COMMONWEALTH OF KENTUCKY

DEPARTMENT OF HIGHWAYS

FRANKFORT

July 25, 1958

ADDRESS REPLY TO
DEPARTMENT OF HIGHWAYS
MATERIALS RESEARCH LABORATORY
132 GRAHAM AVENUE
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MEMO TO: D. V. Terrell
Director of Research

The attached report, "Differential Thermal Analysis of the Freeze-Thaw Mechanisms in Concrete" was presented before the Research Committee on March 11, 1958. The report represents a more or less basic analysis of the freeze-thaw concept but may well have considerable practical application in future durability testing.

Some of the previously unexplained behavior of air-entrained concrete is indeed logical now that the pressure-temperature relationships have been evaluated on a strength and moisture content basis.

Respectfully submitted,

W. B. Drake
Associate Director of Research

WBD:dl
Enc.
cc: Research Committee Members
J. C. Cobb (3)

Commonwealth of Kentucky
Department of Highways

DIFFERENTIAL THERMAL ANALYSIS OF THE FREEZE-THAW MECHANISMS IN CONCRETE

by

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ABSTRACT

The freezing of water in concrete may create highly disruptive internal forces, depending upon the degree of saturation of the voids and the extent of the resulting dilations. Heretofore, it has not been possible to measure the internal pressures accompanying freezing; and it is this aspect of the automatic freeze-thaw testing of concrete with which the present study was concerned. By the use of thermocouples, imbedded in concrete and referenced to an ice-water bath, it was possible to plot, on an automatic multivolt potentiometer recorder, an isothermal phase change for the absorbed water, and to demonstrate a depression of the freezing point of the water with increasing confining pressures. It was also possible, at least in a general way, to relate the progress of damage in the concrete to increased absorption and freezing point depression.

INTRODUCTION

The effects of freezing water in concrete may range from practically none to serious damage or rupture. If damage occurs, it can be attributed to overstressing of the mortar structure or of the aggregate by expansion of the water in converting to ice. This expansion may have no effect so long as the structure is not dilated beyond its natural strain limit. However, if water freezes in a completely filled and sealed container, the vessel must yield or dilate as much as 9 percent by volume or else it will rupture. Likewise, it water completely fills the voids in concrete and is frozen therein, the concrete must theoretically dilate by an amount approximately equal to its moisture content, expressed as a fractional part of its bulk volume, times 9 percent. Thus 10 percent moisture by volume would induce an increase of 0.9 percent in the bulk volume of concrete. This amount of expansion far exceeds the natural strain limit of ordinary concrete, and rupture would be inevitable.

Considering further that the freezing of water is attended by an increase of 9 percent in volume (density of ice = .917, density of water at 0°C = .999841), and if the pores and voids were filled to 91.7 percent of capacity, the volume of ice produced would just equal the volume of voids and no dilation of the concrete would result. Therefore, 91.7 percent saturation of all voids is often described as "critical saturation." The term simply alludes to the degree of saturation beyond which freezing of the water overfills the voids and creates internal expansive forces. While the theoretical meaning of critical saturation is quite clear, its practical meaning, as applied to concrete, is more in the sense of a statistical average and has two possible interpretations: 91.7 percent of the void volume being completely filled, or all voids being filled to 91.7 percent of capacity. The first possibility mentioned would be extremely damaging; whereas, if the second accurately described the condition of the concrete, there could be no damage at all from freezing. This obvious disparity in the interpretations is now unreconcilable by any means of measurement, but it is logical to assume that damage may occur at moisture contents considerably below 91.7 percent saturation and must occur at or above this value.

Concretes, of course, differ greatly in their voids structure, with a particularly great disparity between air entrained and non-air entrained concrete. Voids are created by the entrainment and entrapment of air, by the evaporation of mix-water, and by differences in the volume of reactants and products in the hydration processes. Some types of voids are more easily saturated than others. Those readily saturated affect durability unfavorably while those which are more nearly impermeable are highly favorable to durability. Laboratory experience indicates that damage by freeze-thaw is related but not necessarily proportional to increases in water absorption. Drying of a specimen before beginning freeze-thaw greatly increases the number of cycles required to produce failure. The use of dry aggregate, as contrasted against soaked aggregate, favorably affects durability. Significantly enough, all such effects are somehow related to water absorption and saturation, yet none of them is particularly revealing as to the critical moisture content, degree of saturation or the pressure which actually produces the damage.

In conducting freeze-thaw tests on concrete, it is customary and desirable to monitor weight, natural frequency, and temperature. Heretofore, however, temperature records have simply provided assurance that the concrete has been alternately frozen to 0°F and thawed to 40°F within the desired time intervals. These temperature records are usually obtained by embedding thermocouples in companion specimens of the concrete under test. Automatic recording instruments, of course, have proved to be desirable from the standpoint of convenience. Using such equipment in a study on the freeze-thaw durability of concrete made with a highly porous aggregate, Sawyer, Brown, and Strunk* reported the development of a rather wide isothermal step in the time-temperature curves which, except for a slight depression of the freezing point, corresponded to the normal phase transition from water to ice. This step had been previously observed only as a small tick in the time-temperature records obtained from normal concretes. While these effects had been highly magnified by the large quantity of absorbed water in the porous concrete, it became obvious that they also portrayed certain fundamental physical principles involved in the disruptive action of freeze-thaw on ordinary concrete. The work reported by Sawyer, et al, was accomplished by freezing in air and thawing in water. Thus the isothermal steps were truly manifestations of the latent heat of fusion of the water absorbed in the concrete, and the freezing point depressions were truly manifestations of pressure. These findings suggested

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* Sawyer, D. H.; Brown, C. M.; and Strunk, L. H.; "Studies on the Suitability of Expanded Shale Aggregate for Use in Cement Concrete," Bulletin No. 38, Engineering Experiment Station, University of Kentucky, 1955.

that time-temperature records, if sufficiently accurate, could provide heretofore unavailable information concerning the amount of freezable water in concrete undergoing freeze-and-thaw, the progress of saturation, permeability, the internal pressures induced by freezing at various levels of saturation, and the progress of damage to the concrete. The purpose of the present study, therefore, was to examine these possibilities further and to offer a thoroughly critical and informative analysis of related theories, the extent of their practical application, and the limitations imposed by instrumentations.

