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Interim Report

CORRELATION BETWEEN PORE SIZE DISTRIBUTION AND FREEZE THAW DURABILITY OF COARSE AGGREGATE IN CONCRETE

TO: Harold L. Michael, Director
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FROM: W. L. Dolch, Research Associate
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The attached Report titled "Correlation Between Pore Size Distribution and Freeze Thaw Durability of Coarse Aggregate in Concrete" is submitted as an Interim Report on the HPR Part II Study titled "Improvement of Non-Durable Aggregates in PC Concrete" and the final report on Phase I of this study. The Report has been authored by Makoto Kaneuji, Graduate Instructor in Research on our staff under the direction of Professors W. L. Dolch and D. N. Winslow.

The major findings of the first phase of this research and reported herein are that pore size distribution of aggregates exhibits a good correlation with freezing and thawing durability of concrete and that a correlation equation including pore size characteristics may be very useful in predicting the frost durability of an aggregate. Such prediction does not result in the same acceptability as currently used for ISHC specifications and might provide a more accurate method of determining acceptability of coarse aggregate for use in PC concrete.

A proposal for Phase II of the project has been submitted. This phase would further evaluate the border line between good and poor durability of concrete based on pore size factors and also look at means of improving border line aggregates relative to durability.

The Report is presented to the JHRP Board as partial fulfillment of the objectives of the research. The investigators express considerable optimism about the probable usefulness of the findings in the development of more accurate criteria for acceptance of coarse aggregate relative to durability in PC concrete. Following presentation to the Board the Report will be forwarded for ISHC and FHWA review, comment and acceptance.

Respectfully submitted,

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16. Abstract <p>Studies have shown that the pore characteristics of coarse aggregates have an important role in the freeze-thaw durability of concrete. This study was designed to seek a correlation between pore-size distribution of an aggregate measured by mercury intrusion and the freeze-thaw durability of concrete made with the aggregate.</p> <p>Fourteen aggregates with a variety of pore-size distributions were studied. The rapid freeze-thaw (ASTM C 666A) and a modified critical dilation test were conducted. The absorption and the PCA absorption-adsorption tests were also conducted.</p> <p>A good correlation between the pore-size distribution of an aggregate and its normalized durability factor obtained from the rapid freeze-thaw test was found. The equation relates the expected durability factor to the total pore volume and the median pore size. Larger pore volumes and smaller pore sizes make for poor durability. Aggregates from pavement concrete with varying degrees of D-Cracking were run and, on the basis of the results, tentative expected durability factors were set up to distinguish between potentially good and potentially poor aggregates. Absorption values and the absorption-adsorption test were not as good indicators of performance.</p>			
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Interim Report

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FREEZE THAW DURABILITY OF COARSE AGGREGATE IN CONCRETE

by

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and the

U.S. Department of Transportation
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The contents of this report reflect the views of the author who is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Federal Highway Administration. This report does not constitute a standard, specification, or regulation.

Purdue University
West Lafayette, Indiana
August 2, 1978

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HIGHLIGHT SUMMARY

D-Cracking is one of the most serious durability problems of concrete pavements in freezing climates. It is well known that the main cause of the distress is the coarse aggregate. No available test method is completely successful in predicting freeze-thaw durability. Studies on coarse aggregates relating to freeze-thaw durability have shown that the pore characteristics of the coarse aggregates have an important role in the freeze-thaw durability of the concrete. This study was designed to find the correlation between pore-size distribution of an aggregate measured by the mercury intrusion method and the freeze-thaw durability of concrete made with the aggregate.

Fourteen different types of aggregates with a wide variety of pore-size distributions were studied. Two laboratory freezing tests, the rapid freezing and thawing test (ASTM C 666A) and a modified critical dilation test, were conducted. Also 24-hour absorption and the PCA absorption-adsorption tests were conducted. A good correlation between the pore-size distribution of an aggregate and its durability factor obtained from the rapid freezing and thawing test was found. The modified critical dilation test

results generally agreed with the rapid freezing and thawing test results. The absorption test and PCA absorption-adsorption test were not as good indicators of freeze-thaw durability as pore-size distribution.

A correlation equation between an expected durability factor for an aggregate and its pore-size distribution measured by mercury intrusion was obtained. This equation was then examined for its applicability to the field performance prediction. The aggregates with known field performance were examined, and the existing concrete pavements with various degree of D-cracking were sampled and their aggregates were examined. These studies have shown that the correlation equation is capable of predicting the frost durability of an aggregate. Based on these examinations, border lines separating durable from non-durable aggregates were tentatively determined.

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INTRODUCTION

Statement of the Problem

D-Cracking (Deterioration Line Cracking) is a series of fine cracks parallel and adjacent to the joints and the edge of a portland cement concrete pavement. The source of distress is expansion of water in the concrete when frozen. D-Cracking usually starts at the lower parts of the slab adjacent to the joints, where moisture accumulates, and eventually progresses throughout the entire slab.

In 1945, Woods, Sweet, and Shelburne [1] reported the results of an extensive performance survey of concrete pavements in Indiana. An outstanding correlation was found between the source of coarse aggregate and the deterioration of pavements. Much research has been carried out on the mechanism of deterioration, physical properties of coarse aggregates affecting freeze-thaw durability of concrete, and test methods to predict the field performance of concrete. Much understanding has been obtained through these studies, but the state of the art is far from complete.

The most reliable test methods to predict the freeze-thaw durability of coarse aggregate are probably the laboratory freeze-thaw tests. They are time consuming, costly, and not completely accurate, because the test methods involve many factors affecting the results other than coarse aggregates. A more reliable and

faster test method is needed, especially in heavily populated areas where sound aggregates are becoming depleted and material engineers are forced to use questionable aggregates.

Statement of Objective

It has been reported by many investigators that the pore characteristics of coarse aggregates have important roles in the freeze-thaw durability of concrete. But so far no test involving one or more of the pore properties of the aggregate has been completely successful in predicting freeze-thaw durability of concrete.

Mercury intrusion, first proposed by Washburn [2] as a method to measure the pore size distribution of a porous material, has been successfully used by Winslow and Diamond [3] on hardened portland cement paste. Pore size distributions in the range from 500 microns to 25 angstroms can be readily measured using commercial equipment.

The objective of this study was to find the correlation between the pore size distribution of a coarse aggregate, as measured by mercury intrusion, and the freeze-thaw durability of concrete made with the aggregate.

Literature Review

This literature review covers the freeze-thaw durability of concrete, with the emphasis being placed on the influence of the coarse aggregate. One of the earliest studies on concrete aggregates concerning freeze-thaw durability was made by Reagel [4], who noted the occurrence of popouts in concrete pavements caused by chert particles. Since that time, there have been many investigations on chert. Sweet [5] studied Indiana cherts and reported that: "The most unsound cherts had a ratio of 0.85 or more between the absorption by one hour evacuation and 23 hours immersion and that calculated for one hundred percent saturation. They had an absorption of 3 percent or more, and a bulk specific gravity, saturated surface-dry, of less than 2.50, by A.S.T.M. method C 127-39".

Similar studies conducted by others [6,7] confirmed that unsound coarse aggregates can be characterized by a low bulk specific gravity, a high absorption, and a high degree of saturation.

An extensive field performance survey was made in Indiana covering 3,300 miles of pavements, and results were reported by Woods, Sweet, and Shelburne in 1945 [1]. It was concluded that an outstanding correlation existed between certain sources of coarse aggregates incorporated in the concrete mix and the susceptibility of the finished pavement to blow-ups and map-cracking. No correlation existed between field performance and the type of cement, fine aggregate, the time of year constructed, the type of

subgrade, and other variables. Surveys were made in Kansas [8], Missouri [9], Kentucky [6], and Iowa [10]. It became apparent that coarse aggregate is an important factor in the performance of portland cement concrete pavement. It was further pointed out that these non-durable coarse aggregates met the commonly employed specification limits.

Many investigations attempted to solve the freeze-thaw problem of concrete. The approaches were:

- 1) Comprehensive study of the mechanism of deterioration due to freeze-thaw cycles,
- 2) Study of physical properties of coarse aggregates relating to freeze-thaw deterioration,
- 3) Establishing laboratory freeze-thaw tests.

Powers [11,12,13] contributed much to the study of the failure mechanisms of concrete subjected to freezing and thawing. He proposed the "hydraulic pressure hypothesis" and explained the failure mechanism and the important role of air entrainment. Later in 1953, Powers and Helmuth [14] proposed another hypothesis, "the gel water diffusion mechanism."

Verbeck and Landgren [15] made the first complete analysis of aggregate under freezing and thawing. They analyzed the problem in terms of three phenomena; (1) elastic accommodation, (2) critical size of aggregate (failure due to hydraulic pressure), and (3) expulsion of water from the aggregate into the paste. The details of these hypotheses are discussed later.

In attempts to correlate the physical properties of aggregates to the frost resistance of portland cement concrete, various techniques were employed. In early studies [5,6,7,16], absorption, bulk specific gravity, and degree of saturation were the keys to predict the frost resistance of aggregates. In 1946, Rhoades and Mielenz [17] pointed out the importance of the pore characteristics of aggregates, namely absolute pore volume, size of the pores and their continuity.

In 1948, Sweet [18] studied Indiana aggregates and noted that the volume of voids smaller in diameter than 0.005 mm, expressed as a ratio to the volume of solids, was less than 0.06 for aggregates with good field performance and greater than 0.10 for aggregates with bad service records. The diameter 0.005 mm, which might have been chosen because of the limitation of the microscopic method, has been used to separate "micro-pores", which are supposedly harmful, from "macro-pores" which are not.

Dolch [19,20,21] studied pore characteristics of Indiana limestones, such as density, porosity, absorption, degree of saturation, specific surface area, capillary absorptivity, permeability, and tortuosity factor. He concluded that the rate of increase of the degree of saturation of a material exposed to free water, and the ratio of the absorptivity to the permeability are two indices of frost susceptibility.

Internal surface area was studied as an index of the frost susceptibility by Blaine, Hunt and Tomes [22] and Litvan [23]. It was pointed out that the materials with higher internal surfaces had, on the average, poorer resistance to freezing and thawing than those with lower surface areas.

Lemish, Rush and Hiltrop [24,25] first applied the mercury porosimetry method to measure the pore-size distribution of aggregates and associate it with the frost durability of concrete. The pore size range they measured was from 8 microns to 0.08 microns. Although they did not find any close correlation between pore size distribution alone and service records, they stated; "knowledge of a rock's pore size distribution might be of value in attempting to predict its service record as aggregate."

Pore-size distribution of aggregate measured by mercury porosimetry was also studied by others. Walker and Hsieh [26] found that the amount of pores greater than 8 microns relates to the laboratory freeze-thaw test, in contrast to the results of Sweet. On the contrary, Lange and Modry [27] found that non-durable aggregates had pores in the range of diameter from 0.1 to 0.02 microns. Koh and Kamada [28] found that the pore-size distribution of a "soft rock (non-durable aggregate)" had a peak in the range of diameter between 0.15 and 0.015 microns. The smallest diameter measured in these studies was 0.01 microns.

Studies of physical properties of coarse aggregates relating freezing and thawing durability have led to the qualitative conclusion: non-durable aggregates have a large amount of small pores, a high degree of saturation, a high porosity, a low bulk specific gravity, and a high absorptivity. But the state of knowledge has not reached the stage where one or several physical properties of the coarse aggregate can be used to predict the performance of concrete under freezing and thawing conditions accurately.

Laboratory freeze-thaw tests have been studied and developed by many investigators [7,18,24-27,29-44]. A thorough review of the literature was made by Larson in 1964 [41]. One of the earliest studies was made by Sweet [18], who studied Indiana aggregates and concluded "on the basis of the comparison of field performance, aggregate characteristics, and resistance of laboratory concrete to freezing and thawing, that freezing and thawing tests on concrete beams containing the aggregates can be used to differentiate materials with good field performance from those with poor performance."

