

# Use of Internal-Surface-Area Measurements in Research on Freezing and Thawing of Materials

R. L. BLAINE and C. M. HUNT, *National Bureau of Standards*, and  
L. A. TOMES, *Calcium Chloride Institute*

MEASUREMENTS of surface by low-temperature nitrogen sorption have been made on specimens of building stones, bricks, and hydrated cement. Measurements have also been made on crushed limestones and cherts with good and bad service records as concrete aggregates. Of the materials examined, those with higher internal surfaces had, on the average, poorer resistance to freezing and thawing than those with lower surface areas.

● THERE is some basis for the belief that one of the factors affecting the durability of stones and some other materials of construction is their micropore structure. Russell (1) has reported that the poor weathering properties of building stones was related to the number of pores 5 microns and finer which they contained. Sweet (2) found that the volume of voids with diameters below 5 microns was greater in aggregates which produced poor concrete than in aggregates which produced durable concrete. It has been suggested by Thomas and by Kennedy that the stresses developed when water freezes in building stones (3) and concrete (4) can be relieved by the flow of unfrozen water into unfilled pores in the interior or by extrusion from the specimen. This concept has been developed more fully by T. C. Powers in the hydraulic pressure hypothesis of frost action (5, 6). The permeability of a fine-textured solid would be less than that of a material containing an equal volume of larger pores, and consequently, the forces developed in fine pores could be greater.

A convenient method for assessing the extent of the fine structure in a solid is the measurement of surface area by gas or vapor adsorption. This also makes possible a qualitative estimate of the limiting dimensions which its micropores or particles could have.

Surface areas of certain stones, bricks, hydrated cement, and concrete aggregates have been determined from low-temperature nitrogen-sorption measurements by the Brunauer-Emmett-Teller method (7, 8). Also a few preliminary water-vapor-sorption measurements at 25 C. have been made, using a method

similar to the air-stream method described by Powers and Brownyard (13).

Surface areas have been studied in relation to resistance to freezing and thawing by comparing the areas of materials having different performances in laboratory freezing-and-thawing tests under extremely severe as well as more conventional conditions. Comparisons have also been made of coarse aggregate having good and bad service records in pavement and highway concrete. The work reported here represents preliminary measurements undertaken to see if there is any indication of relationship between surface areas of materials and their performance under natural or artificial freezing and thawing conditions.

## RELATION OF SURFACE TO MICROSTRUCTURE

To illustrate some possible relationships between the surface area and the microstructure of a solid, the surface area per unit weight may be calculated for a number of idealized models. For example, if a solid is composed of uniform spheres, the surface area of the spheres per unit weight would be:

$$S = \frac{6}{dD} \quad (1)$$

where  $S$  is the surface area of the microstructure of the solid in square meters per gram (sq. m. per g.),  
 $d$  is the diameter of each sphere in microns, and  
 $D$  is the density of the solid exclusive of pores in grams per cubic centimeter (g. per cu. cm.).

If a solid is made up of uniform cylinders, long enough that the surface of the ends may be neglected:

$$S = \frac{4}{dD} \quad (2)$$

It is also possible to set up relationships between surface areas and pore diameters for idealized models containing uniform pores distributed uniformly throughout the solid. If the surface of a solid is due to spherical pores arranged side by side in a cubic pattern, the surface area per unit weight would be:

$$S = \frac{6}{d'D} \cdot \frac{\Pi}{6 - \Pi} = \frac{6}{d'D} \times 1.10 \quad (3)$$

where  $d'$  is the pore diameter. However, the amount of surface resulting from pores of a given size decays very rapidly as the pores are spaced farther apart as shown by the relationship:

$$S = \frac{6}{d'D} \cdot \frac{\Pi}{6n^3 - \Pi} \quad (4)$$

where  $n$  is the number of pore diameters between the center of a pore and the centers of its nearest neighbors, and the pores are arranged in a cubic lattice.