BASIS OF THERMAL ANALYSIS

Figure 1 illustrates a typical time-temperature record obtained from an oven-dried specimen of concrete undergoing one cycle of freeze-thaw in automatic freeze-thaw equipment. Since the freezing was done in air, the specimen temperature is seen to lag behind the air temperature, and there are no sharp breaks or steps in the cooling curve. Upon flooding the freezing chamber with water at 40 °F, the specimen temperature rises rapidly, but here again there are no sharp steps or breaks in the curve. Figure 1, therefore, represents a normal freeze-thaw thermograph for dry concrete in the particular equipment used.

In contrast, Figure 2 illustrates a typical thermograph obtained from highly porous, highly absorptive, highly saturated concrete undergoing a single cycle of freeze-thaw. The steps in the cooling and thawing curves occur at approximately the same temperature, near but not exactly at the normal freezing temperature of water (32 °F). The portions of the curves above and below this step have characteristically different curvatures, and the steps are not merely off-sets in otherwise normal cooling and heating curves. However, by graphically projecting these curves through and beyond the steps, according to their characteristic curvatures, the time-durations of the steps are more clearly outlined. The slopes of either or both curves as they approach the step may be described as $\Delta T/\Delta t$. Ideally, ΔT times specific heat times weight/ Δt would give the rate at which heat was being removed from the

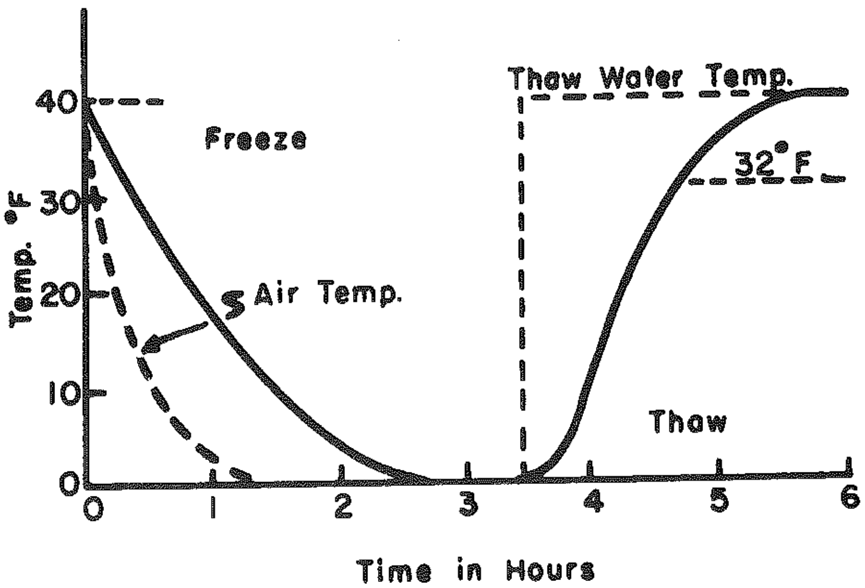

Figure 1: Typical Time-Temperature Record Obtained from Oven-Dried Concrete Undergoing a Single Cycle of Freeze-Thaw.

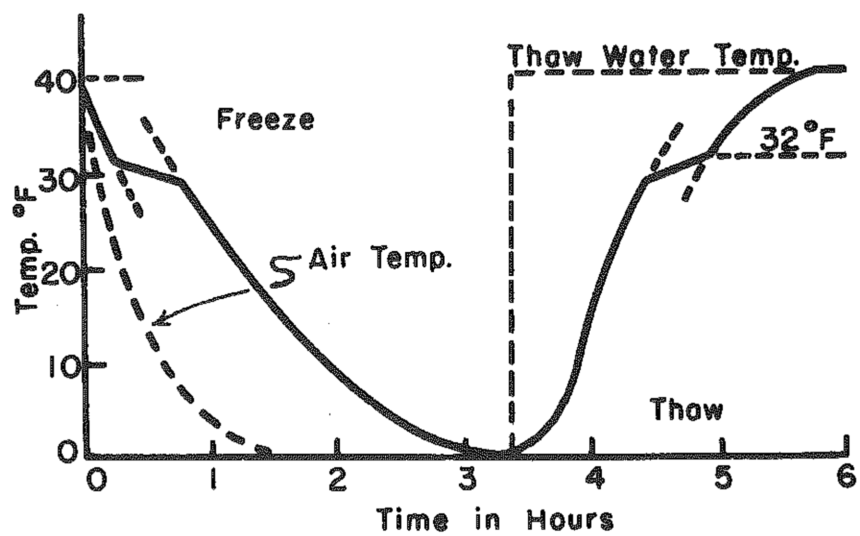

Figure 2: Typical Time-Temperature Record Obtained from Highly Absorptive, Highly Saturated Concrete Undergoing a Single Cycle of Freeze-Thaw.

specimen. Thus, the time-lapse times the average rate of heat removal should correspond approximately with an isothermal change in heat content (ΔH) accompanying the freezing of water in the specimen; and

$$\text{Wt. (water)} = \Delta H/\text{latent heat of fusion (water)}.$$

From Figure 2, it is also apparent that the step itself is sloping slightly downward from 32°F, signifying, of course, that the water began freezing under a normal pressure of 1 atm. (14.7 psi) but finished freezing at 28°F, which corresponds to the freezing point of water under a pressure of approximately 4500 psi. Since there is no apparent depression of the initial freezing point, the effects of solutes and surface forces on the freezing point must be rather small in comparison to the effects of pressure. The depression due to dissolved $Ca(0H)_2$, which is the most abundant solute in hardened concrete, may be estimated roughly to be less than 0.2°F, assuming a solubility of 1.85 gm. per liter of water at 0°C, and assuming 90 percent dissociation.

The possible effects of alkali available from the cement may be similarly estimated by assuming 0.6% alkali by weight of cement and the maximum free water to be approximately equal to the excess mix-water. This quantity of alkali, if available as solute, would depress the initial freezing point a maximum of 2.5°F. Since no such initial depressions are apparent in Figure 2, the concentration of alkali must be rather small, at least while the greater portion of the water is freezing. Since freezing began at or very near 32°F, there were no apparent indications of supercooling.

Verification of the pressures corresponding to freezing-point depressions when attributable entirely to pressure, is provided in Dorsey's Properties of Ordinary Water Substance* and in the International Critical Tables. Both of these sources are based on the work of P. W. Bridgman, published in 1912. Bridgman's complete phase diagram for water is shown in Figure 3. The units of pressure have been changed from atms. to psi. Only a portion of the shaded area is of particular importance to this problem, because of the inherent limitations in the strengths of ordinary concrete. Figure 4 is simply an enlargement of the shaded area in Figure 3, and is included for more precise interpolations.