In 1959, the Highway Research Board Committee on Durability of Concrete-Physical Aspects [42], conducted an extensive research program to evaluate the ASTM tentative methods of test for resistance of concrete specimens to freezing and thawing. They asked 13 laboratories to run the freezing and thawing test on three different concrete mixes using four different methods,

namely, (a) Rapid Freezing and Thawing in Water (C 290),
(b) Rapid Freezing in Air and Thawing in Water (C 291),
(c) Slow Freezing and Thawing in Water or Brine (C 292), and
(d) Slow Freezing in Air and Thawing in Water (C 310). The
conclusions were:

- (1) Freezing in water gave lower durability factors than
did freezing in air,
- (2) Variability among laboratories was small for concrete
with either low or high durability; variability was
large for concrete with mid-range durability,
- (3) Among the four methods, rapid freeze in water (A) showed
the least variability.

In 1955, Powers [43] proposed a new test method. He pointed
out that the condition in the rapid freezing and thawing test is
too severe, compared with natural weathering, that it may reject
aggregates that are immune to frost under natural weather conditions,
and that the important effect of seasonal drying is not taken into
account. His proposed procedure takes this category of field
exposure into account and uses the period of immunity to frost
attack as the primary measure of frost resistance. Based on the
Powers proposal, ASTM set up a new test method, the "Critical
Dilation Test", C 671 and C 682. The State of California has been
using the critical dilation test, which differs in details from
ASTM C 671, successfully. They reported [44] that in some cases,
aggregates were used successfully in the field that has failed the
ASTM C 666 test but that passed their critical dilation test (528-B).

The rapid freezing and thawing test and the critical dilation test are the two laboratory tests most commonly used. These tests seem to correlate with field performance fairly well, but their accuracy is not good enough, because of many factors other than the aggregates that affect the results, such as condition of aggregate and sample, curing of sample, cooling speed etc. They are also time consuming.

Another type of laboratory test is one-cycle slow freezing and thawing test which has limited success [38,40].

Approach Used in This Study

Fifteen quarries with from good to bad field performance records were sampled, and twenty seven different coarse aggregates were obtained. Based on preliminary pore-size distribution studies, eleven aggregates were chosen for further work so as not to have unnecessary duplications. Additionally, three types of brick were obtained to fill gaps in the pore-size distribution ranges. Thus, a total of fourteen samples were chosen for the study.

Rapid freezing and thawing tests were conducted on these aggregates according to ASTM C-666A. A modified critical dilation test developed at Purdue University was also conducted. Absorption tests and the PCA absorption-adsorption test were conducted on the aggregates.

A correlation equation of pore-size distribution and rapid freezing and thawing test results was obtained by multiple regression analysis.

Concrete from existing pavements with various degrees of D-Cracking was sampled. Pore-size distributions of the aggregates concerned were measured, and the correlation equation was examined. Aggregates with known field performance records were also examined, and the borderline between durable and non-durable aggregates was determined based on the pore-size distribution

EXPERIMENTAL WORK

Sampling Aggregates

The main objective in the sampling of aggregates was to get a wide variety in terms of pore-size distribution, with minimum scatter of pore-size distribution in each sample.

Fifteen quarries were chosen so as to have aggregates with from good to bad field performance records. Sampling of artificial products, such as bricks, was also planned in case enough variety of pore-size distribution was not obtained in the natural materials.

From the preliminary study of pore-size distribution of rocks sampled from four quarries, it was found that pore-size distribution varies from ledge to ledge in any quarry. Because the main objective was not to sample the typical aggregate products and evaluate the quarries, but to get aggregate samples with uniform pore-size distributions, each aggregate was sampled from a particular spot in the quarry wall. The color and the texture were examined, and as much as 150 pounds of rock, as uniform as possible, was sampled.

A total of 27 aggregates were sampled from 15 quarries. In addition to these, 9 different types of commercial building bricks were obtained. The next step was to select the aggregates for further study based on the pore-size distributions and homogeneity. Absorption measurements were used for this selection procedure together with pore-size distribution measurements.

Each sample of rock consisted of 5 to 10 pieces of rock weighing from 20 to 50 pounds. Before crushing several small pieces of rock were knocked off each larger piece, and they were subjected to the 24-hour water absorption test. Average values and standard deviations were calculated. Three small pieces with the highest, lowest and medium absorption values respectively were subjected to the pore-size distribution measurement. Almost the same procedure was used for the bricks; they had better homogeneity than the natural rocks.

Based on the uniformity of the pore-size distributions and the absorption values, fourteen aggregates were selected so as to have enough variety in terms of pore-size distribution. Table 1 is the list of these aggregates in order of decreasing pore volume.

Absorption Measurement

Two kinds of absorption, 24-hour soaking and vacuum saturation, were measured. Samples used were 1-inch diameter cores drilled from the pieces of rock. These cylinders were later used for the Absorption-Adsorption test. The samples were vacuum-oven dried, cooled to room temperature in a desiccator, and weighed on an analytical balance.

For 24 hours soaking, the dry samples were soaked in water for 24 hours and weighed in a saturated surface dry condition. A weighing bottle was used to minimize moisture loss. For vacuum

TABLE 1
List of Aggregate Samples

Aggregate Identification	Geological Name
BR-3	Brick
CC-1	Kokomo Limestone
Ke-1	Kokomo Limestone
H-1	Guthries Creek Limestone
F-2	Kokomo Limestone
McC	Geneva Dolomite
BR-5	Brick
BR-1	Brick
PC-1	Mississinewa Shale
MB	Louisville Limestone
Ko	Kokomo Limestone
BM-1	New Albany Shale
H-2	Harrodsburg Limestone
HR-2	St. Genevieve Limestone

saturation, the samples were placed in a filtering flask and evacuated on an aspirator. After 60 minutes of evacuation, water was introduced into the flask while evacuation was continued, and after 23 hours of soaking the samples were weighed in a saturated surface dry condition.

Pore-Size Distribution Measurement

The method used in this study to measure the pore-size distributions of the aggregate was mercury intrusion. The pore-diameter range measurable by mercury porosimetry is approximately from 500 microns to 25 angstroms which covers the entire pore size range of interest. The pores smaller than 25 angstroms are not important, because they are so small that water in them does not freeze under common water temperatures.

Theoretical Background

The surface tension of a non-wetting liquid with a contact angle greater than 90° opposes its entrance into small pores. This is the phenomenon of capillary depression. This opposition is overcome by the application of pressure to the liquid, and then the liquid will enter the pore. The pressure required to force a non-wetting liquid into a pore is a function of the surface properties of the liquid and the solid, and the geometry of the pore.

This relationship, assuming a cylindrical pore was given by Washburn [2]:

$$p = \frac{-4\gamma \cos \theta}{d} \quad (1)$$

where: p = Required external pressure
 γ = Surface energy of the liquid
 θ = Contact angle between the liquid and the solid
 d = Diameter of the pore

Mercury is the commonly used liquid because it has low vapor pressure, it does not react chemically with most solids, and it is non-wetting with most solids. It is reasonable to assume that the quantity $(-4\gamma \cos \theta)$ is constant for a given solid; then the relation between the pressure and the diameter of a pore becomes a linear inverse. The pore size distribution is obtained simply by measuring the volume of intruded mercury at pressures that correspond to diameters of interest.

In most mercury intrusion studies, the values for γ and θ were obtained from the handbook. This sometimes leads to erroneous results. Because each material has its own surface properties, one must obtain actual values for these constants for each material. Instead of measuring γ and θ individually, the whole intrusion constant $(-4\gamma \cos \theta)$ was measured directly by the method of Winslow and Diamond [3], and Winslow and Shapiro [45]. A sample

with drilled holes of a known diameter, measured with a microscope was prepared, and the absolute pressure at which mercury intruded these pores measured. The intrusion constant was obtained as the products of pressure and diameter.

$$k = - 4\gamma \cos \theta = p \times d \quad (2)$$

The contact angle was back-calculated by assuming 484 erg/cm^2 for surface energy of mercury.

Apparatus

The instrument used was a commercial unit, (Catalog No. J5-7125D, American Instrument Company, Silver Spring, Maryland 20910), modified in certain respects, which has a maximum capacity of 60,000 psi. The porosimeter consists essentially of a pressure vessel, pressure generating pump, and measuring instruments for pressure and intrusion. The hydraulic fluid used was a mixture of two parts Transformer 10C oil and one part kerosene. Compressing the hydraulic fluid generates heat and warms it. To minimize the temperature rise an air-circulation fan was attached to the side wall of the cabinet to cool the pressure vessel. The commercial unit has two pressure gages, 0-5000 psi and 0-60,000 psi; a 0-500 psi gage was added to increase the accuracy in the range of pore size from 15 microns to 0.5 microns.

The capacity for intrusion volume is 0.2 ml. The amount of sample necessary for the measurement varies with the porosity of sample, but it is usually from 0.5g to 4g.

Correction of Data

Two kinds of corrections are necessary.

1. In a low pressure measurement (below atmospheric pressure), the volume change of air left in the penetrometer after evacuation should be subtracted from intrusion reading. At higher pressures this volume change becomes negligible.
2. In a high pressure measurement the situation is complicated. As the pressure increases the mercury is compressed and its volume decreases. At the same time the hydraulic fluid is compressed. The compression of the fluid generates heat and causes expansion of the mercury. Furthermore, the temperature of the fluid and the mercury changes as the test proceeds. To correct for all of these problems, blank tests (tests without a sample) were made. It should be noted that the blank test and the real test need to have the same pressuring history because of the time dependent nature of the temperature rise.

The pressure has to be held at each point until the intrusion process reaches equilibrium. The length of time required depends on the pore characteristics of the materials, and it was found that

TABLE 2
Correction Factors in Mercury Porosimetry

Pressure (psi)	Correction (ml/ml of Hg in penetrometer)
50	0.0000
100	0.00001
150	0.00003
200	0.00005
300	0.00007
500	0.00009
700	0.00010
1000	0.00012
1500	0.00015
2000	0.00018
3000	0.00023
5000	0.00029
7000	0.00034
10000	0.00040
15000	0.00047
30000	0.00061
45000	0.00067
60000	0.00076

one minute was enough for the materials used in this study. Eighteen steps of pressure were selected, as shown in Table 2. The correction factors were obtained from blank tests. The correction factors calculated according to this table should be added to the intrusion reading, because the volume increase due to heating is greater than the volume decrease due to compression. When measurement was needed between these predetermined steps, the waiting time was adjusted so as to make the pressure history similar to the standard.

Rapid Freezing and Thawing Test

The rapid freezing and thawing test in water was conducted on air-entrained concrete beams made with fourteen samples in accordance with ASTM C 666A. Four 3 x 4 x 16 inch concrete beams were made with each sample except HR-2 (eight beams were made with HR-2). A total of 60 beams were tested in the laboratory of the Division of Materials and Tests, Indiana State Highway Department. Due to the limited capacity of the freezing and thawing apparatus, half of the beams, which include four beams of HR-2 and two beams of the rest of the aggregate types, were tested at one time and the remainder in a second run.

Preparation of Concrete Beams

1. Materials

Cement: Type I portland cement from one mill was used for all mixes. The physical properties and chemical analysis of the cement, as furnished by the manufacture, are found in Appendix A.

Air-Entraining Agent: Vinsol resin solution was used as an air-entraining agent. One ounce of agent per bag of cement was added to the mix as a standard proportion. Extra amounts of the agent were added as needed for some types of aggregates to get enough air-entrainment.

Fine Aggregate: One type of natural silicious sand was used for all mixes. A sieve analysis of the sand is found in Appendix A.

