SCHOOL OF
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JHRP-85-3

ABSORPTION AND ABSORPTIVITY OF
AGGREGATES AS INDICATORS OF FROST
DURABILITY

FINAL INFORMATIONAL REPORT

Jack Duvall Hunter II

PURDUE UNIVERSITY

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Informational Report

ABSORPTION AND ABSORPTIVITY OF AGGREGATES AS INDICATORS OF FROST DURABILITY

TO: H.L. Michael, Director
Joint Highway Research Project

January 30, 1985

FROM: W.L. Dolch, Head
Materials Engineering Area

File: 5-8

The attached final report of research conducted and authored under my direction by Mr. Jack Duvall Hunter II in partial fulfillment of the requirements for the Master of Science degree in Civil Engineering is forwarded as information to the Board. It did not result from a JHRP or HPR approved project and had no sponsorship or funding, but it is good research and adds to the information reported from earlier research relative to pore size distribution within aggregates and absorption characteristics.

Attempts were made to correlate the Expected Durability Factor (EDF) with various functions of absorptivity and absorption. A function called the Absorptivity Absorption Factor (AAF) was developed. There is a fair relationship between the EDF and the AAF for the less durable materials. The AAF, which is easy and inexpensive to determine, offers the possibility of being a useful indicator of aggregate durability.

The report is furnished as new information on an important subject.

Sincerely,

W.L. Dolch
Research Associate

cc: A.G. Altschaeffl
J.M. Bell
W.F. Chen
W.L. Dolch
R.L. Eskew
J.D. Fricker
W.H. Goetz

G.K. Hallock
J.F. McLaughlin
R.D. Miles
P.L. Owens
B.K. Partridge
G.T. Satterly
C.F. Scholer

R.M. Shanteau
K.C. Sinha
J.R. Skinner
C.A. Venable
L.E. Wood
S.R. Yoder

Civil Engineering Building
West Lafayette, Indiana 47907

INFORMATIONAL REPORT

ABSORPTION AND ABSORPTIVITY OF AGGREGATES
AS INDICATORS OF FROST DURABILITY

by

Jack Duvall Hunter II

Joint Highway Research Project

File: 5-8

This research was performed in the School of Civil Engineering by the author in partial fulfillment of the requirements for the Master of Science degree in Civil Engineering.

Purdue University
West Lafayette, Indiana 47907

January 30, 1985

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ABSTRACT

Hunter, Jack Duval II. MSCE, Purdue University, December 1984. Absorption and Absorptivity of Aggregates as Indicators of Frost Durability. Major Professor: W.L. Dolch.

Eleven aggregate materials were selected, and measurements were made on individual pieces of the absorption, absorptivity, and pore size distribution by mercury intrusion. The Expected Durability Factor (EDF) was calculated from the pore size distribution.

Attempts were made to correlate the EDF with various functions of the absorptivity and absorption. An intermediate absorptivity value may be an indicator of poor durability.

A function called the Absorptivity Absorption Factor (AAF) was developed. There is a fair relationship between the EDF and the AAF for the less durable materials, and the AAF, which is easy and inexpensive to determine, offers the possibility of being a useful indicator of aggregate durability.

INTRODUCTION

Statement of the Problem

D-cracking is the name given to a type of deterioration of concrete, primarily of pavements and other flatwork. The cause of this durability failure is freeze-thaw action on a concrete containing susceptible coarse aggregate that has become critically saturated with water. This problem, once thought more or less under control by judicious selection of materials, has become distressingly common in recent years in states that experience severe winters and, no doubt, elsewhere in the world as well.

D-cracking appears first at those locations -- joints, edges, and pavement bottom -- that most readily become saturated with water. The cracks are more or less parallel to these structural features and to each other. Typically then, the cracking proceeds inward until the pavement is completely destroyed. The problem necessitates a series of patches and early and expensive resurfacing, or even complete replacement of the pavement.

Air entrainment, which protects the paste component of the concrete from similar failure, is of no use when a bad coarse aggregate is the cause of the problem. The only way of avoiding this difficulty is to use a coarse aggregate

that is not susceptible. Therefore, a reliable test method that will detect bad aggregates is obviously desirable. Many have been tried, but so far most have proved unreliable. The best test method, at least until recently, has been to make concrete with the aggregate in question and test the concrete in freezing and thawing exposure. But a reliable test on the aggregate alone, without the necessity of making concrete, would surely be preferable. Such tests, e.g. absorption or sulfate soundness, have been used extensively, but have been shown to have so many exceptions that reliance on them is chancy, to say the least.