The appplication of the principles outlined to the evaluation of concrete depends considerably, of course, upon the precision and accuracy of the time-temperature records and by some mathematical problems in heat transfer. While numerous variations in instrumentation and methods of analysis are foreseeable, the primary objective, at present, is to offer a preliminary insight into the theoretical aspects of thermal analysis and to demonstrate the type of information to be derived therefrom.

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* Dorsey, N. E.; Properties of Ordinary Water-Substance, New York: Reinhold, 1940.

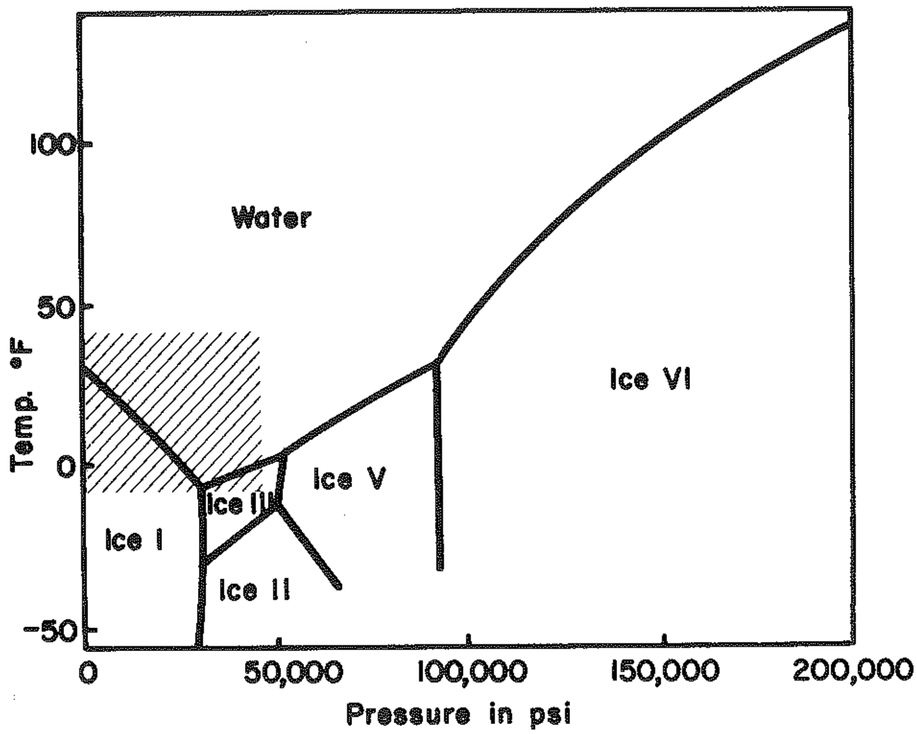

Figure 3: Phase Diagram for Water (from Bridgman).

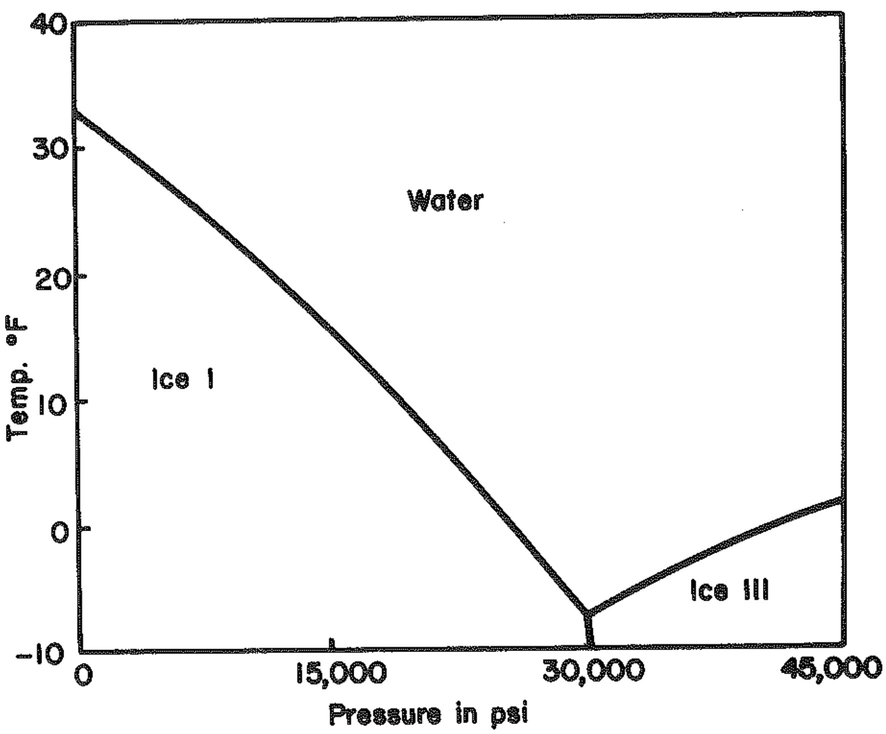

Figure 4: Enlargement of Shaded Area Shown in Figure 3.

PRELIMINARY EXPERIMENTS

In order to further demonstrate the basic principles involved in the application of thermal analysis to concrete, preliminary experiments were made on rather idealized models. First, a quart volume of water, contained in an open vessel, was frozen in air and a time-temperature record was made from a thermocouple positioned near the center of volume. The resulting thermograph, Figure 5, gave a broad step at 32°F as expected, without any noticeable depression of freezing point.

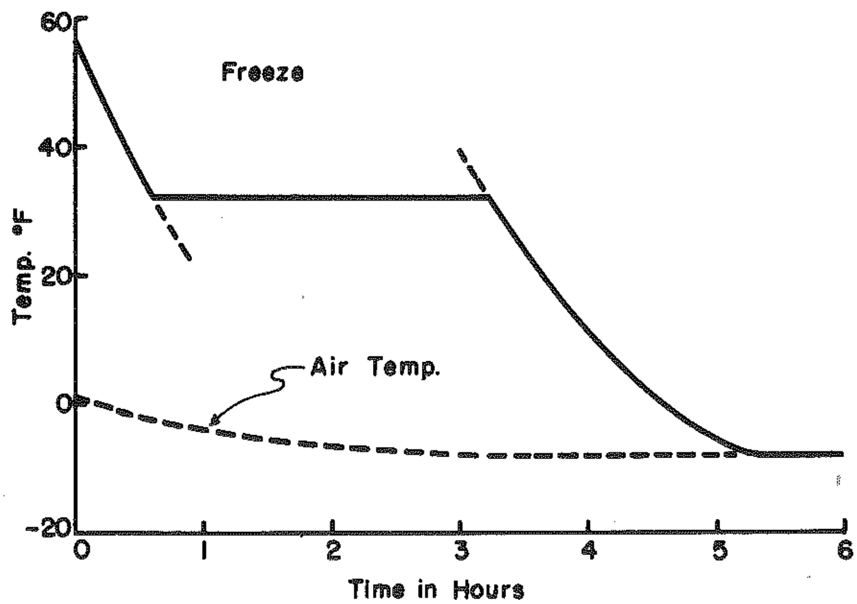

Figure 5: Thermograph Obtained from Freezing of Water in Open Vessel.