For long, uniform, cylindrical pores placed side by side and built up into a rectangular cube, the surface area per unit weight would be:

$$S = \frac{4}{d'D} \cdot \frac{\Pi}{4 - \Pi} = \frac{4}{d'D} \times 3.66 \quad (5)$$

and the surface decays with spacing according to the relationship:

$$S = \frac{4}{d'D} \frac{\Pi}{4n^2 - \Pi} \quad (6)$$

The foregoing equations make it possible to estimate the average particle diameter or to place limiting dimensions on the size of uniform pores which could account for a given experimentally determined surface. They illustrate that a surface area even as large as 1 sq. m. per g. requires the existence of very-fine structure regardless of whether it is due to fine particles or fine pores. The nature of this increase in surface per unit weight is

shown in Figure 1, which is a plot of Equation 1, for a density of 2.65 g. per cu. cm., a representative value for many concrete aggregates. It illustrates graphically how the rate of change of surface with particle size becomes many times greater as the particles become smaller. Even the larger sizes in Figure 1 are in the subsieve range. A similar curve could be plotted to illustrate the relationship between surface area and pore size, if certain simplifying assumptions could be made regarding the size, shape, and distribution of the pores.

The finer the structure in a solid, the higher the surface, and the greater will be the resistance offered to the flow of liquids. If the stresses produced by freezing are hydraulic in

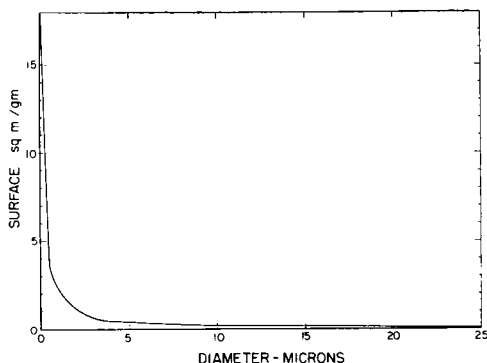


Figure 1. Surface per unit weight of uniform spheres of different diameters and density 2.65 grams per cu. cm.

nature, a finely textured solid could not relieve textured solid. For descriptive purposes the effect of the fineness of the structure may be illustrated by considering the simple case of capillaries of circular cross section. Poiseuille's equation for the rate of flow of liquids through a cylindrical capillary may be put in the form:

$$\frac{\Delta p}{\iota} = \frac{8Q\eta}{\Pi r^4} \quad (7)$$

where  $Q$  is the volume of fluid passing through a cylindrical capillary per unit time,  $r$  is the radius of the capillary,  $\iota$  is the length of the capillary,  $\eta$  is the viscosity of the fluid, and  $\Delta p$  is the pressure difference between the ends of the capillary.

For equal rates of flow (constant  $Q$ ) the pressure gradient is proportional  $1/r^4$ . For equal rates of flow per unit area (constant  $Q/\Pi r^2$ ), the pressure gradient is proportional to  $1/r^2$ . Or, if one considers the case of a capillary completely filled with water and subjected to directional freezing, starting at one end and moving toward the other at a constant rate,  $Q$  would depend on the volume of water frozen per unit time in the capillary and would be proportional to  $\Pi r^2$ . Under these circumstances, the pressure gradient developed in the region of flow would likewise be proportional to  $1/r^2$ . A plot of  $1/r^2$  against  $r$  is given in

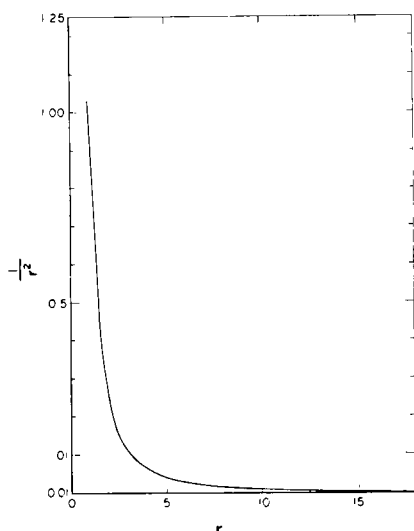


Figure 2. Relationship between  $r$ , the capillary radius, and  $1/r^2$ .