Since the problem concerns the freezing of water that has been absorbed into the coarse aggregate particle, the solution must be related to its pore structure. Recent work has shown that the pore size distribution of the coarse aggregate can be related to the likelihood of the development of freeze-thaw failure and D-cracking (1,2). This relationship may prove to be a reliable diagnostic test that can be performed on the aggregate alone. But even so, the procedure is lengthy and requires comparatively expensive equipment and sophisticated procedures performed by trained personnel. A simple and straightforward method is still to be desired, even if its utility were limited to a rough screening function.

Two parameters of aggregates, which are related to the porosity and pore size distribution of the material, are the absorption and the absorptivity. The determination of these

parameters is simple and rapid and requires only general laboratory equipment. The aim of this investigation was to see if these parameters could be related to the freeze-thaw performance of an aggregate and the likelihood of its causing D-cracking when incorporated into concrete.

Literature Review

Much research has been done and reported on the subject of freeze-thaw durability of concrete and the test methods to analyze and predict it. General reviews are those of Newlon (3), Dolar-Mantuani (4,5), Larson (6), and ACI Committee 201 (7). Freeze-thaw failure can arise in either the paste or coarse aggregate component. That in the paste is completely preventable by the use of proper air entrainment (8), and is of no further concern here. D-cracking is caused by deficiencies of the coarse aggregate.

Deficient aggregates are characterized by relatively high porosity and the consequent high absorption and low bulk specific gravity (9,10). But long ago (11) a pore size factor was also identified as important, with small pores contributing to freeze-thaw problems and consequent D-cracking.

The most reliable test method to detect bad aggregates is the freeze-thaw testing of concrete samples containing them. These tests are reviewed by Newlon (3). But, as previously mentioned, a reliable test of the aggregate alone is obviously desirable.

Many aggregate tests have been proposed and investigated. The list includes absorption, sulfate soundness, specific gravity, degree of saturation, unconfined freeze-thaw resistance, and petrographic examination.

The unreliability of the sulfate soundness test to predict freeze-thaw resistance of an aggregate, in spite of its widespread use, is well documented (5,10). Absorption alone is only slightly better (10). All the others have also so many exceptions and such statistical unreliability that they cannot be relied on with any real degree of confidence.

Recent years have brought newer ideas and test methods. Among them can be mentioned the Iowa Pore Index test (12) and the PCA Absorption-Absorption test (13). The jury may be still out on these; it cannot be said they have proved themselves to be reliable.

The mechanisms of failure of aggregates in freeze-thaw exposure are reasonably well understood (14). Whichever of them may be applicable in a given instance, the pore structure of the aggregate is of primary importance. By pore structure is meant the volume and sizes of pores in the porous solid. There are several ways of characterizing this pore structure, each dependent on some sort of model, but probably the most significant and widely used is the technique of mercury intrusion porosimetry (15).

In the mercury porosimeter, the evacuated sample of porous material is immersed in mercury, and then the amount

intruded into the pores is measured as a function of the applied pressure required to cause its entry. This pressure is related to the size of the pore by means of a model, most usually a bundle of cylindrical pores of various sizes. Several commercial instruments are available, and this has now become the method of choice.

This method was used by Winslow and his coworkers (1,2,16,17) to describe the pore size distribution of coarse aggregates used in Indiana pavements. A good correlation was found between the freeze-thaw behavior of laboratory samples (16) and field pavements (17) and a parameter obtained from the pore size distribution curve of the coarse aggregate used. This parameter was named the Expected Durability Factor, defined as

$$\text{EDF} = C_1/V + C_2\bar{d} + C_3 \quad (1)$$

where EDF = Expected Durability Factor
 V = intruded pore volume for pores
 larger than 45A, cu cm/g of sample
 $\bar{d}$ = average pore diameter, i.e. the
 diameter corresponding to an intrusion
 of V/2, micrometres
 C_1, C_2, C_3 = constants

The values obtained for the constants were: $C_1 = 0.579$, $C_2 = 6.12$, and $C_3 = 3.04$. The smaller the value of the EDF, the worse the aggregate in terms of frost durability.

The second study (17) delineated a critical EDF value of 50. Those pavements containing aggregate more than 10 percent of which had a value less than 50 were found, almost without exception, to have given poor performance in freeze-thaw exposure and to have exhibited consequent D-cracking. If the presently available data are confirmed by further use, the Expected Durability Factor may well become the best diagnostic parameter yet devised to predict the suitability of a coarse aggregate for resistance to frost problems in concrete.