Since the water had been more-or-less unrestrained in the open vessel, a closed vessel or "steel bomb" was devised from a 3"-dia. pipe nipple and two cast iron caps, as shown in Figure 6. A valve and thermocouple well were tapped into the nipple. The bomb was completely filled with water and frozen in air as before,

Figure 6: Steel Bomb, Showing Valve, Thermocouple, and Ruptured End-Cap.

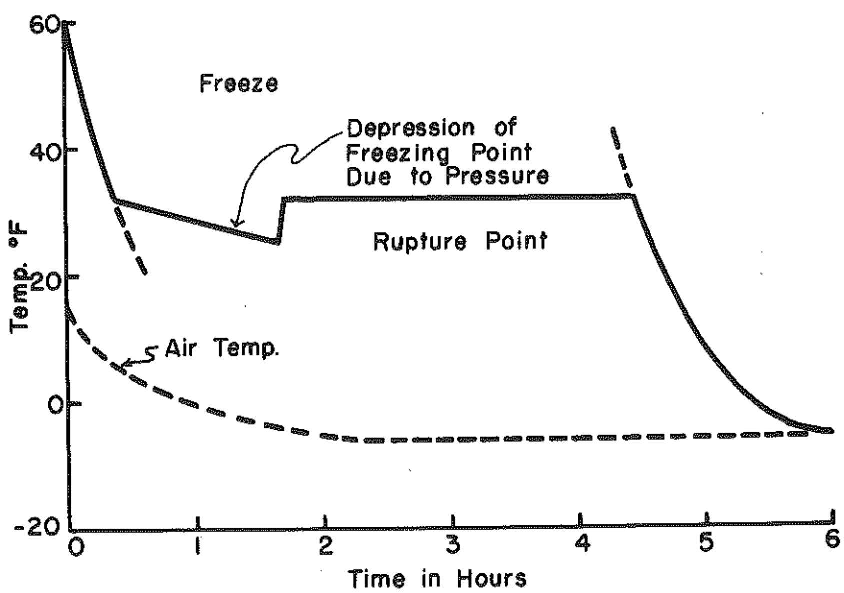

Figure 7: Thermograph Obtained from Freezing Steel Bomb Completely Filled with Water.

and the resulting thermograph is shown in Figure 7. It is apparent that freezing began at 32°F, that the freezing point gradually decreased to 25°F, and then suddenly reverted back to 32°F. According to the phase diagram, Figure 4, a pressure of about 7200 psi. would be required to depress the freezing point of water to 25°F. This pressure is in close agreement with the estimated ultimate strength of the cast iron caps, 7000 psi. Figure 6 shows that explosive rupture of one of the caps actually occurred.

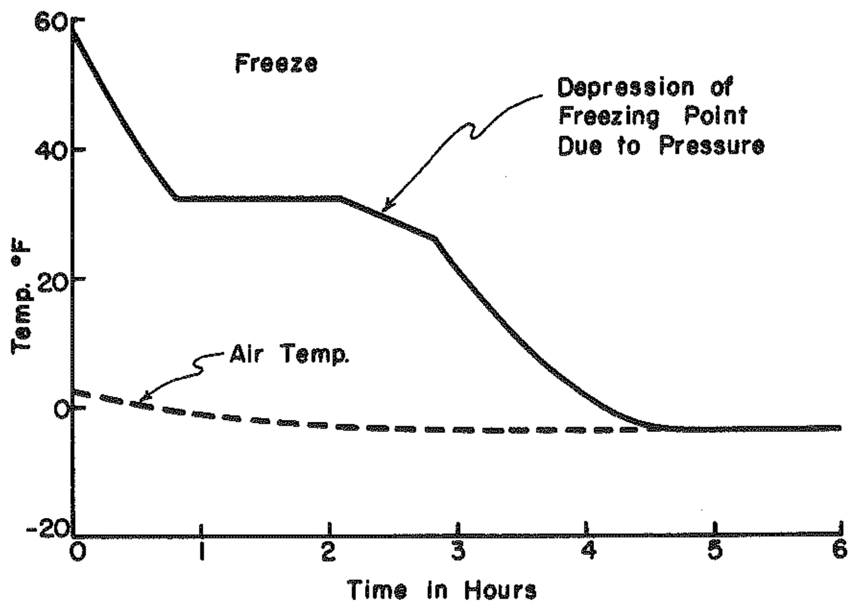

Figure 8: Thermograph Obtained from Freezing Steel Bomb Filled with Water to 96 Percent of its Capacity.

Continuing with these experiments, the ruptured cap was replaced and the bomb filled with water to 96 percent of its capacity. Upon freezing, as before, the thermograph shown as Figure 8 was obtained. Here again the water began freezing at 32°F but there was no immediate depression of the freezing point, and consequently no immediate build-up of pressure. In this case, the development of pressure was delayed until after most of the water had frozen.

Here, there was only 6°F depression of the final freezing point, equivalent to 6200 psi; and, while there was no explosive rupture as shown in Figure 6, the caps yielded considerably under this pressure.

FURTHER EXPERIMENTS WITH LIGHTWEIGHT AND NORMALLY DENSE CONCRETES

While it has already been demonstrated that freezing-point steps can be recorded rather easily when using models or even highly absorptive concrete, it was necessary to demonstrate comparable application of these basic principles to normally dense concretes having much lower absorptive capacity for water. Since previous records from normal concretes had shown only a slight tick at this point, the apparent solution to the problem was to use a more sensitive recording instrument or else to modify the more-or-less standard recorder already in use. The latter seemed more feasible economically.