Figure 2 to illustrate that the pressure gradient could be many times larger in small pores than in an equal cross-sectional area of large pores.

#### SURFACE AREAS AND LABORATORY FREEZING-AND-THAWING TESTS

##### *Comparison of Unrelated Materials*

Specimens  $\frac{5}{8}$  in. in diameter by 2 in. long were cut from bricks and stones with a diamond core drill. Water was admitted to the specimens while they were in an evacuated condition. They were then subjected to repetitions of a freezing-and-thawing cycle which consisted of 30 min. in liquid nitrogen ( $-195$

C.), 30 min. in water at room temperature, and 30 min. in water at about 4 C. Cylinders of hardened cement paste and mortar  $\frac{1}{2}$  by 2 in. in size were subjected to similar cycles, except that the cold-water step was omitted. This process was much more severe than accelerated freezing-and-thawing tests ordinarily used in the laboratory, both in the extremely rapid rate of cooling and in the manner of wetting the specimens. It was shown by Valore (9), in dilatometric measurements of concrete, that vacuum-saturated specimens underwent volume changes during a single freezing many times as great as specimens which were only 65 to 85 percent saturated. The latter degree of saturation probably approximated service conditions more closely than the vacuum-saturated state. The specimens in the present study may not have been fully saturated, but undoubtedly approached this condition more closely than materials merely soaked in water. On the other hand, the factor of small specimen size may have reduced the severity of the test, or at least reduced the tendency for specimens to break. Thomas (3) showed experimentally that smaller specimens of stones incurred less breakage in freezing and thawing than larger specimens.

To determine the role of water in rapid cooling and in heating, specimens of cement paste and mortar were evacuated overnight to remove their free capillary water. They were then placed in glass tubes to keep them dry and given the room temperature to  $-195$  C. cycle. No visible changes were produced in 100 cycles. Companion specimens of wet cement paste cracked in five to eight cycles when subjected to the process in a glass tube. Wet mortar specimens cracked in 20 to 30 cycles of similar treatment when placed in water each cycle, but were more resistant when wet only at the beginning of the experiment. This difference is attributed to the loss of water from the specimens which were not reimmersed between freezings. It is concluded that the degree and type of damage noted in these experiments on freezing at  $-195$  C. was due primarily to the presence of water in the specimens.

Surface areas were measured on companion specimens. Table 1 records the surface areas obtained by nitrogen sorption and the number of cycles of freezing and thawing required to produce the first visible crack in any of three specimens simultaneously subjected to the

freezing-and-thawing test. The values in Table 1 have been plotted in Figure 3, with the exception of the mortar and cement paste (which would require a larger plot). The points group themselves about a curve having a steep branch and a flat branch. Along the steep

TABLE 1  
SURFACE AREA BY NITROGEN SORPTION AND  
CYCLES OF FREEZING AND THAWING  
AT FIRST VISIBLE CRACK

Material	Surface	Cycles of Freezing and Thawing
	sq. m. per g.	
<b>Stones</b>		
Georgia granite .....	0.01	234+
Georgia marble .....	0.01	169
Carrara marble .....	0.04	145
Bedford limestone .....	0.34	34
McDermott sandstone .....	1.17	18
<b>Bricks</b>		
Fire-clay brick .....	0.03	70
Red shale brick (A) .....	0.20	30
Red shale brick (B) .....	0.37	30
Red shale brick (C) .....	0.40	8
<b>Hydrated cement and mortar</b>		
1:3 mortar (14 day cure) (a) .....	5.0 <sup>a</sup>	7
Water/cement ratio 0.5 (b) .....	5.0	5
<b>Hardened paste (14 day cure) (a) .....</b>		
Water/cement ratio 0.5 (b) .....	22.0 <sup>a</sup>	1
	21.8	1

<sup>a</sup> The (b) samples contained 0.01% vinsol; (a) samples contained no vinsol.