The absorptivity is a parameter of a porous solid related to the rate at which it imbibes a liquid, usually water, by capillary action. It was defined by Powers and Brownyard (18) as

$$V^2/A^2 = K_a t \quad (2)$$

where V = volume of liquid absorbed in time t
 A = cross sectional area of porous solid,
 normal to the flow direction of the
 liquid
 t = time from the start of imbibition
 K_a = absorptivity

The SI units of absorptivity are m²/s, but others are more often used. The initial surface absorption (19), which is a British Standard used to characterize pavements and other concrete surfaces, is a similar parameter. The Iowa Pore

Index (12) has analogous aspects, since it determines the amount of water absorbed in a given time and under a given pressure, after a short initial absorption has first taken place. Both of these differ importantly from the absorptivity in that they employ a pressure applied to the water being absorbed, whereas in the absorptivity test the driving force is only the capillary pressure of the liquid meniscus in the porous sample.

The absorptivity has been used only a little in the study of aggregates (21); the indication was that bad limestone aggregates had a comparatively large value of K_a . The method was also used on mortar samples, as a measure of the effectiveness of applied curing (22).

Approach Used in this Work

A suite of samples of aggregates from Indiana was selected. Absorptivity, absorption, and pore size distribution were determined on the same individual pieces. The resulting values were correlated with each other and with the calculated Expected Durability Factor.

EXPERIMENTAL WORK

Samples

The samples used were the residues from those used by Kaneuji (1), so his report should be consulted for details. In that work several gaps in the properties of the materials were filled with three locally obtained bricks. The samples used in the present work were all of the stone samples used by Kaneuji and one of the bricks. They are listed in Table 1.

Sample Preparation

Several pieces of typical appearance were selected from each of the sample sources. Working samples were then prepared either by coring with a small diamond bit if the piece was large enough, or by sawing out small roughly prismatic pieces with a diamond blade saw. The dimensions of these pieces were of the order of a few cm, and their weights were a corresponding few grams.

It is important to state that the comparisons made later apply, deliberately, only to the individual piece tested. No implication is made of wider applicability. Indeed the original quarry samples were taken with an eye only toward obvious uniformity, and no implication was ever

Table 1. Samples Used.

<u>Sample No.</u> *	<u>Geologic Origin</u>
CC-1	Kokomo limestone
Ke-1	Kokomo limestone
H-1	Guthries Creek limestone
McC	Geneva dolomite
BR-1	(Brick sample)
PC-1	Mississinewa shale
MB	Louisville limestone
Ko	Kokomo limestone
BM-1	New Albany shale
H-2	Harrodsburg limestone
HR-2	St. Genevieve limestone

* These designations are the same as those used by Kaneuji (1).

made that they are representative of the quarries from which they came.

After the samples of aggregate were formed, each was cut and polished on an end so as to have a smooth face with an area that could be determined by regular geometric methods. For the samples that were cored, this would mean the area was calculated by measuring the diameter. For the other samples, the shape was prismatic and the area was calculated by measuring the average width and height of the base of the sample with vernier calipers.

The samples were cut on a small diamond-blade saw operating at slow speed. After the samples were cut, they were polished using a lap plate with a water based, medium grit grinding compound. Care was taken to achieve the sharpest edge possible to minimize error in measuring the area of the sample.

The samples were then washed free of all grit and were rubbed firmly to remove any loose fragments or jagged edges. This was done so that during the drying process none of the samples would break or disintegrate.

The general procedure was first to trim and shape the sample, then to oven dry it at 110 C. Next the absorptivity was determined. Then the piece was immersed for 24 hours, and its absorption was determined. Then it was dried again and the mercury intrusion was performed, giving the pore size distribution curve, from which the Expected Durability Factor was calculated.

Absorptivity

The absorptivity was determined as follows. The oven dry piece of sample was weighed to the nearest 0.1 mg. Several pieces of filter paper were put in the bottom of a Petri dish, and water was added until the paper was thoroughly soaked and the surface was essentially a free water surface, as judged by the appearance of free water when the surface of the soaked papers was lightly touched. Then the polished face of the piece, whose area had been previously measured, was placed on the wet surface at time zero, and an electric stopwatch was started. At suitable times thereafter the process was interrupted, the bottom of the piece was surface dried by touching it to a wet, well-wrung cloth, and the piece was reweighed. This interruption typically took about 20 seconds. It is assumed that no significant redistribution of water occurred within the piece during this period. Then the piece was replaced on the wet surface, and the watch was restarted. In this way several sets of data satisfying equation (2) were accumulated. The conversion of weight of water absorbed to its volume was made by assuming a density of 1 g/cu cm.