Temperature Records

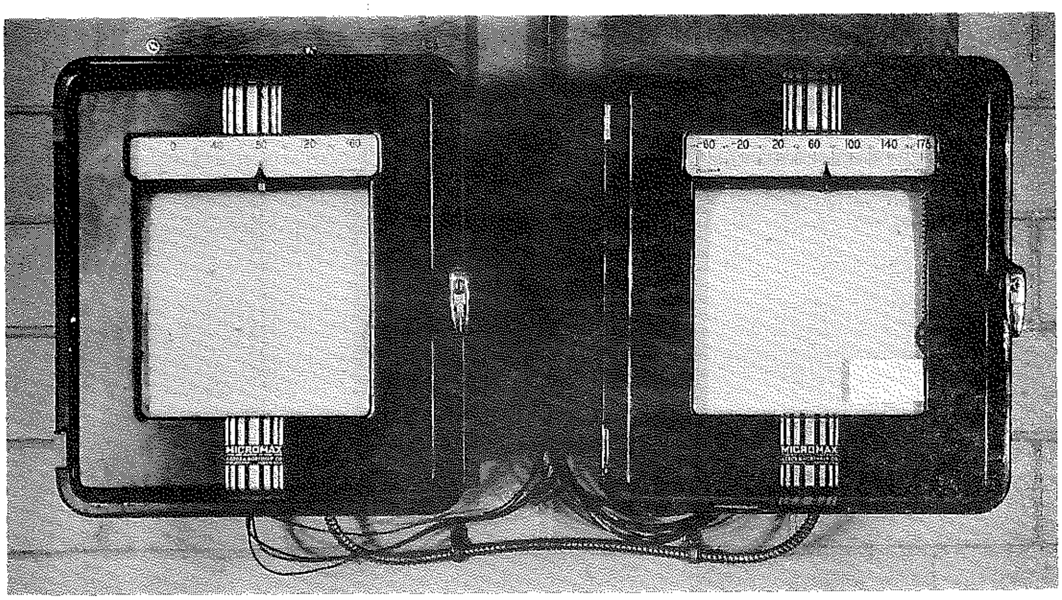

Figure 9: Automatic Temperature Recorder.

The temperature recorder was an 8-point, potentiometer-type instrument, a Leeds and Northrup, Model S, Micromax, using iron and constantan thermocouples and having a range of -75° to 175°F, shown above on the right-hand side of Figure 9. The ideal full-scale range, of course, for this particular application would be only slightly greater than 0° to 40°F. In order to obtain a commensurate expansion of scale, two thermocouples were cast in the concrete specimens instead of the usual one. These were connected alternately in series with two other thermocouples in a constant temperature ice-water bath. Since the recorder itself had a compensating reference junction at 77°F, the relationship between the actual temperature of the specimen and the recorded temperature was given by t = 141° - 2t, where t was the indicated temperature and T the actual temperature of the specimen. Thus, when the concrete was at 0°F, the registered temperature was 141°F. When the actual temperature was 40°F, the instrument registered 61°F. This, in effect, expanded the scale by a factor of 2. Had one additional series of junctions been provided, the scale could have been expanded by a factor of 3.

All eight points of the recorder were used in common in order to register the temperature at two-minute intervals. The chart speed was 2-3/4 inches per hour; consequently all the time-temperature curves included herein were re-plotted to a more appropriate scale from the actual record.

Automatic Freeze-Thaw Equipment

A schematic drawing of the freeze-thaw equipment is provided in Figure 10. Operationally, it is fully automatic and consistent with ASTM C-291-57T.

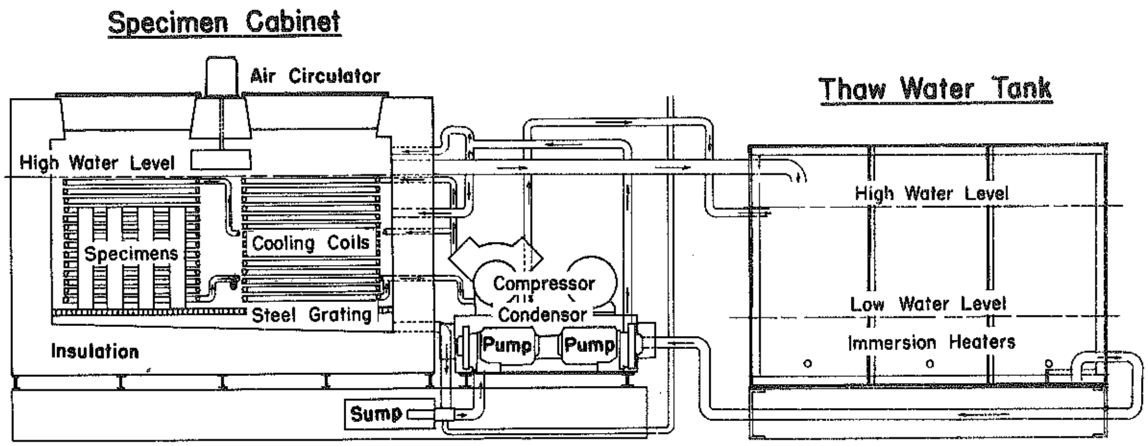

Figure 10: Schematic Diagram of Automatic Freeze-Thaw Equipment.

Description of Concrete Specimens

Two types of concrete, both having a cement factor of 1.5, one made with dense limestone coarse aggregate and natural silica sand, the other made with expanded shale coarse aggregate and natural silica sand, were cast in 6-inch cubes with thermocouples imbedded near their centers. The essential difference in the two concretes lay in the fact that the expanded shale aggregate was capable of absorbing as much as 10 percent water by weight* whereas the absorption of the limestone was in the order of 0.7 percent. The air content of the dense concrete ranged between 1.5 and 2.5 percent. Two cubes were cast from each of the two types of concrete and cured in a 100-percent humidity room for 14 days at 72°F. After curing normally for 14 days, one cube of lightweight concrete and both of the dense concrete were oven-dried to constant weight. All four were then subjected to 30 cycles of freeze-thaw.

* Sawyer, et al: op. cit.

While casting the normal concrete cubes, a portion of the batch was placed in a metal container and thermocouples imbedded therein. Immediately afterwards it was exposed to a standard cycle of freeze-thaw.

Analyses of Time-Temperature Records

The resulting thermograph from the freshly mixed concrete is shown in Figure 11 and indicates an isothermal freezing step at 32°F. Since there was no depression of the freezing point there was no build-up of pressure attending the freezing.