Coarse Aggregate: Coarse aggregates were crushed and graded according to the proportion given in Appendix A. This is the same gradation as that used by Blackburn [30], and was found to be efficient in utilizing as much of the material from the crusher as possible.

Coarse aggregates and brick samples were vacuum saturated before mixing. The crushed and graded samples were washed thoroughly and oven dried, and they were placed under the vacuum (25 mmHg absolute pressure) for an hour.

Then water was introduced into the system while evacuating and the aggregates were soaked in water overnight. Just before mixing they were taken out of the water and excess free water was wiped off to get a saturated surface dry condition.

2. Mix Design

In order to obtain concrete similar to that used in the field, the mix design specified by the Indiana State Highway Commission was followed as closely as possible. Maximum size of coarse aggregate was reduced to one inch because of the beam size limitation. A water cement ratio of 0.5 by weight and a cement factor of 6 bags per cubic yard were used for all mixes. The amount of fine aggregate was 40% of the total aggregate. The mix proportion was thus: 1.0: 2.1: 3.2 for cement, fine aggregates, and coarse aggregate by weight. The mix proportion for 0.75 cu. ft. of concrete, which was enough to make four 3 x 4 x 16 inch beams and three 3 x 6 inch cylinders is given in Appendix A.

3. Mixing and Curing

Mixing of concrete was done in a Lancaster Counter Current Batch Mixer, Type SKG. The sequence of the operation was as follows:

1. The mixing pan was thoroughly wetted and the free water was wiped off.

2. The coarse aggregate in a saturated surface-dry condition and the sand in an air-dry condition were placed in the mixing pan, and mixing was started.
3. The cement was added.
4. The mixing water, containing the air-entraining agent, was added and timing was started.
5. Mixing was continued for 3 minutes, followed by 3 minutes rest, followed by 2 minutes further mixing.
6. Air content was measured according to ASTM C 231 using Air Meter Type B (White meter). When the air content was less than 5%, more air-entraining agent was added and the batch was remixed for 1 minute. This process was continued until 5% air content was obtained.
7. Slump was measured in accordance with ASTM C 143.
8. Fresh concrete was placed in the oiled steel beam molds in three layers, and was consolidated on the vibrating table. Cardboard molds were used for the 3 x 6 inch cylinders. The samples were prepared according to ASTM C 192.
9. The surface was finished with a trowel and was covered with plastic sheets and damp cloths.
10. The samples were demolded 24 hours after casting and cured in the moist room.
11. At the age of three months, the beam samples were wrapped in damp cloths and plastic bags and transported to the Division of Materials and Tests Laboratory. They were

soaked in water 4 days before the first testing and 81 days before the second. The age at the first testing varied with sample from 61 days to 99 days. See Table 5 for details.

Testing Procedure

The rapid freezing and thawing test was run in a Conrad Freeze-Thaw Chamber with Honeywell instrumentation, in accordance with ASTM C 666. Procedure A, rapid freezing and thawing in water, was chosen because this procedure seems to give a better correlation with field performance [18,34]. One complete freezing and thawing cycle takes three hours, cooling from 40°F to 0°F in two hours and warming from 0°F to 40°F in one hour. The temperature was measured by a thermocouple embedded in the center of a dummy specimen.

Approximately every five cycles the freeze-thaw unit was held in a thaw condition, and at the temperature of 45°F the beams were removed from the chamber. Fifteen minutes after removal from the cans the beams were tested for resonant frequency according to ASTM C 215. The deterioration of the beams was recorded by sketching the cracking and scaling. During the fifteen minutes of waiting period all the cans were cleaned of debris and tested for leaks.

After recording the resonant frequency and deterioration the beams were replaced in the cans and returned to freezing and thawing.

Calculation of Durability Factor

The Durability factor was calculated as defined in ASTM C 666,

$$DF = \frac{PN}{M} \quad (3)$$

where: DF = Durability factor of specimen,
P = Relative dynamic modulus of elasticity at N
cycles, percent,
N = Number of cycles at which P reaches the specified
minimum value for discontinuing the test or
the specified number of cycles at which the
exposure is to be terminated, whichever is
less, and
M = Specified number of cycles at which the ex-
posure to be terminated.

It is specified in C 666 that freezing and thawing is to be continued until the specimen has been subjected to 300 cycles or until its relative dynamic modulus of elasticity reaches 60 percent of the initial values, whichever comes first. Since freezing and thawing was terminated before 300 cycles for all specimens in this study, the durability factor was calculated by the following equation:

$$DF = \frac{(60) \cdot N}{300} \quad (4)$$

N, number of cycles when P reached 60, was obtained by linear interpolation between two points, before and after P dropped below 60.

Modified Critical Dilation Test

A modified version of the critical dilation test developed by Famili [46] was conducted on fourteen aggregates. This test method has two features that differ from the critical dilation tests of ASTM C 671 and C 682, and California DOT 528-B.

1. Cooling proceeds in one direction only: In a real concrete pavement cooling usually proceeds from the surface to the bottom. Therefore, one-directional cooling is more realistic.
2. The sample specimen consists of a single cylinder of the sample material surrounded by air-entrained mortar.

This test was first intended to comprise only one cycle of freezing, but it was found during the preliminary study that one cycle of freezing is not adequate to measure the frost durability of aggregate. The sample with Ke-1 aggregate, which is notorious for being non-durable, showed no expansion in the first cycle of freezing, but a large expansion in the second cycle, after two additional weeks of soaking the composite

sample in water. Some other aggregates showed small expansion in the second or third cycles, and some others showed none even in the sixth cycle. Therefore, the freezing test was repeated every two weeks until the dilation exceeded a critical value.

Preparation of Sample

1. Materials

Aggregate: A cylinder, 11/16 inches in diameter and $1\frac{1}{2}$ inches long, was taken from a larger piece of each aggregate. The axis of the cylinder was perpendicular to the bedding plane. A thermistor for temperature measurement was glued on the side of the cylinder at mid-point. The sample was vacuum saturated and then soaked in water for a week before casting.

Cement: Type I portland cement, the same as used for the concrete beams, was used.

Air-Entraining Agent: One ounce of vinsol resin per bag of cement gave satisfactory air-entrainment.

Sand: Ottawa sand (ASTM C 109) was used as a fine aggregate.

2. Mix Design

The water cement ratio used was 0.55. A lower water cement ratio caused difficulties in placing and consolidation, because the mold was small. The ratio of 0.55 gave satisfactory workability. The ratio of cement to sand was 1.0: 2.75, which was taken from ASTM C-109.

3. Casting and Curing

The mixing procedure specified in ASTM C 305 was followed.

The dimension of the composite sample specimen was $1\frac{1}{2}$ inches in diameter and $3\frac{1}{2}$ inches long as shown in Figure 1. The sample was cast on the copper plate which was to be attached to the cooling box in the freezing test.

The mold of plexiglass had six holes for the purpose of holding the aggregate sample in the middle while the mortar was cast around it. A sample aggregate was taken out of water and placed in the middle of the mold by the aid of a jig. Aggregate supports with sharp edges were inserted into the holes of the mold to suspend the aggregate. The nylon strings glued to the top of the aggregate were also fixed to the mold. Now, the aggregate was suspended by two nylon strings and six aggregate supports. Holes and slits in the mold were covered by plastic tape to make it water tight.

The mold was filled with mortar and consolidated in three layers, on a vibrating table. When the mortar was filled above the aggregate supports, they were taken out and the holes were covered by plastic tape. This casting procedure was successful in placing the aggregate in the middle of the specimen, surrounded by an air-entrained mortar. The sample was covered by damp cloths and a plastic bag. The sample was demolded nine hours after casting and placed in water.

Figure 1

Sample and Casting Mold

Apparatus

The apparatus consisted of two main units, a cooling unit and a recording unit. A diagram is shown in Figure 2.

Cooling Unit: The coolant (a mixture of water and ethylene glycol) is stored and cooled in the freezer, circulated by the pump through the cooling box in which the sample is placed, and returned to the freezer. The cooling box consists of a copper plate and an insulated housing. The coolant flows through the copper plate on which the sample is placed.

Recording Unit: The temperature of the sample was measured by a thermistor (YSI Thermilinear Component 44203, Yellow Spring Instrument Company) mounted on the side of the aggregate piece, whose accuracy was $\pm 0.15^{\circ}\text{C}$ and whose temperature range was from -30°C to 50°C . The diameter change was measured by a linear variable differential transformer (Type PCA 220-020, Schaevitz Engineering), which was attached at the end of invar steel measuring arms. The diameter change measuring device is shown in Figure 3. The fused quartz rods attached at the mid point of the arms pressed against the specimen. At the points where the quartz rods touch the specimen, a small amount of grease was used to prevent the build-up of frost during freezing. The LVDT needs to be kept at constant temperature, because it is sensitive to

Figure 2

Schematic Diagram of Apparatus

temperature change. Accordingly, the LVDT was placed in the constant-temperature jacket in which a mixture of water and ethylene glycol at 0°C was circulated. The signals from the thermistor and the LVDT were sent to an X-Y recorder, and the diameter change with temperature was recorded automatically. All the units except the X-Y recorder were placed in the cold room in which the temperature was kept constant at 0°C .

Testing Procedure

The sample of aggregate embedded in mortar was taken out of the soaking, and excess free water was wiped off. A small amount of grease was put on the copper plate to improve the heat transfer and the sample was placed on the cooling box. The measuring arms were pressed against the sample, and the sample was covered by a styrofoam insulator. A desiccant was placed around the LVDT to keep the contact points of the LVDT dry. Another styrofoam insulation box was used to cover the entire cooling box. The freezer and circulation pump were turned on to start the test. One cycle of freezing, from 10°C to -12°C was completed in 6 hours.

Figure 3

Diameter Change Measuring Device

PCA Absorption-Adsorption Test

Klieger et al. [34] proposed a test method to identify non-durable aggregates by a combination of their absorption and adsorption values. The absorption value is a rough indicator of pore volume and the water vapor adsorption value at 92 percent relative humidity is a rough indicator of the total surface area. The authors established a pass-fail criterion for aggregates based on their field performance records.

Testing Procedure

The aggregate samples used were 1 inch diameter cores that had been previously used for the absorption test. The specimens were cut with a low speed saw (Isomet 11-1180, Buehler Ltd.) into 1/16 to 1/8 inch thick slices with alternate slices being set aside for absorption and adsorption measurements.

Absorption: The slices were vacuum-oven dried for 48 hours, then transferred to a desiccator and cooled to room temperature. They were then placed in a weighing bottle and weighed on an analytical balance. The slices were next vacuum saturated with boiled distilled water and, on alternate days, removed, towel dried to the saturated surface-dry condition, and placed in the weighing bottle for reweighing. This weighing procedure was repeated until weight gains were no longer recorded. The absorption of the test material was determined from the

difference between the final and oven dry weights divided by the oven dry weight.

Adsorption: The adsorption measurements were made on the alternate of slices. These were first crushed to the 8 to 16 sieve size, than vacuum oven dried and placed in a weighing bottle of known tare weight. The material was next cooled to room temperature in a desiccator containing calcium chloride. The weighing bottle with sample was then stoppered and weighed on the analytical balance to obtain the oven dry weight. The bottle was next opened and placed, together with the stopper, in a desiccator containing a saturated KNO_3 solution which, at $23 \pm 1^\circ\text{C}$ maintains a relative humidity of 92 percent. After one day of storage, and on alternative days, the sample was weighed in the stoppered weighing bottle until a weight increase was no longer recorded. The adsorption was determined by dividing the total weight gain by the oven dry weight of the sample.