Equation (2) can be rectified by taking logarithms, so it should plot as a straight line with a slope of 0.5 on a log-log plot. Such plots were made for each run, and K_a was then determined by taking the ordinate

at a time corresponding to one minute. An example of the absorptivity plots is shown in Figure 1. The reported units for K_a are cm^2/min . The minimum number of data points taken for any sample was three, and the maximum was thirteen.

Absorption

After the absorptivity run, the piece was immersed in water for 24 hr, surface dried, and weighed. The absorption was then calculated in the usual way, i.e. the water absorbed per unit weight of dry solid.

Pore Size Distribution

After the absorption was measured, the piece was redried in the oven for 24 hr. It was then cooled in a desiccator.

The mercury intrusion instrument was an Aminco porosimeter operating to a maximum pressure of 60000 psi. The techniques used and the corrections applied to the data were the same as those used by Kaneuji (1), with one exception. The Washburn equation relating the applied pressure to the pore size that will be entered by mercury at that pressure is

$$P = -4 \gamma \cos \theta / d \quad (3)$$

where P = applied pressure
 γ = surface tension of mercury
 θ = contact angle of mercury on the
 solid sample

Figure 1. Absorptivity Curve, Sample Ko

d = diameter of assumed cylindrical pore

In Kaneuji's work (1,16) the numerator of the right side of equation (3), which is constant for a given sample, was determined directly by using samples with small drilled holes of known size. A back calculation, assuming a surface tension of 484 dynes/cm, gave contact angles ranging from 118° to 130° , and averaging 125° . This is the value that was assumed here, as was also done by Lindgren (2,17). A surface tension of 480 dynes/cm was also assumed. The maximum error that would have been introduced into Kaneuji's data by this assumption would have been about 30 percent in the calculated pore size, and the average error was probably much less.

If the piece of sample was too large for the penetrometer chamber, it was broken into smaller pieces, and in any event, the face used for the absorptivity determination was included in the portion used for the pore size distribution determination. An example of the pore size distribution curves is shown in Figure 2.

Figure 2. Pore Size Distribution Curve, Sample Ke-1

DATA

Several individual pieces from each source were run in the absorptivity determinations, and the data curves were plotted. A selection of only one sample was then made for the further determinations of absorption and pore size distribution. This selection was made on the basis of the absorptivity curve being "normal", without deviations or kinks that would indicate some internal heterogeneity of the piece in question.

What was required was data from a suite of substances with differences that would more or less span the spectrum that might be encountered in the field. Runs on several pieces from the same source would give results closely similar to each other and would be pointless in the present context. Further, there was no attempt made to associate these results with any special source or with the field experience of these materials. The comparisons to follow are all internal and self consistent.

An example of the absorptivity curves is shown in Figure 1. This curve has the theoretical slope of $1/2$, and most of the others had this slope or one reasonably close to it. There were, however, exceptions. The curves

for the Ke-1 samples had slopes of roughly 0.9; those for H-1 were about 0.7; those for CC-1 and BR-1 were variable, down to about 0.1.

The reasons for these differences are not understood. They seem not to be due to experimental error, because individual curves are fairly reproducible. The differing slopes mean that the exponent in equation (2) is something other than 2; indeed the differences can be large. But if the process of imbibition of a liquid by a porous solid is analyzed, the result is an expression, analogous to equation (2), that has an exponent of 2 (21). This analysis is for a model of equal-sized, non-circular, tortuous pores. The exponent 2 is the consequence of an integration and has nothing to do with the model. The only assumptions of the analysis are that all forces are small with the exception of the capillary force causing ingress of the liquid and the viscous force causing its retardation. So the only speculation that can be made is that the actual porous system in these exceptional rocks is so much different from a bundle of capillary tubes that the model does not nearly apply. But this goes against the common sense that there is no logical reason why these rocks should be different from the majority in this regard.

In any event, the absorptivities for these rocks were calculated from the absorptions at one minute exposure, so the values are formally correct even in those instances where the data seem not to follow equation (2).

The data obtained are presented in Table 2. The absorptivity values are given as pK_a where $pK_a = \log (1/K_a)$. In the calculation the units on K_a were cm^2/min . The absorptions are given as fractions. The Expected Durability Factors were computed from the pore size distribution curves, using equation (1). Also given are the Expected Durability Factors reported on these same materials in the earlier study (1), as a matter of interest and to show that the samples used here were substantially the same.