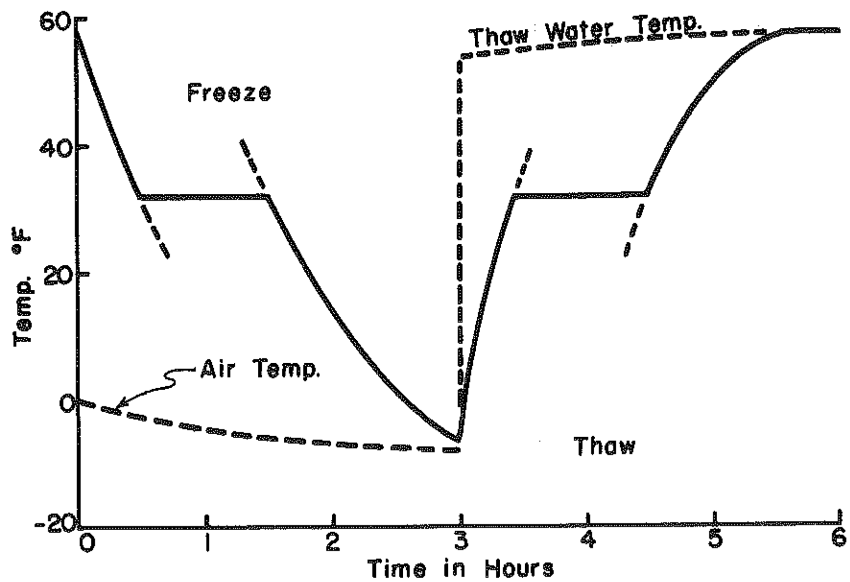

Figure 11: Thermograph Obtained from Freshly Mixed Concrete Subjected to Freeze-Thaw.

The lightweight concrete cube, oven dried, gave no freezing-point step during the first cycle, Figure 12; but during the second cycle a rather broad step developed without any noticeable depression of the final freezing point. During the third cycle the step broadened further, and there was an obvious depression of the freezing point. Both the width of the step and the depression increased until about

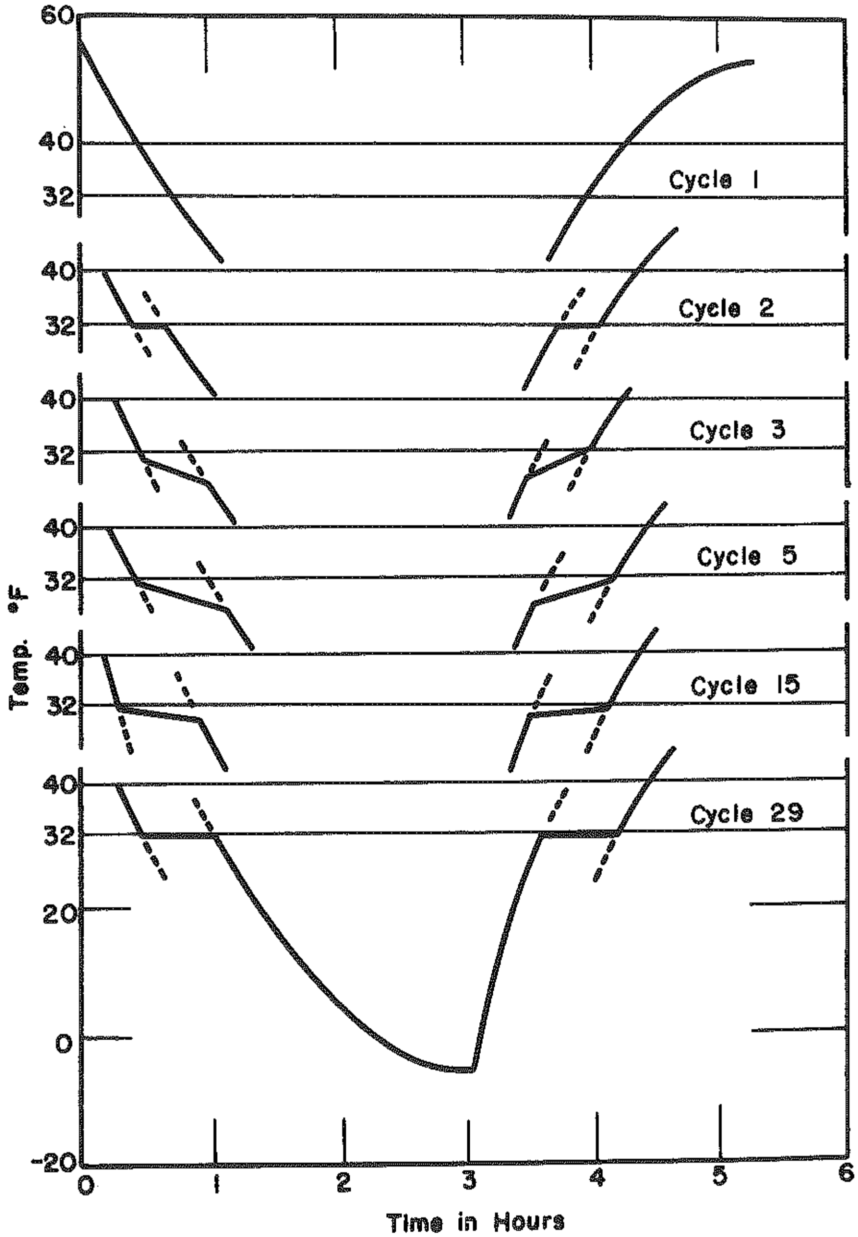

Figure 12: Time-Temperature Records from Lightweight Concrete Cube, Moist-Cured 14 Days, Oven Dried, Frozen in Air, Thawed in Water.

the tenth cycle; beyond this the depression began to diminish and after the 29th cycle was no longer detectable. At this point, the sample was almost a complete ruin.

According to Figure 15, Curve A, most of the increase in weight due to water absorption occurred during the first 5 cycles and there were only slight gains in weight thereafter. According to some elementary calculations the maximum gain in weight corresponds to approximately 30 percent of the bulk volume of the concrete specimen, whereas the total percentage of voids in the concrete was calculated to be about 36 percent. The maximum freezing-point depression was about 4°F, which corresponds to a pressure of 4500 psi.

The companion specimen of expanded shale concrete which was also cured in a moist atmosphere for 14 days but not oven-dried, gave both a wide step and a freezing-point depression during the first cycle, Figure 13. After the first few cycles, the performance of the specimen closely paralleled that of its oven-dried companion. Curve B, Figure 15, shows only a slight increase in weight due to absorption.

