperatures of interest here is greater than the entropy of ice at the same temperature.

One of the fundamental thermodynamic relationships is

$$\left(\frac{\partial F}{\partial T}\right)_P = -S$$

which says that the change in free energy of a given component produced by a change in temperature with pressure held constant is equal to its entropy but opposite in sign to the change in temperature. Therefore, if the entropy of the ice is smaller than the entropy of water to be extracted from the gel, a decrease in temperature will produce a greater change in the free energy of the ice than the change in free energy of the gel water. Hence, if the starting point is one of equilibrium (where the two free energies are equal), lowering the temperature will destroy the equilibrium and create a free-energy potential.

The energy data already cited show that such a potential is produced between the unfrozen gel water and the capillary ice when the temperature is lowered. This demonstrates that a change in the system will take place in such a way as to restore equilibrium. In the present case, the theoretically possible change would produce either a contraction or an expansion, according to circumstances, as discussed in this paper. The expected changes were observed to take place.

Thus, though the experimental evidence for diffusion is more complicated than that for hydraulic pressure, it is just as conclusive.

The beginnings of the diffusion theory developed here were mentioned in the 1945 paper in connection with the hypothesis advanced by Collins (6), which was, in turn, based upon the "segregation" theory of Taber (4). It was pointed out that a transfer of gel water to capillary ice is thermodynamically possible and that it should result in expansion. However, at that time it did not seem possible to account for the protective effect of air by such a mechanism. Since air voids did control frost action and since the method of control of hydraulic pressure by air voids was clear, it seemed necessary to assume that hydraulic pressure was the principal cause of damage. Confronted with data such as given in this paper, we reconsidered the diffusion theory and found that it, too, could account for the protective effect of air and that the explanation was compatible with that given for the control of hydraulic pressure.

The explanation of pressure generation through the adsorbed film between the ice body and the solid is essentially like that advanced by Taber in 1930 for the growth of ice lenses in soils (4). However, the "lenses" in paste are microscopic bodies, and the forces set up are of a nature peculiar to cement paste.

Both mechanisms of frost action on cement paste are predicated on the peculiarities of the paste. Hydraulic pressure would be no factor at all if it were not for the particular combinations of permeability, strength, and porosity found in paste, together with typical distances between air voids in non-air-entrained concrete. Also, diffusion phenomena of the kind described are possible because cement pastes are capable of holding some freezable water that cannot be frozen in place, along with some that can be frozen in place.

Although we did not bring it out explicitly in the preceding discussions, the reader may have seen that the water movements discussed are reversible, or mostly so. When water is extracted from the paste to the air voids during a period of freezing, it will return from the voids to the paste during a period of thawing. Thus, water that was expelled or that diffused to the air voids during freezing will be extracted from the air voids during thawing. This accounts for the persistence of the pro-

tective effect of entrained air. When air voids are absent, water extracted from the gel to the capillary cavities will return to the gel during thawing.

A question remains as to which of the two mechanisms is principally responsible for expansion when expansion occurs. It is clear that the answer will depend mainly upon the rate at which the sample is cooled and the length of time it remains at a subfreezing temperature and the permeability of the paste. At the rates of cooling normally used in laboratory freezing-and-thawing tests, most of the expansion of average non-air-entrained concrete that takes place while the cooling is going on at customary rates may be due to hydraulic pressure. If, however, the specimen is held in the freezer for a time after the minimum temperature is reached, continued expansion may take place through the other mechanism. Concrete in the field cools slowly, and low temperatures may be maintained for many hours or days. If the paste is not protected with entrained air, it is liable to be damaged by both mechanisms: first, by hydraulic pressure, and then by growth of the ice bodies. The lower the temperature, the more severe the final effect.

With air-entrained concrete, the role played by hydraulic pressure will depend upon the degree to which the paste is protected by the air voids. If the air voids are close together and if the rate of cooling is not excessive, hydraulic pressure is exceedingly transitory, and diffusion to the air voids dominates the process almost immediately. If the air voids are too far apart for adequate protection of the paste, hydraulic pressure may play a more prominent role. The dominant influence of the spacing factor cannot be overemphasized.

SUMMARY

Water freezing in capillary cavities produces hydraulic pressure and consequent dilation. At any temperature below the temperature at which the ice in a cavity was formed, gel water can diffuse to that cavity and cause the ice body to grow, producing expansion. Both processes can occur simultaneously in different parts of the paste. Since diffusion is slow, expansion is due mainly to hydraulic pressure when freezing is rapid, as in laboratory tests.

When air voids are present, they limit the hydraulic pressure according to the thickness

of the layers of paste between them. Also, the ice they contain draws water from the paste, causing the paste to shrink. Since the ice in the capillary cavities generally has a higher free energy than that in the air voids, the ice in the air void may eventually draw the excess from both the gel and the frozen cavities, producing over-all contraction. Expansion due to growth of ice in the capillary cavities is prevented if the air voids are close enough together, as is also expansion due to hydraulic pressure.

During thawing, the water that was extracted from the paste by the ice in the air voids diffuses back. In a paste free of air voids, the ice in the capillary cavities melts progressively, and the water drawn from the gel during freezing is returned to the gel.

Expansion or contraction during cooling at constant rate occurs in the manner expected from the theory. Also, the effects of changes in rate of cooling are in accord with the theory.

The function of the air voids is to limit hydraulic pressure and to limit the time during which capillary ice can increase by diffusion of gel water. The spacing factor controls the effectiveness of the voids for either mechanism.

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