Table 2. Data

<u>Sample No.</u>	<u>pK_a</u>	<u>Absorption</u>	<u>Expected Durability Factor</u>	
			<u>This Study</u>	<u>Earlier Study (1)</u>
Ko	4.89	0.0190	33.8	31.3
Br-1	4.07	0.0202	20.8	21.9
McC	2.72	0.0482	24.2	29.3
CC-1	1.17	0.1016	38.1	37.8
H-1	3.30	0.0668	12.0	11.3
Ke-1	2.26	0.0934	16.5	20.0
H-2	6.26	0.0067	75.8	98.2
BM-1	6.36	0.0222	44.6	76.4
HR-2	6.11	0.0057	293.	----
MB	4.68	0.0173	27.2	24.9
PC-1	3.99	0.0413	18.4	18.9

DISCUSSION

In this discussion the values of pK_a were calculated from K_a values in cm^2/min . The absorption values in the combined parameters were fractions, but for convention's sake, when absorptions alone are plotted the unit is percent.

It is implicitly assumed in most of what follows that the earlier studies were correct, and that there is a direct relationship between EDF and the durability, or more exactly the tendency toward D-cracking of concrete made with the aggregate. So when reference is made to a 'durable' aggregate, what is meant is one whose EDF is relatively high, greater than about 50, and which would not cause D-cracking of the concrete pavements in which it was used.

Durability and Absorption

Absorption has long been used as an indicator of the durability of an aggregate, no doubt because of the simplicity of its measurement and because of the inherent logic involved. It stands to reason that the more water an aggregate can absorb, the poorer will be its performance in freeze-thaw exposure. Limits of the order of 3 percent

or 5 percent have frequently been imposed in specifications. But the relation between absorption and durability, as measured by some laboratory test, has been shown to be widely scattered (10), while being roughly in the expected direction. Work on Indiana aggregates (2,17) has shown that a large number of the non-durable aggregates would nevertheless pass the current state highway specifications; indeed, they did, or they would not have been used in pavements from which they were extracted.

The relationship between the EDF and absorption for the aggregates used in this study is shown in Figure 3. It can be seen that the two rocks with the smallest absorption, H-2 and HR-2, are durable and the others are not. This is only what would be expected from the definition of the Expected Durability Factor. It can be seen from inspection of equation (1) that a material with a pore volume of less than about $1.2 \text{ cm}^3/\text{g}$ will have an EDF larger than the critical 50 no matter what its pore size. The absorption is not, of course, equal to the pore volume, unless the degree of saturation is 100 percent, but still there is at least a rough correspondence between the two. So perhaps it can be said that a material with an absorption less than about one and one-half percent ought to be durable no matter what its other characteristics.

It should be pointed out that this durability would not necessarily be the result of the aggregate being in the

Figure 3. EDF vs. Absorption

class called elastic accomodators by Verbeck and Landgren (14). These rocks, which cannot be harmed by freezing under any circumstances, have maximum absorptions of perhaps a few tenths of a percent.

The samples with higher absorptions, while all non-durable, have no relationship between their EDF and absorption values. The data for these rocks, plotted to a larger vertical scale, are shown in Figure 4. Unfortunately, in this study there were no samples from the class of aggregates that are durable because of their large average pore size. Equation (1) shows that materials with an average pore size larger than about 8 microns will be durable no matter what their absorptions.

Absorptivity and Absorption

The absorption is the weight of water absorbed per unit of oven dry weight of the sample. To avoid ambiguity the conditions of the experiment should be stated. The absorptions reported here are for 24-hr immersion, and if this is the case, the usual practice is to omit the qualifying phrase and refer merely to the 'absorption'.

If the dynamics of the absorption of water into a porous solid are analyzed, it is possible to relate the absorptivity to the properties of the solid (21). For a model of pores that are round, straight cylinders the result is

Figure 4. EDF vs. Absorption for Non-Durable Samples

$$K_a = Cdn^2 \quad (3)$$

where d = pore diameter
 n = porosity
 C = a constant involving only properties of the liquid

The porosity is the volume of voids per unit of total, or bulk, volume of the material. So the relationship between the porosity and the absorption is

$$n = \frac{Ax_b}{S_w x_w} \quad (4)$$

where A = absorption
 S_w = degree of saturation
 x_w = unit weight of water
 x_b = bulk unit weight of sample

The degree of saturation is the fraction of the pore volume that is occupied by water. It is usually high, in the region of 0.8-0.9 for non-durable aggregates after 24 hr immersion.

If the porosity is eliminated from equations (3) and (4) the result is

$$K_a = \frac{Cx_b^2 d A^2}{S_w^2 x_w^2} \quad (5)$$

Therefore it can be seen that the absorptivity is directly proportional to the pore size and the square of the absorption.

As a matter of somewhat peripheral interest, the values for pK_a and absorption are plotted in Figure 5. The relationship is that implied by equation (5), i.e., the higher the absorption, the higher the absorptivity and, therefore, the lower its negative logarithm, which is pK_a .