The normally dense concrete specimens, oven-dry, likewise failed to show a freezing-point step during the first cycle but developed one during the second. A significant depression of the final freezing point developed during the third cycle and persisted thereafter through the 30th. While the specimens gave no outward indications of damage at the end of 30 cycles, it is apparent from Figure 14 that the pressures of freezing were becoming increasingly severe. Since both specimens exhibited these same general tendencies, only one series

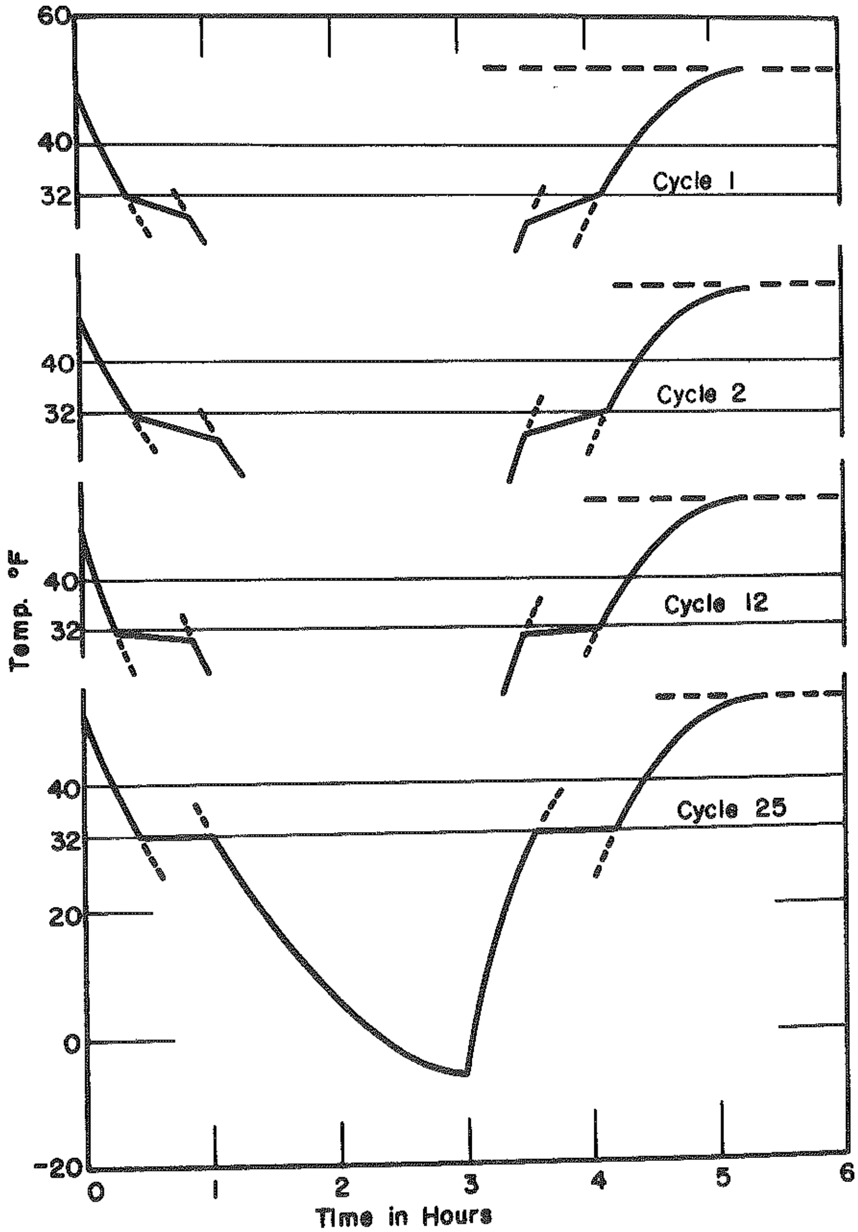

Figure 13: Time-Temperature Records from Lightweight Concrete Cube, Moist-Cured 14 Days, Frozen in Air, Thawed in Water, No Intermediate Drying.

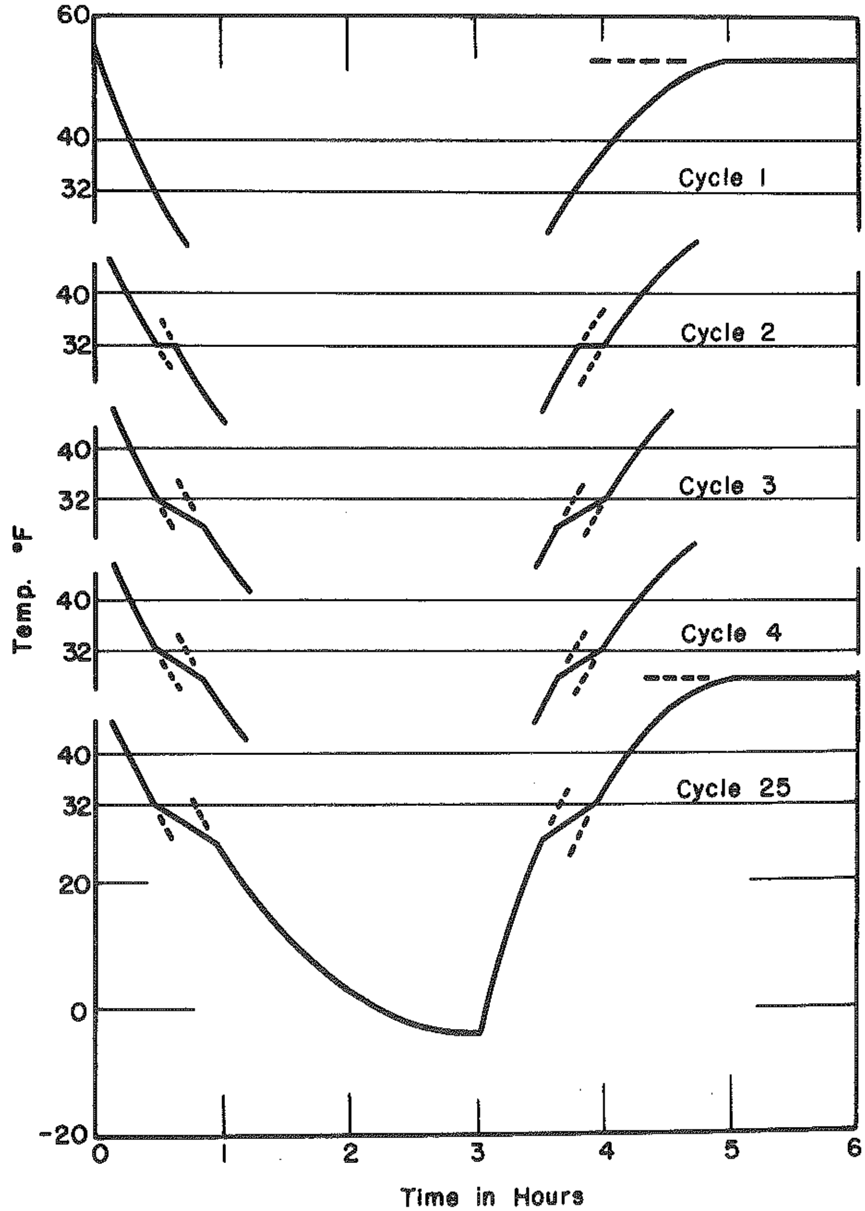

Figure 14: Time-Temperature Records from Normally Dense Concrete Cube, Moist-Cured 14 days, Oven-Dried, Frozen in Air, Thawed in Water.