RESULTS

Absorption

In Table 3 are presented the absorption measurement data. Two cylinders of each aggregate type (three of Ke-1) were tested for 24 hours soaking and vacuum saturation. Each test was performed twice on the same sample. The test was not completed on BM-1 aggregate because this particular aggregate was laminated and too fragile to take core samples. The samples with * had axes parallel to the bedding plane, and the rest of the samples had axes perpendicular to the bedding plane. Columns 1 and 2 are the 24 hours soaking adsorption values of two repeat tests and columns 3 and 4 are the vacuum saturation adsorption values. Columns 5 and 6 are the average values of 24 hours soaking and vacuum saturation respectively, and column 7 is the ratio of the 24 hours soaking value to the vacuum saturation value.

Intrusion Constant

In Table 4 are given the intrusion constants for the sample materials, measured as described before. Column 1 is the average diameter of the drilled holes in microns, column 2 is the pressure to intrude in mmHg, column 3 is the intrusion constant K

in $\mu\text{m}\cdot\text{psi}$, and column 4 is the contact angle, θ , in degree obtained by assuming 484 erg/cm^2 for the surface free energy of mercury. The unit ($\mu\text{m}\cdot\text{psi}$) was used for the intrusion constant k , because the diameter of the pore in microns is readily obtained by dividing the constant by the intruded pressure in psi . The intrusion constant for aggregate BM-1 was not measured because this particular aggregate continued to out-gas throughout this test. This was not a problem in the high pressure measurement. The intrusion constant of 160 was used for BM-1 and other aggregates not subjected to this test because 160 was the most frequently observed value and close to the average value of all the aggregates, excluding bricks, that was 157.5.

Pore Size Distribution

As described before, the pore size distribution was measured for all the aggregates for the purpose of selecting samples more critically. After the aggregates were selected, based on the pore-size distributions and their homogeneity, they were crushed and graded to make concrete beams for freezing and thawing tests. Since the main purpose of this study was to find out the correlation between pore-size distribution of aggregate and frost durability, it was felt necessary to obtain the representative or average pore-size distribution of the aggregates actually mixed in the concrete beams.

TABLE 3
Absorption Test Results

Absorption - Percent								
Sample		1	2	3	4	Average		7
		24 Hours	Soaking	Vacuum Saturation		24 Hrs Soaking	Vacuum Sat.	Ratio S=5/16
BR-3	1	10.35	10.27	14.23	14.20	10.31	14.22	0.73
	2	11.52	11.48	14.87	14.88	11.50	14.88	0.77
CC-1	1	8.71	8.51	11.84	11.85	8.61	11.85	0.73
	2	8.55	8.11	11.77	11.77	8.33	11.77	0.77
Ke-1	1	8.29	8.39	10.89	10.87	8.34	10.88	0.77
	*2	8.40	8.43	10.87	10.85	8.42	10.86	0.78
	3	6.52	6.38	8.66	8.65	6.45	8.66	0.74
H-1	1	7.98	8.08	9.38	9.39	8.03	9.39	0.86
	*2	7.79	7.81	9.10	9.13	7.80	9.12	0.86
F-2	1	6.29	6.12	9.68	9.66	6.21	9.67	0.64
	2	6.41	6.22	9.66	9.64	6.32	9.65	0.65
McC	1	6.17	6.02	8.95	8.94	6.10	8.95	0.68
	2	6.17	5.93	8.78	8.75	6.05	8.77	0.69
BR-5	1	5.56	5.54	7.68	7.68	5.55	7.68	0.72
	2	5.68	5.64	7.80	7.80	5.66	7.80	0.73
BR-1	1	3.75	3.71	5.94	5.93	3.73	5.94	0.63
	2	3.61	3.60	5.66	5.65	3.61	5.66	0.64
PC-1	*1	4.58	4.65	4.74	4.73	4.62	4.74	0.97
	2	4.51	4.55	4.75	4.73	4.53	4.74	0.96
MB	1	2.07	2.03	3.38	3.38	2.05	3.38	0.61
	2	2.21	2.26	3.41	3.40	2.24	3.41	0.66
Ko	1	1.96	1.96	2.53	2.53	1.96	2.53	0.77
	2	2.03	2.02	2.51	2.50	2.03	2.51	0.81
H-2	1	0.75	0.74	0.87	0.87	0.75	0.87	0.86
	2	0.78	0.79	0.91	0.91	0.79	0.91	0.87
HR-2	1	0.04	0.04	0.06	0.06	0.04	0.06	0.67
	2	0.09	0.08	0.09	0.10	0.08	0.10	0.80

* The sample has axis parallel to the bedding plane.

TABLE 4

Intrusion Constant and Contact Angle

Sample	1	2	3	4
	Average Diameter of Drilled Holes d(μ m)	Pressure P(mmHg)	Intrusion Constant $K = p \times d$ (psi $\times \mu$ m)	Contact Angle θ (degree)
BR-3	617	12.9	154	123
CC-1	633	13.2	162	125
Ke-1	710	9.7	133	118
H-1	640	10.8	134	118
F-2	649	12.7	159	124
McC	665	11.5	148	122
BR-5	611	11.6	137	119
BR-1	596	15.0	173	130
PC-1	610	13.55	160	125
MB	628	13.2	160	125
Ko	614	12.9	153	123
BM-1	---	----	(160)	(125)
H-2	638	13.3	164	126
HR-2	663	13.6	174	128

LIMITING PORE SIZE DISTRIBUTION OF AGGREGATE SAMPLES

Figure 4 . Pore-Size Distribution of Aggregate Samples

Preliminary tests showed that the pore size distribution of one portion of a rock might be somewhat different from that of another portion of the same rock. When individual pieces were tested the worst situation showed a spread in total intruded pore volume of about 20% with a lesser spread in pore diameters. However, even in such a severe case, it was found that distributions from about five individual pieces were sufficient to give good values for the upper and lower bounds of the pore volume. This was found to be true as long as a single type of rock was involved. Therefore, by placing several approximately equal sized peices of rock in the porosimeter at the same time, a single test was able to give an approximate "average" distribution.

Nine pieces of aggregate were picked from the pile of crushed and graded aggregate by a "blind pick" method. A small particle of about 0.5 gram was broken from each individual aggregate piece using a hammer and a cold chisel. Three of these were put together for a pore-size distribution measurement and three pore-size distribution curves were obtained for each aggregate type. The results are shown in Appendix B. Figure 4 shows the pore-size distributions of the fourteen aggregates in one graph.

Rapid Freezing and Thawing Test

The results of the rapid freezing and thawing test (ASTM C 666A) are shown in Table 5. Columns 1 and 2 are the durability factors of the individual concrete beams in the first

testing, column 3 is their average value, and column 4 is the age of the concrete beams at the time the first testing started. Column 5 through 8 are the results of the second testing in the same order as the first testing.

The first measurement of the resonance frequency was done after 5 cycles in the first testing, but after 13 cycles in the second testing. This happened due to a misunderstanding, and it affected the results of the specimens with lower durability. The zero values obtained in the second test could have been somewhat higher if measurements had been made after fewer cycles. These zero values were eliminated from the further analysis because of their uncertainty. One datum of HR-2 (3.51) was also regarded as an experimental error because that particular value was far from the rest of the results.

Modified Critical Dilation Test

Figure 5 shows a typical temperature-diameter diagram of an air-entrained mortar specimen. As the temperature went down the diameter of the specimen decreased. A change in the slope was noticed at around -1°C . The rate of contraction was greater below this temperature. The specimen with HR-2 aggregate, which is a durable aggregate with almost no porosity, showed the same type of curve except its slope was different. This type of curve with two approximately linear portions is regarded as an indication of a frost-durable sample.

TABLE 5

Rapid Freezing and Thawing Test Results

Sample	First Testing				Second Testing			
	Durability Factor				Durability Factor			
	Ave.			Age (Days)	Ave.			Age (Days)
BR-3	0.6	0.7	0.6	77	3.7	3.4	3.5	154
CC-1	11.7	5.9	8.8	96	3.1	9.5	6.3	173
Ke-1	9.0	1.9	5.5	105	0	2.8	1.6	182
H-1	0.9	0.7	0.3	105	0	0	0	182
F-2	11.3	8.8	10.0	95	12.8	10.5	11.7	172
McC	5.2	9.2	7.2	101	7.8	3.2	5.5	178
BR-5	4.1	3.6	3.9	66	3.1	3.3	3.2	143
BR-1	3.7	5.0	4.3	101	4.9	5.0	5.0	178
PC-1	5.7	2.7	4.2	101	3.3	0	1.7	178
MB	12.0	8.8	10.4	93	7.8	4.7	6.2	170
Ko	10.0	11.1	10.6	89	6.3	2.3	4.3	166
BM-1	8.9	19.9	14.4	88	24.5	19.7	22.1	165
H-2	22.9	22.5	22.7	90	20.5	23.3	21.9	167
HR-2	30.8	25.3	24.2	101	3.5	27.3	17.5	178
	10.5	30.2			15.2	24.2		

In Figure 5, one example of an unsound specimen is also shown. The curve shows a deviation from the "sound" curve. The temperature at which the curve starts to deviate from the linear varied with the sample. The largest deviation, Δd , was measured as a dilation as shown in the figure. This method is different from that of ASTM C 671, which measures, as dilation, the largest deviation from the initial thermal contraction line above 0°C. The ASTM Method does not consider the fact that an air-entrained sample shows more contraction after the freezing starts, therefore, it measures an erroneously small dialtion.

The dilation was measured as a deviation from the results of the frist freezing cycle in the case where the cycle first showed no expansion, and the curve of HR-2 was used as the basis for deviations in the case where the sample showed expansion in the first freezing cycle. The dilation Δd was devided by the diameter of the specimen $d = 38.1\text{mm}$, and the strain $\epsilon = \Delta d/d$ was obtained.

In Table 6 are given the results for the aggregates. The first freezing test was done at the age of one week, and the freezing test was repeated every two weeks. The sample was soaked in water between each freezing test. The test was terminated when the measured dilation strain exceeded 100×10^{-6} , or when the number of freezing tests reached six, whichever came first.

All the data are found in Appendix C.

Figure 5

Temperature-Dilation Diagram of an
Air-Entrained Mortar, HR-2, and an Unsound Specimen

TABLE 6
Modified Critical Dilation Test Results

Maximum Dilation ($\times 10^{-6}$, Strain ϵ)

Test No.	1	2	3	4	5	6
Sample (Age)	(1 wk)	(3 wks)	(5 wks)	(7 wks)	(9 wks)	(11 wks)
BR-3	>500	-				
CC-1	0	24	26	42	76	131
Ke-1	0	197	--	--	--	---
H-1	95	500	--	--	--	---
F-2	0	0	0	0	0	0
McC	18	250	--	--	--	---
BR-5	157	---	--	--	--	---
BR-1	300	---	--	--	--	----
PC-1	68	236	--	--	--	---
MB	13	34	97	194	--	---
Ko	0	31	66	283	--	---
*BM-1	0	0	0	0	0	0
H-2	0	0	13	19	32	26
HR-2	0	0	0	0	0	0

*BM-1 Sample used in this test is different from that used in other tests. It has the same type of pore-size distribution with less total pore volume. Its pore-size distribution is found in Figure B-14 in Appendix B.

PCA Absorption - Adsorption Test

In Table 7 are given PCA Absorption - Adsorption test results of 14 aggregates. The maximum adsorption was obtained in one day to two weeks depending on the aggregates.

TABLE 7

PCA Absorption - Adsorption Test Results

Sample	Absorption Weight %	Adsorption Weight %
BR-3	13.6	0.10
CC-1	11.8	0.09
Ke-1	10.7	0.60
H-1	9.3	0.85
F-2	9.7	0.14
McC	9.5	0.11
BR-5	7.5	0.06
BR-1	5.6	0.04
PC-1	4.6	2.46
MB	3.2	0.43
Ko	2.1	0.53
BM-1	2.9	2.09
H-2	1.0	0.19
HR-2	0.1	0.03

DISCUSSION

Summary of Knowledge

As a beginning of the discussion, the knowledge about freezing and thawing durability of concrete will be briefly summarized with the emphasis on coarse aggregate.