Durability and Absorptivity

The only other work in which the absorptivity of aggregates was measured (21) indicated that the less durable aggregates had the higher absorptivities. The relationship for the materials studied here is shown in Figure 6. The value for Hr-2 is omitted ($EDF = 293.$, $pK_a = 6.11$). The EDF values for HR-2 and H-2 are probably the least accurate of any, because they are based on small values of the total porosity. So any errors in its measurement would cause relatively large errors in the calculated value of EDF.

Figure 6 seems to show an intermediate region of lowest EDF and worst durability. High values of pK_a correspond to low values of absorptivity, mostly due to low porosity values. Such materials ought to have high EDF and durability, as they seem to. At lower values of pK_a the durability is reduced because of higher porosity (and absorption). But at still lower values the indication is of an increased EDF, probably because of a larger pore size becoming influential

Figure 5. pK_a vs. Absorption.

Figure 6. EDF vs. pK_a

in the calculation. The material with the lowest pK_a is CC-1, which has the highest absorption (10.16%), but its average pore size is 5.0 microns. The next highest pK_a is that of Ke-1, whose porosity is almost as high as that of CC-1, with an absorption of 9.34% but a pore size of only 1.3 microns and therefore a considerably smaller EDF than CC-1.

It is of interest to see that the implications of Figure 6 are somewhat confirmed by the data from the earlier study (21). Five aggregates were tested then, two of which had good field histories while the other three had been non-durable in pavement concrete. The 'good' materials had pK_a 's of 6.65 and 6.23, while those of the 'bad' aggregates were 5.14, 2.96, and 4.40. It can be seen that these five values conform to the implications of Figure 6 with respect to their probable EDF's.

So Figure 6 offers the possibility of using the absorptivity alone as an indicator of the probable durability of an aggregate material. More samples would have to be run before such a recommendation could be made, but the possibility exists. Especially needed are data for the aforementioned aggregates with large pore sizes. The so-called reef rocks of central Indiana are one example.

The 'Logical' Analysis

A relationship among absorption, absorptivity, and durability can be derived in a relatively straightforward or 'logical' manner as follows.

Equation (1) is

$$EDF = \frac{C_1}{V} + C_2d + C_3 \quad (1)$$

The value of C_3 is approximately 3, which is small compared with most values of EDF. Therefore, if C_3 is eliminated from (1) and the bar over d is henceforth understood, equation (1) becomes

$$EDF = \frac{C_1}{V} + C_2d \quad (6)$$

As previously discussed, the pore volume is proportional to the porosity and roughly equal to the absorption. So equation (3) can be transformed to

$$K_a = C_4dA^2 \quad (7)$$

Now, if this value for d is inserted into equation (6) and A is substituted for V , (6) becomes

$$EDF = \frac{C_5}{A} + \frac{C_6K_a}{A^2} \quad (8)$$

If now (8) is multiplied by A and rearranged, it becomes

$$\frac{K_a}{A} = C_7 + C_8 A(\text{EDF}) \quad (9)$$

which is linear in K_a/A and $A(\text{EDF})$.

These results are plotted in Figure 7, except for those for CC-1 ($1000K_a/A = 665$, $A(\text{EDF}) = 3.87$), which would be off the page by a ten factor.

The point lying farthest to the right and almost on the x axis is that for HR-2. If this one is also considered extraneous and eliminated, the remaining points are shown on Figure 8. The least squares line is shown and has a coefficient of variation of $r = 0.87$. This relationship is fair, but only because it is essentially a 'three point' curve, i.e. the two highest values have a statistical weight disproportionate to their importance, because the others are so closely grouped.

A possible reason for the poor agreement is that equation (3), and therefore equation (7), omits an important property of the porous material. As previously stated, equation (3) is the result of the analysis of a model of a porous material with round, straight pores. But real porous materials, and specifically the rocks in question in this study, have pores that are irregular in cross section and through which a flowing fluid takes a tortuous rather than a straight path.

Figure 7. K_a/A vs. $A(EDF)$

Figure 8. K_a/A vs. $A(EDF)$ (Nine Samples)

If the analysis is made for a material with tortuous pores of irregular cross section, the result is

$$K_a = \frac{C'dn^2}{k_o k_t} \quad (10)$$

where k_o = a shape factor for the pore cross section

k_t = tortuosity

The shape factor is 2 for a round pore and has been shown to be about 2.7 for porous materials of the kind considered here (23). The tortuosity is the square of the ratio of the length of the real, microscopic, tortuous flow path to the macroscopic or 'nominal' length of flow path (21, 24). The value of the tortuosity is, obviously, unity for a straight tube. For a bead pack of more or less equal sized spheres the measured value (20) is about 2.0. Values for consolidated porous media, such as those in question here, are higher. For aggregates, values measured by an electrical conductivity method (21) have varied from about ten to a few hundred, with the higher values being for the less porous rocks, which is only to be expected.