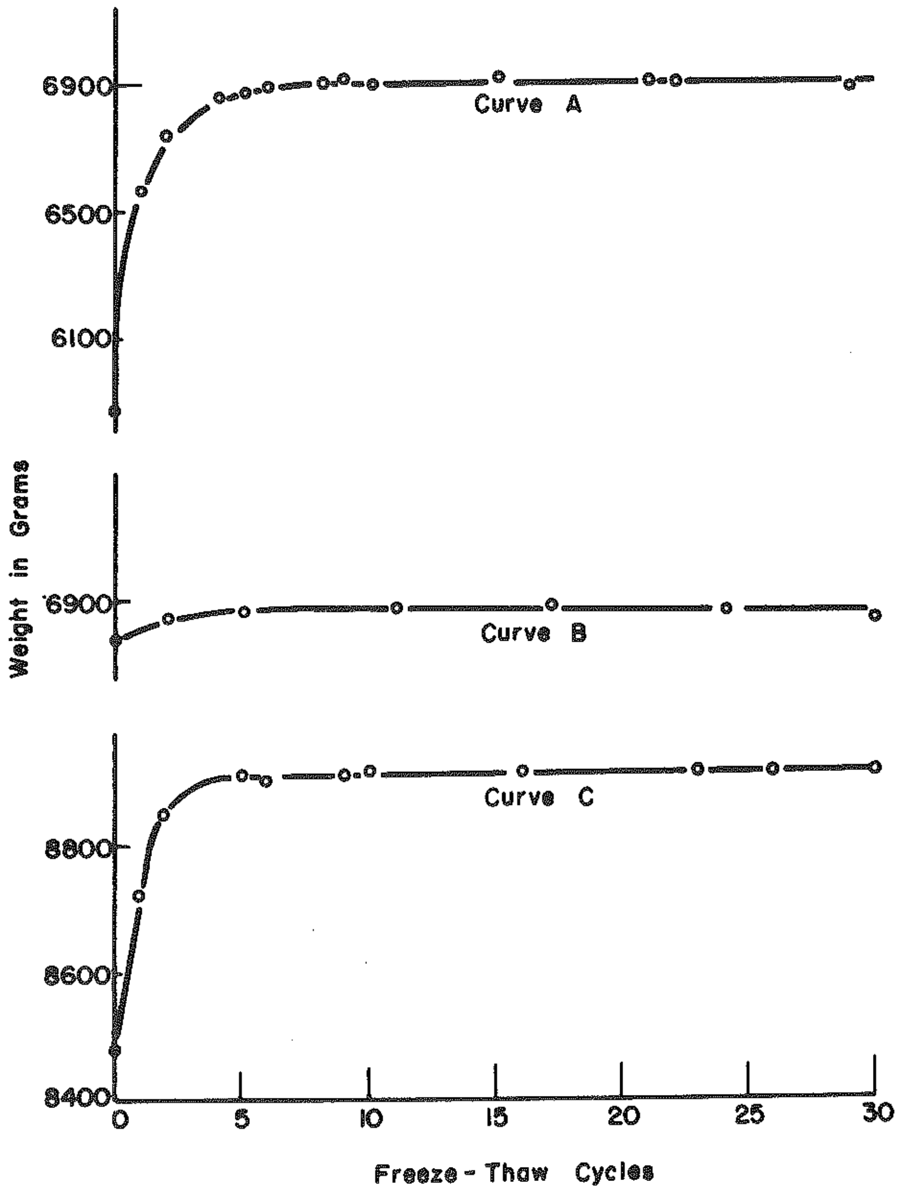

Figure 15: Curves Showing Gains in Weight Due to Absorption of Water During Freeze-Thaw. Curve A: Oven-Dried Lightweight Concrete; Curve B: Undried Lightweight Concrete; Curve C: Oven-Dried Normally Dense Concrete.

of thermographs is included. A corresponding absorption curve is given in Figure 15, Curve C. Here, as in the case of the oven-dry expanded shale concrete, most of the absorption occurred within the first few cycles.

CONCLUSIONS

The time-temperature histories recorded in these experiments, while perhaps not the ultimate in precision and accuracy, reveal valuable information regarding basic freeze-thaw mechanisms in concrete. The work clearly demonstrates a direct application of the elementary principles of thermal analysis. The specific conclusions drawn from the work are as follows:

1. Differential, multiple-junction thermocouples provide an effective method of increasing the temperature sensitivity of potentiometer-type recorders. Since each depression of the freezing point by 1°F corresponds to approximately 1000 psi, and since the maximum depression expected to develop in concrete is about 6°F, a sensitivity in the order of 10°F per inch of scale is necessary to define clearly the development of the freezing-point step. An ice-water bath provides a convenient reference temperature for calibration of the instrument.

2. In every case where a freezing-point step was registered, freezing began at or very near 32°F. Consequently, there was no noticeable indication of supercooling.

3. Since there were no indications, within the accuracy of the records obtained, of any depressions in initial freezing points, the effects of dissolved solutes and surface forces on the freezing point of the absorbed water are very slight in comparison to to the effect of pressure.

4. Since both of the oven-dried concretes registered a freezing-point step in the second cycle and showed no depression of the final freezing point, the water in these concretes at this stage froze in much the same manner as pure, unrestrained water. Since both of these concretes later developed significant depressions of the final freezing points and since the two concrete specimens carried to failure showed a complete subsidence of any depression in the final freezing point, the depressions that occurred during the intermediate cycles are attributable entirely to pressure.

5. The maximum pressures produced by the freezing of absorbed water are in the same order of magnitude as the compressive strength of the concrete.

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