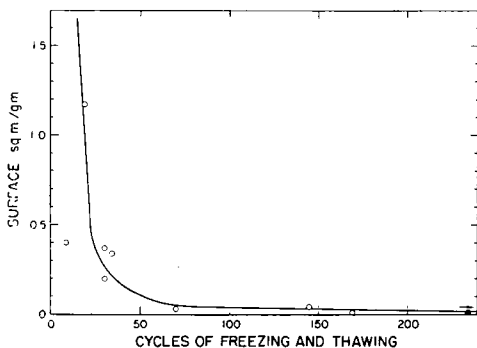


Figure 3. Surface area of stones and bricks versus the number of cycles of freezing and thawing required to produce the first visible crack.

branch the range of surface areas is comparatively large, while the number of cycles of freezing and thawing required for the first crack is comparatively small. Along the flat branch the range of surface areas is narrow, but the number of cycles of freezing and thawing is comparatively large.

The results in Figure 3 are qualitatively consistent with the hydraulic-pressure hypothesis. That is, the earliest failures occurred in the samples where the greatest stresses would be expected and the curvature is in the direction which might be predicted by the hypothesis. However, surface-area measurements without supplementary data do not make possible a rigorous test of this concept.

While the cement paste and mortar showed comparatively large surface areas and poor resistance to freezing and thawing under the conditions of the test, it is doubtful whether surface-area measurements would adequately predict differences in frost resistance among different cement pastes and mortars. For example, no consistent difference between the surface areas of cement pastes and mortars with and without air-entraining agent was found, despite the amply demonstrated fact that air-entrained concrete can be much more durable in service and in laboratory freezing and thawing than concrete without air entrainment. From this it is concluded that the air voids were too large (Equation 3), or spaced too far apart (Equation 4) to be evident from surface area measurements. Thus surface-area measurements readily detected the existence of micropores but were relatively insensitive to large pores and did not afford information regarding pore-size distribution. It is believed that vacuum wetting tended to minimize or eliminate the protective action of large internal pores which may have existed in any of the materials included in Table 3.

#### Comparison of Indiana Limestones

Kessler and Sligh (10) determined the performance of a number of Indiana limestones in a freezing-and-thawing test. They also determined compressive strengths parallel and perpendicular to the bedding planes, as well as total porosity and other properties. Surface-area measurements have been made on  $\frac{5}{8}$ -by 2-in. cylinders of some of these limestones.<sup>1</sup> The number of cycles of freezing and thawing required to reach the condition of greatest damage considered by Kessler and Sligh before removing the sample from the test have been averaged and are summarized in Table 2 along with porosity values and the average of the compressive strengths taken

<sup>1</sup> These specimens were supplied by Arthur Hockman and D. W. Kessler of the National Bureau of Standards.

parallel and perpendicular to the bedding plane. Each surface-area value is an average for two specimens. One is referred to Kessler and Sligh's paper for the details of the freezing-and-thawing test, but it was essentially a

TABLE 2  
PERFORMANCE IN FREEZING-AND-THAWING TEST, SURFACE AREA, COMPRESSIVE STRENGTH, AND POROSITY OF LIMESTONE CORES

Ref. No. <sup>a</sup>	Cycles <sup>a</sup> Freezing and Thawing (Average 3 Specimens)	Average <sup>a</sup> Compressive Strength (Perpen- dicular and Parallel to Bedding Plane)	Porosity <sup>a</sup>	Average Surface by N <sub>2</sub> Sorption	
				%	sq. m. per g.
8	2,643+	7,630	16.2		0.25
14	663	8,680	12.9		0.56
34	3,068+	8,600	12.9		0.33
38	167	6,600	16.2		0.49
53	142	3,550	20.2		0.40
54	600	8,100	14.7		0.28
57	158	4,950	17.3		0.37
65	360	7,100	18.0		0.26
74	733	7,580	13.2		0.34
87	1,525+	6,300	11.8		0.37
89	3,068+	9,280	14.0		0.24
91	83	3,200	18.4		0.57
96	433	7,650	12.9		0.38
100	567	9,300	15.4		0.53

<sup>a</sup> Data condensed from Bureau of Standards Technological Paper #T349 by D. W. Kessler and W. H. Sligh.