The shape factor k_o is fairly constant, and so is not important to the relationship under discussion. But equations (7-9) ignore the tortuosity, and this neglect is surely the reason for at least part of the poor agreement found in Figures 7 and 8. Practically speaking, this is

a moot point, because the tortuosity is difficult to measure. So, the data shown here probably do not justify the use of equation (9) to calculate the EDF from measured values of the absorption and the absorptivity.

Absorptivity Absorption Factor (AAF)

The failure of the 'logical' approach brought about a search for an empirical factor that could be used to relate absorption, absorptivity, and durability. That was, after all, the main purpose of this study.

A large number of correlations were made. Originally, the measure of durability used was the Normalized Durability Factor of Kaneuji (1). This factor was the result of freeze-thaw testing of concrete containing these aggregates. The test used was ASTM C 666. The aggregates were batched in the vacuum saturated condition. Durability factors were calculated, as per C 666, and then they were normalized to a value of 100 for the highest. This Normalized Durability Factor (NDF) was then correlated with the pore size distribution curve to establish the definition of the Expected Durability Factor (EDF), equation (1). The NDF values, obtained in the earlier study (1), are listed in Table 3.

Many correlations were attempted, using standard techniques of linear regression, between the NDF values and various functions of the absorption and absorptivity. These generally took the form of A^n , K_a^n , and $(\log K_a)^n$,

Table 3. Normalized Durability
Factors (NDF) (1)

<u>Sample No.</u>	<u>NDF</u>
Ko	31.8
Br-1	19.9
McC	27.2
CC-1	36.0
H-1	3.5
Ke-1	19.6
H-2	95.5
BM-1	78.1
HR-2	100.0
MB	35.6
PC-1	16.7

where n was small positive or negative integers. No good correlations were found with any simple function of the absorption alone or the absorptivity alone. Combined functions of the absorption and absorptivity were then tried, using multiple regression analysis obtained with the Purdue University SPSS (Statistical Package for the Social Sciences) program. The best correlation obtained was with a function of the form $C_1A + C_2(\log K_a)(1/A)$. This combined function was termed the Absorptivity Absorption Factor.

Later it was decided to attempt the correlation with the EDF of the specific test piece itself used as the measure of durability. The reasons for this choice were several. First, the NDF values are averages of the results of several freeze-thaw tests, sometimes varying rather widely (1). As such they represent general rather than specific behavior, even though they correlated well with the EDF calculated in the earlier study. Also, the rationale of this study changed toward an attempt to relate the specific absorbing properties of an individual sample with the durability it would have, assuming the EDF calculated from its pore size distribution curve to be a good measure of that quality. If the EDF is a good measure of durability, as it seems to be, then the question is whether it can be predicted with reasonable accuracy from the absorption and absorptivity values. Therefore, the EDF of the specific

piece is obviously the property of interest in the attempted correlation. Said another way, the correlation is really with the pore size distribution curve, which is a property of the specific test piece, as are its absorption and absorptivity.

The result of the multiple regression analysis was

$$AAF = -40.1 + 691A + 0.227(pK_a/A) \quad (11)$$

where the logarithmic term was put in terms of the pK_a . The calculated AAF values are given in Table 4, along with the EDF values and the residuals. Also given are the specific values of the second ($691A$) and third ($0.227(pK_a/A)$) terms of equation (11), to show explicitly how the final result is influenced by them.

It can be seen that for rocks with a low porosity and absorption (e.g. H-2 and HR-2) the second term is small, and the AAF value is governed primarily by the third term, the one involving the absorptivity. On the other hand, when the absorption is large, as for CC-1 and Ke-1, the third term is small, and the final result is primarily governed by the second term, the one involving only the absorption.