MECHANISM OF FREEZE-THAW FAILURE: The mechanism of freeze-thaw failure of aggregate in concrete has been analyzed by Verbeck and Landgren [15]. They postulated three classes of phenomena.

(1) Elastic accomodation: The excess volume of water created by the freezing of a critically saturated aggregate can be accomodated by the elastic expansion of aggregate within the limit of the tensile strength of the material. In this case no place for the excess water to escape is considered. Even though this situation is not realistic, aggregates with low porosity can accomodate the volume increase of water by elastic expansion. However, the surrounding paste may not be able to accomodate this expansion elastically. The following equation gives the tensile stress of the aggregate required to accomodate the expansion without any failure [15].

$$P = \frac{0.09W_t E}{3(1-2\mu)} \quad (5)$$

where: P = aggregate tensile stress required.

W_t = volumetric fraction of freezable water in aggregate

E = Young's modulus of elasticity of aggregate, and

μ = Poisson's ratio of aggregate.

(2) Unconfined freezing and critical size of aggregate:

The excess volume of water created by the expansion of water due to freezing has to move through the porous solid, and this movement of water generates hydraulic pressure. The magnitude of the hydraulic pressure depends upon the rate of freezing, strength and permeability of the material, and the distance the water has to travel to an "escape place". This hydraulic pressure hypothesis was first proposed by Powers [11]. In it the critical distance is defined as the maximum distance the water can travel through the porous material without generating a hydraulic pressure higher than the material's tensile strength. If it is smaller than the size of aggregate, the aggregate will fail internally. The maximum permissible size, or critical size, of the aggregate can be calculated by the following equation [15].

$$L_{\max} = \frac{27.7 K_1 T}{0.09 dW/dt} \quad (6)$$

where: $L_{\max}$ = critical size of aggregate, diameter
 K_1 = permeability coefficient of aggregate, cm per sec.
 T = tensile strength of aggregate, psi, and
 dW/dt = rate of freezing of water.

Typical values for $L_{\max}$, as given by Verbeck and Landgren [15], are 0.5 inch for the chert and 33 inches for a dolomite aggregate with a high permeability, assuming a freezing rate of 1.5 inches per hour (1.06×10^{-3} cm/sec).

(3) Freezing while confined by hardened cement paste (or mortar):

If the porosity of the aggregate is too great for elastic accomodation and the aggregate is critically saturated, the excess water due to freezing must be expelled. If the size of aggregate is smaller than the critical size, the aggregate will not fail internally due to the hydraulic pressure. The excess water will be expelled into the surrounding paste that typically has a low and a small critical distance. If the paste is not air-entrained, the paste will fail; if it is air entrained and the volume of air voids in the surrounding paste within its critical distance (roughly 0.01 inch) is greater than the volume of water to be expelled, those air voids will accomodate the excess water and the paste will not fail. Otherwise, the usual case, the paste adjacent to the piece of aggregate will fail. This is the "expulsion into the paste" mechanism of Verbeck and Landgren.

The failure of the air entrained concrete due to freezing is caused by either hydraulic pressure within the aggregate or expulsion-into-the-paste. With the type of aggregate subject to hydraulic pressure failure, the permeability of the aggregate is the most important factor. Those aggregates with low permeability have small sizes of pores, and they are saturated critically by high capillary force.

With the aggregates that fail by the expulsion-into-the-paste mechanism, the pore volume of the aggregate is the most important factor. But pore size is also important in terms of the degree of saturation. The surrounding paste typically has a smaller pore size and a higher capillary attraction than the aggregate. If the pore size of the aggregate is far larger than that of the paste, the paste will pull water away from the aggregate and the aggregate will rarely become critically saturated. Therefore, the aggregate with low permeability, small pore size, and high porosity is most vulnerable to freezing problems in concrete.

FREEZING POINT DEPRESSION OF WATER IN PORES: There is another thing to be mentioned here; that is the freezing point depression of the water in small pores. The water in small pores does not freeze at normal freezing temperatures [47,48,49,50]. The smaller the pore, the lower the freezing temperature. Helmuth [50] noted that ice crystal growth is restricted in small pores. The water first freezes in the large pores, and the ice crystals in the larger pores grow by incorporating unfrozen water from the smaller capillaries.

Discussion of Results

Rapid Freezing and Thawing Test

The durability factor, as defined, has values between 0 and 100. A durability factor of 100 is assigned to a concrete that shows no decrease of dynamic modules of elasticity after 300 cycles of freezing and thawing. Usually durable concretes show a high durability factor, higher than 80, and values lower than 50 are regarded as non durable, although the pass-fail criteria differ among different testing laboratories.

The data obtained in this study showed considerably lower values, and no beam survived more than 155 cycles. The reasons for the low durability factors are:

1. All the aggregates were vacuum saturated before mixing whereas the most frequently used methods of treating aggregates are oven-drying or 24 hour soaking in water. As seen in Table 3, Column 7, the saturation ratios between 24 hour soaking and vacuum saturation are lower than the critical degree of saturation, 0.91, except for aggregate PC-1. Thus, the treatment used in this test was much more severe than is normal. All of the aggregates in this study may have been critically saturated when the freeze-thaw testing began. Even a 24 hour soaking in water would probably have yielded many non-critically saturated specimens. Such specimens would have required

more cycles to become critically saturated and resulted in higher durability values. The reason that vacuum saturation was used is that it brings all aggregates to nearly the same moisture content whereas 24 hour soaking leaves aggregates in widely varying moisture contents depending upon their pore structures. Oven-drying was not used because it represents an unrealistic state for an aggregate.

2. The test was conducted according to Procedure A of ASTM C-666 with freezing and thawing both being done in water. This is generally a more severe method than Procedure B in which the freezing takes place in air.

To make sure that the concrete was properly air entrained, the air content was measured on the hardened concrete by the point counting method, ASTM C 457. A 3 x 6 cylinder was cut in half and polished for microscopic analysis. The results are given in Table 8, and show all the specimens to have been properly air entrained. Therefore, all the test results seem to reflect the the frost durability of the coarse aggregate, even though the obtained durability factors are low.

Among all the aggregates, HR-2 is the "control" aggregate which is supposed to be one of the most durable aggregates in the state. It has a low absorption value (0.1% vacuum absorption), and no appreciable pore volume was found in the mercury porosimetry test. This aggregate had the highest durability factor, an average of 23.35. In order to give enough spread to the range of durability

factors, all were multiplied by $(100/23.35)$. These new values were called the "Normalized Durability Factor (NDF)" and are used in the rest of this report.

When the results of the first and second tests (Table 5) are compared, nine aggregates showed lower average durability factors in the second test and four showed vice versa. But when the individual values are compared, only two aggregates had two lower values in the second test. Because of its longer soaking period in water, the second test showed lower durability factors in general. But when the scatter of the results are taken into account, the differences in two tests are not significant. So, the results of both tests were equally used for the further analysis. In Table 9 are given the Normalized Durability Factors and their average value.

TABLE 8
Air Content Measurement

Air Content (Volume %)		
Aggregate	Fresh Concrete (ASTM C 231 Type B)	Hardened Concrete (ASTM C 457)
BR-3	7.2	4.4
CC-1	7.5	4.4
Ke-1	6.8	3.8
H-1	6.2	3.3
F-2	9.0	4.5
McC	7.5	3.6
BR-5	6.2	3.5
BR-1	7.0	5.1
PC-1	8.0	3.9
MB	6.5	3.4
Ko	6.5	4.4
BM-1	6.5	3.6
H-2	6.0	5.2
HR-2	8.5	4.4

TABLE 9
Normalized Durability Factors

Sample	Normalized Durability Factor NDF				Average
BR-3	2.4	2.8	15.9	14.4	8.9
CC-1	45.7	56.7	22.3	19.4	36.0
Ke-1	38.5	8.3	11.9		19.6
H-1	4.0	2.9			3.5
F-2	48.4	37.6	55.0	45.0	46.5
McC	22.3	39.3	33.3	13.9	27.2
BR-5	17.5	15.6	13.9	14.3	15.3
BR-1	15.9	21.2	21.0	21.4	19.9
PC-1	24.4	11.6	14.1		16.7
MB	51.4	37.8	33.2	20.0	35.6
Ko	43.0	47.4	27.2	9.9	31.8
BM-1	38.3	85.1	104.8	84.4	78.1
H-2	98.2	96.4	87.9	99.6	95.5
HR-2					100.0

Pore-Size Distribution of Aggregate and Freeze-Thaw Durability

In Figure 6 are shown the pore-size distributions of the samples along with the normalized durability factors (NDF) of the concretes made with them.

In Figure 7 are shown three aggregates, McC, BR-5, and H-1; their pore volumes are approximately equal ($McC = 0.080$, $BR-5 = 0.073$, $H-1 = 0.083$ cc/g), but their pore sizes are different. H-1 has the smallest pore size and the lowest NDF among the three. It is clearly seen that, at constant pore volume, the smaller the pore size, the lower the durability.

Figure 8 shows another comparison of two aggregates with equal pore volume and different pore sizes. BR-1 and PC-1 have about the same pore volume, 0.040 and 0.037 cc/g respectively, but their pore sizes are quite different. PC-1 with smaller pore size showed lower durability. But the difference of NDF between these two aggregates is much smaller than the differences among the aggregates shown in Figure 7.

In Figure 9 are shown two aggregates, Ko and BM-1. Ko has a pore volume of 0.021 cc/g and BM-1 has a pore volume of 0.015 cc/g, but the pore-size distribution curve indicates that BM-1 has more pore volume in the range smaller than $25 \overset{\circ}{\text{A}}$ in diameter. The vacuum saturation absorption (Table 10) value for BM-1 was 2.91 percent. Therefore, BM-1 has a little more pore volume than Ko, and its

pore size is much smaller than K_o . But the trend in durability factors is reversed. NDF values were 31.84 for K_o and 78.13 for BM-1. This can be explained by the fact that the water in extremely small pores does not freeze under normal outdoor temperatures. Some, or most of the pores in BM-1 aggregate are too small for the water to freeze in situ at 0°F , which is the lowest temperature to which it was exposed.

In Figure 10 are shown three aggregates, BR-3, BR-5 and BR-1. These three aggregates have approximately equal pore sizes and different pore volumes. The higher the pore volume, the lower the durability factor. The same trend can be seen in Figure 11, which shows two aggregates with same pore size, CC-1 and F-2.

It has been shown that pore size and pore volume of the coarse aggregate are two important factors that affect the durability of concrete under freezing and thawing. There is another factor that might be of importance; that is, the shape of the pore-size distribution, or the range of pore sizes over which the distribution is spread. The effect of the spread in a distribution cannot be examined with a simple comparison of pore size distribution curves and will be discussed later in the section on quantitative correlation between pore size distributions and frost durability of aggregates.

LIMITING PORE DIAMETER IN MICRONS

Figure 6 Pore-Size Distribution and Normalized Durability Factor of Aggregate Samples

Figure 7 Comparison of Samples McC, BR-5, and H-1

Figure 8 Comparison of Samples BR-1 and PC-1

Figure 9 Comparison of Samples Ko and BM-1

Modified Critical Dilation Test

As shown in Figure 5, the temperature-diameter curve of the mortar specimen consisted of two lines. The first part of the line was the simple linear thermal contraction. After the temperature reached the freezing point (super cooling was noticed, to around -1°C), the slope of the line became steeper. This can be explained by the "gel water diffusion process" of Powers and Helmuth [14]. At the point A, the water in large pores started to freeze and the water in small pores remained unfrozen. No expansion was observed at this point because the mortar was air entrained and all the excess volume of water could escape to the air voids. As the temperature went down, the unfrozen water in small pores started to migrate to the ice bodies in large pores and air voids. The ice in the pores is at a higher free energy level than air voids ice, because the ice in the pores is under a higher pressure if there is no free space in the pores. Therefore, the unfrozen water in the small pores migrates to the air voids ice rather than the ice in the pores. The paste shows an over all contraction, and together with the thermal contraction the slope of the curve becomes steeper than in the first part.