TABLE 3  
SURFACE AREA AND PERFORMANCE OF AGGREGATES USED IN PAVEMENT CONCRETE

Material	Surface	Order of Performance <sup>a</sup>
	sq. m. per g.	
Crushed limestone C	0.26	1 (best)
Crushed limestone D	1.8	2
Chert A		
Light fraction	2.2	3
Dark fraction	2.4	
Chert B		
Light fraction	5.2	4 (poorest)
Dark fraction	4.5	

<sup>a</sup> Based on information supplied by T. F. Willis and E. O. Axon, of the Missouri Highway Commission. The reported order was the same both in laboratory freezing-and-thawing tests of concrete specimens and in-service records of concrete pavements.

2-to-3-cycle-per-day process, operating between about 20 and -14 C., freezing in air and thawing in water.

In Figure 4, surface area has been plotted against the average number of cycles required to reach the most severely damaged state

considered by Kessler and Sligh, in which a considerable amount of the specimens had broken off. These points do not appear to fit a curve as well as those in Figure 3; however, the ratio between the highest and the lowest surfaces in Figure 3 is 117 to 1 while the ratio in Figure 4 is 2.4 to 1. Also, the slower freez-

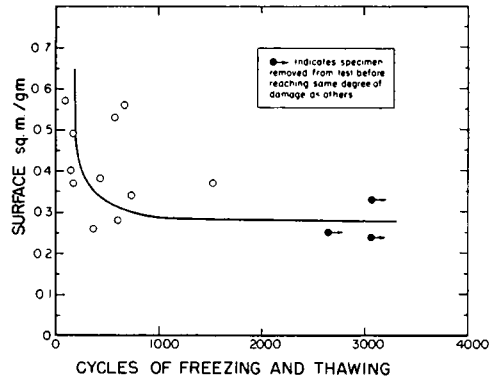


Figure 4. Surface area of Indiana limestones versus performance in laboratory freezing-and-thawing test.

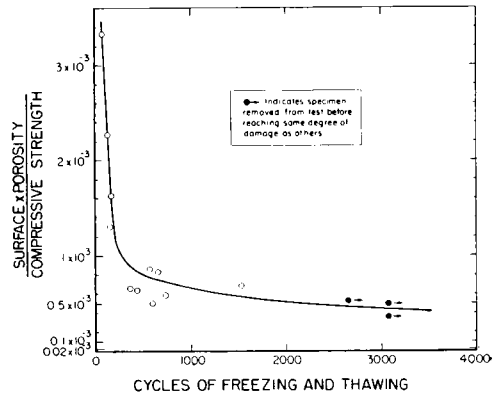


Figure 5. Surface area  $\times$  porosity/compressive strength versus performance in laboratory freezing-and-thawing test.

ing-and-thawing process and the partial saturation of the specimens had the effect of increasing the number of cycles required to produce a given degree of damage.

Figure 5 is obtained by plotting the empirical relationship

$$\frac{\text{surface area} \times \text{porosity}}{\text{compressive strength}}$$

against the number of cycles of freezing and thawing. This affords a closer grouping of the points about a curve than when surface area alone is considered.

#### SURFACE AREAS OF CONCRETE AGGREGATES WITH GOOD AND POOR SERVICE RECORDS

The relationship between the surface area of the aggregate and the resistance to freezing and thawing of concrete is probably even more complicated than the cases considered in the preceding section where the surface area is considered more or less representative of the entire material. As Rhoades and Mielenz have pointed out (11) and earlier English workers have demonstrated experimentally with stones (12), fine capillaries can withdraw water from coarser capillaries, and remain saturated after the coarser capillaries in contact with them have become dry. Thus, water in a complex mixture like concrete might go to and remain most persistently in that part of the structure where the pores are the smallest.