These results are plotted in Figure 9, which shows the AAF values calculated from (11) vs. the EDF values determined from the mercury intrusion results. The equation of the best line in Figure 9 is

Table 4. Absorptivity Absorption Factors

<u>Sample No.</u>	<u>AAF</u>	<u>EDF</u>	<u>Residual</u>	<u>Second Term*</u>	<u>Third Term**</u>
Ko	31.5	33.8	2.3	13.1	58.4
Br-1	19.6	20.8	1.2	14.0	45.7
McC	6.0	24.2	18.2	33.1	12.8
CC-1	32.7	38.1	5.4	70.2	2.6
H-1	17.3	12.0	- 5.3	46.2	11.2
Ke-1	29.9	16.5	- 13.4	64.5	5.5
H-2	177.	75.8	-101.	4.6	212.
BM-1	40.3	44.6	4.3	15.3	65.0
HR-2	207.	293.	86.	3.9	243.
MB	33.3	27.2	- 6.1	12.0	61.4
PC-1	10.4	18.4	8.0	28.5	21.9

* 691A

** $0.227(pK_a/A)$

Figure 9. AAF vs. EDF (All Samples)

$$AAF = 15.3 + 0.722(EDF) \quad (12)$$

and the correlation coefficient is $r = 0.85$.

This curve is no doubt strongly influenced by the lone values with the high durability numbers. Therefore, the largest of these (HR-2) was eliminated, and the remaining results were replotted as Figure 10. The equation of this best line is

$$AAF = -34.3 + 2.38(EDF) \quad (13)$$

and its correlation coefficient is 0.90, and is so high mainly because it represents essentially a 'two-point' curve. Therefore, the lone value (H-2) was removed, and the remaining nine points for the more absorptive and less durable materials are shown in Figure 11. The equation for this best line is

$$AAF = 5.63 + 0.723(EDF) \quad (14)$$

with a correlation coefficient of $r = 0.67$. It is interesting, but probably accidental, that the slopes of equations (12) and (14) are almost identical. Also, the intercept is suitably small.

The exclusion of the lone points of Figure 9 can be justified in a practical sense by the aforementioned fact that if the absorption is low enough, less than perhaps one and a half percent, the aggregate will be durable with an EDF greater than 50, no matter what its pore size or absorptivity.

Figure 10. AAF vs. EDF (Ten Samples)

Figure 11. AAF vs. EDF (Nine Samples)

So the emphasis should be on the region of lower durability, and a parameter that will discriminate in the region of comparatively low EDF is what is desired. It does not, after all, matter much whether the EDF is 100 or 200, but it is desirable to be able to distinguish between an aggregate with an EDF of 40 and one of 60.

The presence of K_a in the numerator of equation (11) is reasonable, since K_a is proportional to the 'pore size' of the porous medium, and so is the EDF. A problem, however, with the use of K_a is that it is much more variable among a suite of samples than are either the absorption or the durability, however measured. The absorptivity varies over several orders of magnitude, while the absorption and the durability vary by only perhaps one. One of the reasons for this large variability of K_a is the influence of the tortuosity, which in general increases as absorption and pore size decrease. Therefore, the influence of the tortuosity is to magnify the influence of pore size and absorption as can be seen from equation (10). So perhaps this influence justifies the otherwise arbitrary use of the logarithm, since this function greatly reduces the variability of the argument to which it is applied.

The presence of the absorption in the denominator of the third term of (11) is also in the 'logical' direction, because its increase should result in a lower durability value.

But the presence of the absorption in the second term, in which its increase causes an increase rather than a decrease in the durability, is another matter. Here it seems to operate in the 'wrong' direction. On the grounds that perhaps the second term is not really needed to evaluate the samples of comparatively low durability, Figure 12 was constructed, in which pK_a is plotted vs. EDF for the same nine samples shown in Figure 11. The equation of this best line is

$$\frac{pK_a}{A} = 4.96 + 5.13(EDF)$$

with a correlation coefficient of $r = 0.49$, clearly a poorer agreement than that of Figure 11. So it seems the second term is a benefit to the agreement, logical or not.

It is, in the last analysis, probably a mistake to try to rationalize the equation for the AAF parameter. The only real question is whether it is a useful correlation or not. The correlation shown in Figure 11 is not good. Whether equation (11) and the concept of the Absorptivity Absorption Factor is good enough can probably be determined only by further testing with a wider variety of aggregate materials. In the meantime, considering the simplicity of its determination, the AAF is probably a useful value to be included in the test results by which the acceptability of aggregates is evaluated. But it cannot, at least yet, replace the EDF, determined in the usual way.

Figure 12. pK_a/A vs. EDF

CONCLUSIONS

The following conclusions seem reasonable:

1. Absorptivity may be a fair indicator of the durability of an aggregate. Those with an intermediate pK_a , between about 1 and 6, will probably be non-durable. Higher values probably indicate durable materials, and lower values may do so as well.

2. The Absorptivity Absorption Factor, defined in equation (11), is a fair indicator of durability. The AAF should be interpreted in the same way as the EDF, with values less than 50 being indicators of non-durable aggregate.

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