The same phenomena are observed with specimens having a sound aggregate, such as HR-2. The only difference is the slope of the curve. The slope of the gel water diffusion process with specimen HR-2 is flatter than that of the mortar specimen because the specimen HR-2 has a lesser amount of paste.

The lines in the temperature-diameter curve are not exactly linear. This is because the temperature and diameter are measured at one point of the specimen, while the temperature in other parts of the specimen are not the same, owing to the one directional freezing.

With the aggregate F-2 which has large pore sizes, temperature rise at the freezing point was observed as shown in Figure 12. These aggregates have pores of 10μ to 1μ in diameter whereas the pores in the paste are smaller than 0.1μ [3]. After the super-cooling period the water in the aggregate starts freezing, and because the pore volume of the aggregate is so large and the pore size range is so narrow, the freezing of water occurs quickly, and the temperature rises. No expansion was observed at this temperature rise, this means that the aggregate was not critically saturated. Because the pore size of the aggregate was far larger than that of the surrounding paste, the water was pulled out of the aggregate by the paste. The main cause of this is the self-desiccation of the paste. This effect was surprisingly large and seems to control the degree of saturation of aggregates. Because of this effect the time of demolding had a large effect on the test results. The sooner the sample was demolded, the higher the degree of saturation was and the larger the expansion. For the purpose of accelerating the test, all the samples were demolded 9 hours, instead of 24 hours, after the casting.

In Figure 12 are also the results from three aggregates, BR-3, H-1, and PC-1. These three aggregates showed expansion in the first

Figure 10 Comparison of Samples BR-3, BR-5, and BR-1

Figure 11 Comparison of Samples CC-1 and F-2

Figure 12

Temperature-Dilation Diagram of Samples F-2, BR-3, H-1, and PC-1

freezing test but at different temperatures. The sample BR-3 with the median pore-diameter (MD) of $0.6\ \mu$ started to expand at -1°C . The sample H-1 with MD of $0.18\ \mu$ started to expand around -3°C , and PC-1 with MD of $0.18\ \mu$ at -5°C . The smaller the pore size, the lower the freezing temperature. The pore size of BR-3 was larger than the threshold pore size of the paste, $0.1\ \mu$, but the degree of saturation of the aggregate remained higher than the critical value and the sample showed a large expansion.

Figure 13 shows the critical dilation test results with the average normalized durability factors obtained from rapid freezing and thawing tests. The ordinate is the dilation ($\epsilon = \Delta d/d$) up to 100×10^{-6} , and the abscissa is the freezing cycles and the soaking period. Three aggregates, BR-3, BR-5, and BR-1 exceeded the critical dilation (100×10^{-6}) in the first freezing cycle. Four other aggregates, H-1, PC-1, McC, and Ke-1, exceeded the critical dilation in the second freezing cycle. Among these seven aggregates which exceeded the critical dilation within two cycles, McC was the only aggregate which had NDF of greater than 20. Three aggregates, ME, Ko, and CC-1, showed gradual increase in dilation and failed at the fourth and sixth cycle. The sample H-2 showed a small dilation in the third cycle, and the dilation gradually increased with the number of cycles but became stable at the 5th and 6th cycles. Even though the test was terminated at 6 cycles (11 weeks), H-2 is not likely to continue to increase in dilation, because it has such a low porosity ($0.006\ \text{cc/g}$ by mercury porosimetry).

Figure 13

Modified Critical-Dilation Test Results

Three samples, HR-2, BM-1 and F-2, showed no dilation after six cycles of freezing and 11 weeks of soaking in water. The sample HR-2 is the control sample aggregate and has no appreciable porosity. The sample BM-1 has a small pore-size and a low porosity (the pore volume of the particular sample used for this test was only half that of the sample used for the rapid freezing and thawing test). Because these two aggregates have a low porosity, it is understandable that they showed no dilation. On the contrary, F-2 aggregate has a large pore volume (0.091 cc/g by mercury porosimetry), and its pore size is from 10 μ to 1 μ in diameter. Because of its large pore size the aggregate was not critically saturated, or, even if the degree of saturation was higher than 0.91, the excess volume of water due to freezing was small enough to be accommodated by the surrounding air voids in the paste.

The results of this modified critical dilation test generally agreed with the rapid freezing and thawing test results. But two differences were noticed. First, two aggregates, CC-1 and F-2, with a large pore size ($MD = 4.8\mu$) showed better durability in this test. As mentioned earlier, because of its slow cooling rate, the freezing front does not proceed as a plane but the freezing starts in the large pores. With the sample CC-1 and F-2, the freezing first starts in the aggregate and the excess volume of water due to freezing can escape to the surrounding paste and air voids. On the other hand, the cooling rate of the rapid freezing-thaw test is much faster, and the specimen is cooled from an exterior surface. Therefore, the freezing starts from the exterior surface and progresses inwards.

The aggregates located in the middle of the specimen do not have any place for the excess volume of water to escape. The aggregates with large pore-sizes seems to benefit by this slow and one-directional freezing test.

Second, three bricks (BR-1, BR-3, BR-5) showed lower durability in this test. The possible reason for this is their pore structure. The comparison of the adsorption values and the surface area calculated from the mercury pore-size distribution, which will be shown later (Figure 18), indicates that bricks have ink-bottle type pores, because their adsorption values are too low, compared with their surface area by mercury porosimetry. If the aggregate has ink bottle pores, the freezing will start at the large pores, which are connected with smaller pores, and excess water has to move through these small pores generating high hydraulic pressures. The permeability is controlled by these small pores. Because the ink bottle pores are scattered in the aggregate, the migration of the excess water will be blocked by the ice body and this will cause a high pressure in the aggregate. If the aggregate does not have ink bottle type pores, the freezing will progress in one direction in the aggregate, and excess water can escape to the surrounding paste and air voids. The retention of water in the aggregate is controlled by the entrance pore diameter instead of by the inside diameter of the ink-bottle pore, so the degree of saturation will be as high as the other natural aggregate with the same pore size distribution.

Absorption Test

Absorption is a rough measure of pore volume. Generally the aggregate with a higher absorption is less durable, as shown in Figure 14. But the absorption by itself is not a precise indicator of durability.

In Figure 15 are compared the pore size (median diameter MD) and the ratio of 24 hours soaking and vacuum saturation absorption values (absorption ratio S). The aggregates with smaller diameters of pores have the higher values of S, because of the higher capillary attraction of the smaller pores.

PCA Absorption - Adsorption Test

Test results are shown in Figure 16. The line in the graph is the border line dividing sound aggregates from aggregates that cause D-cracking, according to the PCA report [34]. The aggregates used in the present study has a three times broader range in adsorption and twice the range in absorption than those used in the PCA study.

The aggregate H-2, which is rated as durable in the rapid freezing and thawing test (NDF = 95.5), is in the region of supposedly D-cracking aggregates. The sample BM-1 (NDF = 78.1), which is also durable, is in the region of pop-out and D-cracking aggregates. These results are probably due to the very small size of their pores, which have therefore a large surface area and a high value of adsorption. Aggregate BR-1 and BR-5, which are

Figure 14 Absorption and Normalized Durability Factor

Figure 15

Median Diameter and Saturation Ratio

Figure 16

PCA Absorption-Adsorption Test Results

rated as non-durable are in the region of sound aggregates. This is also because of their pore structures. Despite a high pore volume, these bricks have low surface areas and this brings them into the sound aggregate region. Considering that their threshold pore diameter is small (about 1μ), these bricks seem to have ink bottle pores.

Generally speaking, an evaluation of aggregates by the absorption-adsorption test does not correlate well with the rapid freezing and thawing test results. From a comparison of the pore-size distribution of the aggregates and the results of the rapid freezing and thawing test, it was found that the pore-size affects the durability greatly in the diameter range of 10μ to 0.1μ . As the pore size becomes smaller its effect on the durability becomes less, and very small pores do not affect the durability at all because the water in those small pores does not freeze at normal outdoor temperatures. Hence, the adsorption value is sensitive to the small pores, leading to the erroneous prediction of the absorption-adsorption test.

Internal Surface Area

It was reported by Blaine et al. [22] that the internal surface area is an indicator of frost durability of aggregates and building materials. The large surface area generally means small pore diameter, low permeability, and high capillary attraction. If so, the material retains water in its pores and the freezing of water generates high hydraulic pressure.

In their studies the internal surface area was measured by sorption method, but it can also be calculated from the results of mercury intrusion measurements. The equation is given by Rootare and Frenzlou [51] as follows:

$$A = \frac{-1}{\cos \theta \gamma_L} \int_0^{V_{\max}} P dv \quad (7)$$

where: A = internal surface area per gram of sample,

θ = contact angle,

γ_L = surface energy of mercury,

P = absolute pressure,

V = intruded pore volume per gram of sample, and

$V_{\max}$ = total intruded pore volume.

This calculation is based on the assumptions of cylindrical pores and non ink-bottle pores. They reported some data that showed that the calculated values agree well with those from sorption measurement by BET.

In Table 10 and Figure 17 are given the calculated internal surface area of aggregates and their normalized durability factors. Except for four aggregates (BM-1, PC-1, H-2, Ko) those with higher surface area showed lower durability. These four exceptional aggregates had small pore diameters (smaller than 0.1μ). The surface area is very sensitive to the pores of small size. On the other hand, the comparison of pore-size distribution and rapid

freezing and thawing test results indicates that the difference of pore size does not affect the durability greatly if the size is small enough (smaller than 0.1μ in diameter).

The surface area is also affected by pore volume, and many combinations of pore volume and pore size can have the same surface area. For instance, BR-1 and H-2 have the same surface area, but different pore volume, pore diameter and durability as shown in Table 11.

TABLE 10
Surface Areas from Mercury Porosimetry Measurement

Sample	Surface Area (m ² /g)				NDF
				Ave.	
BR-3	3.51	2.22	3.32	3.02	8.9
CC-1	0.25	0.25	0.23	0.24	36.0
Ke-1	1.77	1.56	1.96	1.76	19.6
H-1	4.00	4.50	4.04	4.18	3.5
F-2	0.30	0.26	0.23	0.26	46.5
McC	0.84	0.51	0.62	0.66	27.2
BR-5	0.81	0.65	0.56	0.67	15.3
BR-1	0.56	0.59	0.54	0.56	19.9
PC-1	12.82	11.46	11.21	11.83	16.7
MB	0.87	1.29	1.23	1.13	35.6
Ko	2.42	2.89	2.69	2.70	31.8
BM-1	9.92	9.51	9.22	9.55	78.1
H-2	0.58	0.56	0.55	0.56	95.5

Figure 17

Surface Area from Mercury Pore-Size Distribution and Normalized Durability Factor

Figure 18

Surface Area from Mercury Pore-Size Distribution
and Adsorption at 92% RH

TABLE 11
Comparison of BR-1 and H-2

Sample	Surface Area $A(m^2/g)$	Pore Volume (cc/g)	Median Pore Diameter MD(μ)	Durability NDF
BR-1	0.56	0.0392	0.67	19.9
H-2	0.56	0.0061	0.054	95.5

Therefore, the surface area is not an accurate indicator of frost durability.

Adsorption measurement at 92% RH (PCA Test) is also an indicator of surface area. Adsorption values and the calculated surface area values are compared in Figure 13. The 92% RH adsorption values are not biased by the existence of the ink-bottle pores. It is noticed that three bricks (BR-1, BR-3, BR-5) have low adsorption values compared to their surface area calculated from mercury pore-size distribution. This is an indication that these bricks have ink-bottle pores. The rest of the aggregates, which are natural aggregates, have good correlation between adsorption and surface area.

Correlation Between Pore-Size Distribution of Aggregate and Its Frost Durability

The test results show that the pore-size distribution of an aggregate has a good correlation with its frost durability. Neither the absorption, PCA absorption-adsorption, nor surface area has a better correlation.

In this section the quantitative correlation between pore-size distribution of the aggregates and the rapid freezing and thawing test results is obtained by multiple regression analysis. Then this correlation equation will be examined by comparing its predictions with the actual field performance data.

Correlation Equation

In order to obtain a quantitative correlation the multiple regression analysis was made with the aid of a computer.

It is necessary to describe the pore-size distribution numerically. As mentioned before, the pore volume and the pore-size are the two important factors. The median diameter of pores (50-percentile) was chosen to represent the pore-size, and the intruded pore volume was used for pore volume. In addition to these two factors, another factor was chosen to represent the shape of the pore-size distribution curve, or the range of pore-size. This was done by taking the ratio of 25-percentile diameter to the median diameter, and this was named "spread factor (SF)".

The general formula of the correlation equation is:

$$\text{EDF} = f(\text{PV}, \text{MD}, \text{SF}) \quad (8)$$

where:

- EDF = expected durability factor
- PV = intruded pore volume, cc/g,
- MD = median diameter of pores in μ as measured by mercury intrusion, and
- SF = spread factor.

Because the aggregate BM-1 has exceptionally small pores and it is known that some of these small pores are not harmful under freezing, the best fitting formula was first found without including BM-1. Then the pore-size distribution was arbitrarily terminated at various diameters from 70 $\text{\AA}$ to 30 $\text{\AA}$, and the BM-1 data were included. Best fit was obtained with a limiting lower diameter of 45 $\text{\AA}$.

The spread factor (SF) was not as significant as the other two factors, and the range of SF values found with the samples used in this study was not wide enough. Therefore, the spread factor was not considered in the development of the final equation. The following equation was obtained as the best fit.

$$\text{EDF} = \frac{0.579}{\text{PV}} + 6.12 (\text{MD}) + 3.04 \quad (9)$$

where:

- PV = intruded volume of pores larger than 45 $\text{\AA}$,
 MD = median diameter of pores larger than 45 $\text{\AA}$ as
 measured by mercury porosimetry.

The normalized durability factors of the individual concrete beams rather than average values were used as input data. The average value of three pore-size distribution was used as input data for PV, MD, and SF. The examination of the regression equation showed that Equation (9) was statistically significant. 95% Confidence Intervals of the equation constants B_1 ($= 0.579$), B_2 ($= 6.12$), and B_0 ($= 3.04$) were:

$$B_1 = 0.493 \sim 0.664$$

$$B_2 = 3.99 \sim 8.26$$

$$B_0 = 3.74 \sim 9.83$$

In Table 12 are given Expected Durability Factors (EDF) and the residuals. The examination of the residuals showed no particular relation with aggregate type, pore volume, or pore size.

The correlation equation as given by Equation (9) is shown in Figure 19. The ordinate is PV (cc/g) and the abscissa is MD (μ). The NDF values of aggregates are also shown in the graph and they are predicted well by the correlation equation. For the aggregates with MD smaller than 0.1 μ , EDF values are controlled by PV. As MD becomes larger EDF values gradually increase.

TABLE 12
Expected Durability Factor

Sample	Pore Volume PV (cc/g)	Median Diameter MD (μ)	Spread Factor SF	Normalized Durability Factor NDF	Expected Durability Factor EDF	Residual
BR-3	0.1241	0.610	1.37	2.40	11.44	-9.04
				2.78		-8.66
				15.93		4.49
				14.35		2.91
CC-1	0.1107	4.818	1.10	45.74	37.75	7.99
				56.70		18.95
				22.27		-15.48
				19.40		
Ke-1	0.0866	1.185	1.41	38.46	19.98	21.48
				8.27		-8.71
				11.91		-5.07
H-1	0.0832	0.185	1.82	3.98	11.13	-7.15
				2.91		-8.22
F-2	0.0912	4.806	1.21	48.35	38.82	9.53
				37.60		-1.22
				54.95		16.13
				44.97		6.15
McC	0.0791	3.091	1.35	22.31	29.27	-6.96
				39.31		10.04
				33.28		4.01
				13.88		-15.39
BR-5	0.0726	0.792	1.30	17.47	15.87	1.60
				15.59		-0.28
				13.19		-2.68
				14.30		-1.57
BR-1	0.0392	0.670	1.44	15.85	21.91	-6.06
				21.20		-0.71
				20.99		-0.92
				21.41		-0.50

TABLE 12 (con't)

Sample	Pore Volume PV (cc/g)	Median Diameter MD (μ)	Spread Factor SF	Normalized Durability Factor NDF	Expected Durability Factor EDF	Residual
PC-1	0.0368	0.0188	1.72	24.41	18.88	5.53
				11.56		-7.32
				14.13		-4.75
MB	0.0310	0.521	1.86	51.43	24.90	26.53
				37.82		12.92
				33.23		8.33
				20.04		-4.86
Ko	0.0208	0.070	1.82	43.00	31.29	11.71
				47.37		16.08
				27.15		-4.14
				9.85		-21.44
BM-1	0.0079	0.0098	2.97	38.29	76.35	-38.06
				85.05		8.70
				104.80		28.45
				84.37		8.02
H-2	0.0061	0.054	1.56	98.24	98.23	0.01
				96.40		-1.83
				87.92		-10.31
				99.61		1.38

Comparison With Field Performance Data

Since the correlation equation was found to be successful in predicting an aggregate's performance in the rapid freezing and thawing test, this result was compared with the field performance on the aggregates. The final objective is to find the borderline, or pass-fail criterion, based on the field performance record of the aggregates. Basically two approaches were made.

The first approach, A, was to take samples from the existing concrete pavements and examine the correlation equation. This approach is highly reliable because the aggregate sample is taken from the existing concrete pavement. This is possible with this test method because the amount necessary for the mercury porosimetry is small. The second approach, B, was to examine the aggregates whose field performance records were available. Because these aggregate samples were taken from certain ledges of the quarries and the amounts of aggregates obtained were so small, the information obtained from these samples were less reliable compared to the first approach, A.

Approach A

The descriptions of seven samples are given below together with their expected durability factors calculated by equation (9). The first two digits of sample number indicates the number of

Figure 19

Correlation Equation

highway except sample 501. The ages at sampling are given, but they are not the ages when D-cracking started. In the descriptions, the existence of internal cracks are given in case they are clearly seen. The pore-size distribution curves of the samples are found in Appendix D.

(1) Sample No. 651 (Figure D-1, Appendix D)

Location: I-65 at SR 58

Age at Sampling: 17 years

Aggregate: Crushed Stone

Deterioration: A core sample was taken at the center joint where D-cracking showed. Severe deterioration was found in core sample, especially the bottom part was badly cracked.

Air Content: Air content was measured on two core samples.
A = 2.3% and 3.4%

Test Results:

<u>Aggregate No.</u>	<u>Description</u>	<u>EDF</u>
1	Crack through aggregate	35.9
2	" " "	24.1
3	" " "	40.3
4	" " "	19.7
5	No crack	50.6

(2) Sample No. 741 (Figure D-2, Appendix D)

Location: I-74, west of SR 58

Age at Sampling: 14 years

Aggregate: Gravel

Deterioration: D-cracking was found at every joint. Core sample showed cracks through aggregates. Many different rock types were found.

Air Content: $A = 4.0\%$

Test Results:

Aggregate No.	Description	EDF
1	Light green & gray, crack	22.3
2	Gray & black band, fine cracks, not like D-cracking but aggregate's original cracks	77.0
3	Tan, fine crack	57.7
4	Yellowish brown, crack	49.2
5	Yellow, crack	21.1
6	Dark brown	39.4
7	Tan, crack	19.1
8	Tan, no crack	80.7

(3) Sample No. 311 (Figure D-3, Appendix D)

Location: US 31, R-3

Age at Sampling: 30 years or more

Aggregate: Crushed

Deterioration: Only minor D-cracking was found at some joints. Rated as good field performance. Cores were taken, and no crack was found with core sample.

Air Content: $A = 4.7\%$

Test Results:

Aggregate No.	Description	EDF
1	Light, gray, no crack	98.2
2	" " "	365.2
3	" " "	196.2
4	" " "	98.2
5	" " "	50.7
6	" " "	46.0
7	" " "	121.4
8	Tan, looks like a piece of gravel.	23.0

(4) Sample No. 691 (Figure D-4, Appendix D)

Location: I-69, at SR-26

Age at Sampling: 14 years

Aggregate: Gravel

Deterioration: D-Cracking at the joints, No core was taken, but broken pieces of concrete were taken.

Test Results:

Aggregate No.	Description	EDF
1	Gray	13.0
2	Brown	over 100
3	Gray & tan	29.6
4	Brown	122.1

(5) Sample No. 692 (Figure D-5, Appendix D)

Location: I-69

Age at Sampling: 14 years

Aggregate: Crushed stone

Deterioration: D-cracking at joints. No core was taken, but broken pieces of concrete were sampled.

Aggregate No.	Description	EDF
1	Gray	29.3
2	Light tan	36.8
3	Whitish gray	34.1
4	" "	35.9
5	" "	31.6

(6) Sample No. 693 (Figure D-6, Appendix D)

Location: I-69 at SR-18

Age at Sampling: 14 years

Aggregate: Crushed stone

Deterioration: D-cracking at joints. No core was taken, but broken pieces of concrete were sampled.

Aggregate No.	Description	EDF
1	Gray	32.4
2	"	23.9
3	"	57.8
4	"	37.0

(7) Sample No. 501 (Figure D-7, Appendix D)

Location: Private driveway, Lafayette

Age at Sampling: 35 years or more

Aggregate: Gravel

Deterioration: Deterioration was found at the age of 35 years. Sample is a big piece of aggregate (2" diameter).

Aggregate No.	Description	EDF
1	Tan	52.7
2	Tan	59.5

Approach B

Three aggregates with good field performance records and four aggregates with bad field performance records are listed below together with their EDF values.

(1) Aggregates with good field performance

No.	Aggregate Source	EDF
202	Reef Rock, Bluffton	170.0
212	Liston Creek Limestone (1-1S, studied by Dolch [19])	278.9
213	St. Genevieve Limestone (67-2S, studied by Dolch [19])	134.8

(2) Aggregate with bad field performance

No.	Aggregate Source	EDF
301	Jeffersonville Limestone (3-1S, studied by Dolch [19])	35.9
302	Iowa	21.0
695	Pipecreek	29.2
	Probable aggregate source for I-69, No. 692 and No. 693 in Approach A	26.5 36.9
Ke-1	Kenneth (Used in this study as Ke-1)	17.1

In Approach A, a difficulty was found with gravel aggregate. Because of its heterogeneity many different pore-size distributions and EDF values were found. It is difficult to point out the aggregate particle as responsible for D-cracking. Therefore, the gravel sample was regarded as supporting data. Each gravel concrete contained aggregates with low EDF values. With crushed stone aggregates, the situation was far better, but the concretes contained small amounts of different types of aggregates. Even if any crack was found through the aggregate it was not completely clear whether that particular aggregate caused cracking or not.

Borderline

The decision of where to establish the borderline was mostly based on the information obtained through Approach A. Sample 651 was regarded as the typical "borderline" because the D-cracking was first found about 15 years after the construction, and the extension of D-cracking in the region was not severe. The sampled core showed some cracking. Aggregates 2 and 4 were badly cracked. Aggregates 1 through 4 seem to be responsible for cracking. Sample 741 was one of the non-durable aggregates. D-cracking was developed extensively at every joint. But unfortunately it had gravel aggregates and showed a variety of pore-size distributions and EDF values. Three out of eight aggregates had EDF lower than 23. Sample 311 is an example of durable aggregate. Aggregate 1 through

7 were the same type of aggregates having EDF higher than 46.0, but No. 8 was a completely different type of aggregate which looked like a piece of gravel with a round shape.

Sample 691 was also a gravel aggregate. One had quite a low EDF value, 13, and another had 29.6. The rest were over 100. Sample 692 and 693 had basically the same aggregate. Eight out of nine aggregates had EDF lower than 37.0. In Approach B, all the aggregates with good field performance had EDF over 100. The equation (9) can give EDF values larger than 100 for aggregates with a sufficiently small pore volume because of the nature of the equation. The aggregates with bad field performance had EDF values lower than 27.0.

Considering all the information, the following regions were set up.

EDF	Predicted Durability
up to 40	Non-durable
40 to 50	Marginal
over 50	Durable

This decision concerning the borderline needs more supporting data, but the ones given seem to predict the field performance well for the limited samples available to date.

If the pore volume is smaller than $0.012(\text{cc/g})$, the aggregate will have EDF values greater than 50 no matter how small the pore size is. If the median pore diameter (MD) is larger than 6.80μ , the aggregate will have EDF values larger than 50 even if the pore volume is larger than $0.10(\text{cc/g})$. If the proportion of the aggregate with low EDF value is small, the concrete seems to have better durability as a whole.

The aggregate on which the correlation equation is based on cover wide ranges of pore volume and pore size. Practically, most of the natural aggregates pore size distributions have been covered. The amount and distribution of these macro pores are variable, but if they are distributed well through the aggregate and not saturated with water, they will work as air voids in paste. But how much these macro-pores improve the frost durability of aggregates is uncertain. Therefore, it is recommended to calculate EDF based on the pore size distribution in the range smaller than 15μ and count the macro pores as uncertainty on the plus side.

Ink-bottle pore is another unique case. The mercury intrusion method measures only the entrance diameter of pore and fails to measure the inside diameter. As mentioned earlier the entrance diameter controls the retention of water and the permeability, and hence the hydraulic pressure. The correlation equation will give the right durability prediction if the ink bottle pores are saturated with water. If they are not saturated, the larger diameter inside will control the capillarity and the durability will be better than EDF prediction. But, in practice, the correlation equation gives the "safe" value in terms of durability prediction.

Sampling aggregate is important in the practice of durability prediction. It is recommended to sample ledges instead of stock piles. Proper amounts of aggregates should be sampled from each ledge and the EDF values for each ledge should be calculated. When only one ledge shows a low EDF value, selective quarrying is advised.

Mechanism of Failure

According to present ideas, aggregates failure during freezing and thawing is caused by either a large hydraulic pressure or an expulsion of water into the paste. If a sufficiently large hydraulic pressure is generated the aggregate will fail internally, and if enough water is expelled a crack will start in the surrounding paste.

These two hypotheses are based on the assumption that the freezing front proceeds as a plane through the concrete and that all the water on that plane starts to freeze at the same time. This freezing is not always realistic with a material that has a wide variety of pore sizes. The current study has revealed that the freezing may start in the large pores first and then later in the smaller pores. The smaller the pore, the more delayed will be this latter freezing. At the same time, the temperature in the concrete near the surface is probably lower than in the bottom because the concrete pavement is cooled from the surface. Therefore, the process of freezing of water in porous material depends on the pore-size distribution and the cooling rate.

In the modified critical dilation test, the aggregates with small pore size (PC-1, H-1) showed expansion at low temperatures, for example -5°C with PC-1 (Figure 12). The process of freezing would be as follows: The freezing starts in the largest pores in the paste at around -1°C . The excess water escapes to the nearest air-voids and the sample does not show any expansion. The water in smaller pores in the paste, which are too small for the water to freeze in situ at that temperature, migrate to the ice bodies in the air voids and in the capillaries to freeze. The sample shows more contraction because of the loss of water from small pores (gel pores). The freezing also proceeds to the water in aggregates whose pores are so small that the water remains unfrozen. The water near the aggregates's surface migrates to the ice body in the surrounding paste and starts to freeze. The excess water is pushed toward the center of aggregate where water still remains unfrozen. The unsaturated space in the aggregate becomes filled with water, and when all the unfilled space is saturated the aggregate starts to expand as the freezing proceeds. This is the situation that the freezing starts at the exterior and proceeds to the center of aggregates, and the aggregate will show internal fracture when the expansion exceeds the elastic limit. In the situation that the cooling rate is faster and the freezing proceeds in one direction in the aggregate, the excess water moves through the aggregate and generates hydraulic pressure. If the hydraulic pressure is higher

than the aggregate's tensile strength, the aggregate will fail internally, and if not the excess water will be expelled into the paste. By the time the excess water is expelled into the paste, the water in large pores in the paste is already frozen and practically there is no space for the water to escape. In either case, the aggregate is confined in the frozen paste before the water in the aggregate starts to freeze. This happens with the aggregate with small pore sizes, and this is different from what Verbeck and Landgren analyzed by expulsion into the paste mechanism.

Therefore, the pore size of aggregate has three important roles in the freezing and thawing durability of concrete: (1) retention of water by capillary attraction, (2) permeability, relating hydraulic pressure, and (3) freezing temperature, relating freezing process.

CONCLUSIONS

1. Pore-size distribution of aggregates measured by mercury porosimetry has a good correlation with freezing and thawing durability of concrete as measured by ASTM C 666. Pore volume and median pore diameter are the two most important properties of an aggregate affecting its frost durability. The larger the pore volume, the lower the durability. The smaller the pore diameter, the lower the durability. However, pores smaller than 45 $\text{\AA}$ ^o do not affect the durability, probably because they are so small that the water does not freeze in them at ordinary outdoor temperatures. In the pore-size range larger than 1 μ in diameter, the durability of concrete drastically decreases as pore diameter decreases.

2. The following correlation equation was found between the pore-size distribution of the aggregates and the frost durability of concrete.

$$\text{EDF} = \frac{0.579}{\text{PV}} + 6.12 (\text{MD}) + 3.04$$

where:

EDF = expected durability factor

PV = intruded volume of pores larger than 45 Å^o
in diameter, cc/g,

MD = median diameter of pores larger than 45 Å^o
in diameter, μ, as measured by mercury
porosimetry.

This equation can be used to predict the frost durability of an aggregate. Based on comparisons with field performance data, the following border lines were determined.

EDF	Predicted Durability
up to 40	Non-durable
40 to 50	Marginal
over 50	Durable

Further experience with this equation may dictate small changes in these dividing lines.

3. The water in aggregates with small pores freezes after the much of the water in the surrounding hardened cement paste has frozen and confined the aggregate. Therefore, when the water in the aggregate expands on freezing, a dilation type of failure occurs that is neither a critical distance nor an expulsion into the paste mechanism.

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APPENDICES

APPENDIX A

APPENDIX A

In this appendix, the analyses of the materials used and the mix design of the concrete for the rapid freezing and thawing test (ASTM C 666A) are shown.

TABLE A-1
Analysis of Cement

<u>Chemical Analysis, percent</u>		<u>Fineness:</u>	
SiO ₂	21.33	325, % Passing	86.3
Al ₂ O ₃	4.96	Wagner, cm ² /g	1820
Fe ₂ O ₃	2.44	Blaine, cm ² /g	3610
CaO	64.71		
MgO	1.14	<u>Compressive Strength, psi:</u>	
SO ₃	3.32	1-Day	2095
Na ₂ O	0.07	3-Day	3650
K ₂ O	0.72	7-Day	4550
T.A. as Na ₂ O	0.54	28-Day	5780
Ignition Loss	1.18		
Insoluble Residue	0.33		
F	2.50		
R	2.88		
A/F	2.03		
<u>Potential Compound Composition, percent</u>			
C ₃ S	55.05		
C ₂ S	19.62		
C ₃ A	9.02		
C ₄ AF	7.42		
CaSO ₄	5.64		

TABLE A-2

Sieve Analysis of Sand for ASTM C-666 Test

<u>Sieve No.</u>	<u>Wt. % Retained on Sieve</u>
4	0
8	2
16	10
30	29
50	45
100	12
Passing 100	2
Fineness Modulus = 2.39	

TABLE A-3

Gradation of Coarse Aggregate for ASTM C-666 Test

Sieve Size in.		
Passing	Retained	Wt. %
1	1	0
3/4	3/4	25
1/2	1/2	33
3/8	3/8	17
	No. 4	25

TABLE A-4

Mix Design of Concrete for ASTM C-666 Test

Mix Design for 0.75 cu. ft. of Concrete	
Cement	15.6 lbs.
Water	7.8 lbs.
Fine Aggregate	33.0 lbs.
Coarse Aggregate	50.0 lbs.
Air Entraining Agent, Master Builders MBVR	sufficient to provide 5% air

APPENDIX B

APPENDIX B

This appendix contains the pore-size distribution curves of the aggregate used in this study.

Aggregate	Figure No.
BR-3	B-1
CC-1	B-2
Ke-1	B-3
H-1	B-4
F-2	B-5
McC	B-6
BR-5	B-7
BR-1	B-8
PC-1	B-9
MB	B-10
Ko	B-11
BM-1	B-12
H-2	B-13
BM-1*	B-14

* This particular sample was used for the modified critical dilation test.

Figure B-1 Sample BR-3

Figure B-2 Sample CC-1

Figure B-3 Sample Ke-1

Figure B-4 Sample H-1

Figure B-5 Sample F-2

Figure B-6 Sample McC

Figure B-7 Sample BR-5

Figure B-8 Sample BR-1

Figure B-9 Sample PC-1

Figure B-10 Sample MB

Figure B-11 Sample Ko

Figure B-12 Sample BM-1

Figure B-13 Sample H-2

Figure B-14 Sample BM-1

APPENDIX C

APPENDIX C

Modified Critical Dilation Test Results

The temperature-dilation diagrams of the samples are shown in Figures C-1 through C-12. In each figure the ordinate is the dilative strain and the abscissa is the temperature. In some cases, the sample dilated upon the first freezing cycle. In these cases, the results of the non-dilative HR-2 sample are also shown for comparison. The small numbers in the circles indicate the freezing cycle from which the indicated curve was obtained. Each diagram also lists the maximum dilation observed on each freezing cycle. The results of samples F-2, BM-1 and HR-2 are shown in the same figure, each by one diagram, since these three specimens showed no dilation during the tests.

Figure C-1 Sample BR-3

Figure C-2 Sample CC-1

Figure C-3 Sample Ke-1

Figure C-4 Sample H-1

Figure C-5 Sample McC

Figure C-6 Sample BR-5

Figure C-7 Sample BR-1

Figure C-8 Sample PC-1

Figure C-9 Sample MB

Figure C-10 Sample Ko

Figure C-11 Sample H-2

Figure C-12 Sample F-2, BM-1, HR-2

APPENDIX D

APPENDIX D

This appendix contains the pore-size distributions of the aggregates sampled from the existing concrete pavements and of aggregates with known field performance.

Sample	Figure No.
No. 651	D-1
No. 741	D-2
No. 311	D-3
No. 691	D-4
No. 692	D-5
No. 693	D-6
No. 501	D-7
No. 202	D-8
No. 212	D-9
No. 213	D-10
No. 301	D-11
No. 302	D-12
No. 695	D-13

Figure D-1 Sample No. 651

Figure D-2 Sample No. 741

Figure D-3 Sample No. 311

Figure D-3 Sample No. 691

Figure D-5 Sample No. 692

Figure D-6 Sample No. 693

Figure D-7 Sample No. 501

Figure D-8 Sample No. 202

Figure D-9 Sample No. 212

Figure D-10 Sample No. 213

Figure D-11 Sample No. 301

Figure D-12 Sample No. 302

Figure D-13 Sample No. 695