It would seem pointless to attempt to relate the durability of concrete to the surface area of the aggregate, because the surface area of cement paste is higher than the surface area of any aggregate tested. However, according to the concepts set forth by Powers and Brownvard (13), hardened cement paste contains both capillary pores and gel pores. The measured surface area of the paste is probably largely a function of the gel pores. Aggregates undoubtedly have much larger pores than the gel pores of cement paste, but the aggregate pores are not necessarily larger than the capillary pores of the paste. If it be postulated that all or part of the gel water does not freeze under natural freezing conditions, and there may be some justification for this (13), then the greatest forces would be generated in the pores of the aggregates or the capillary pores of the cement, depending on which were smaller. Whether the above mechanism is correct or not, there is no lack of evidence that the quality and condition of the aggregate affects the durability of the concrete, even when there is no clear-cut demonstration of alkali-aggregate reactivity. A fairly extensive bibliography on this and other aspects of concrete durability is given by Walker and Bloem (14). It has also been

pointed out that the composition and brand of cement is a factor in the durability of concrete made from a given aggregate (15, 16).

Two chert and two limestone aggregates were supplied by T. F. Willis of the Missouri State Highway Commission. These aggregates had been used in pavement and other concrete and represented materials with good and bad service records. Surface-area measurements were made on these and the values are shown in Table 3, along with information supplied by Willis and Axon relating to the performance of these aggregates in concrete pavements and in laboratory freezing-and-thawing tests.

The performance of concrete made from these aggregates were reported to be in the same order, both in laboratory freezing-and-thawing tests and in actual service, as pre-

TABLE 4  
SURFACE AREAS AND SERVICE RECORDS OF  
CRUSHED LIMESTONES USED IN  
HIGHWAY CONCRETES

Lime-stone	Surface Area	Reported Service Records
No.	sq. m. per g.	
1	0.30	Excellent service record
2	0.78	Good service record
3	0.78	Good service record
4	1.18	Bad service record, quarry condemned
5	2.26	Bad service record, quarry condemned
6	3.63	Bad service record, unsatisfactory performance

dicted from their surface areas, irrespective of the type of aggregate. The alignment of these samples in the order expected from their surface areas suggests that aggregates with larger surface areas may produce concrete of lower durability on the average than similar aggregates with smaller surface areas.

Surface areas have also been determined on six samples of crushed limestone with good and bad service records in highway concrete.<sup>2</sup> The surface areas and reported service records of these aggregates are given in Table 4.

The data in Tables 3 and 4 indicate that surface area or the fine structure which it represents is very likely one of the properties of an aggregate which influences the durability of concrete.

<sup>2</sup> These samples and information concerning their service records were supplied by J. E. Gray of the National Crushed Stone Association.

## WATER-VAPOR SORPTION

Since water is the liquid which permeates the specimen and exerts pressure according to the hydraulic pressure hypothesis, there would be a reasonable basis for expecting that surface areas measured by water-vapor sorption would have greater significance in predicting durability behavior than surface areas measured by nitrogen sorption.<sup>3</sup>

Water-vapor sorption measurements have been made on a few specimens at 25 C., using an apparatus similar to the air-stream apparatus described by Powers and Brownyard (13) but using nitrogen to transport the water vapor instead of air. In Table 5 surface areas by water-vapor sorption are given for some of the same specimens whose nitrogen surfaces

TABLE 5  
WATER-VAPOR SORPTION BY STONES  
AND BRICKS

Material	Surface <sup>a</sup> by Water Sorption	Water Sorption at 94% R.H.	Surface H <sub>2</sub> O Surface N <sub>2</sub>
	sq. m. per g.	mg. per g.	
<b>Stones</b>			
Georgia granite .....	0.5+	0.66	50+
Georgia marble .....	0.17	0.04	17
Carrarra marble .....	0.14	0.21	3.5
Bedford limestone .....	0.5	0.84	1+
McDermott sand- stone .....	4.0	9.41	3.4
<b>Bricks</b>			
Fire clay brick .....	0.15-0.25	0.02	7
Red shale brick (A) .....	0.26	0.33	1.3
Red shale brick (B) .....	0.57	1.03	1.5
Red shale brick (C) .....	0.61	0.63	1.5

<sup>a</sup> Each water molecule was assumed to cover 10.6 sq. Å.

are reported in Table 1. After the determination of surface by water sorption, these specimens were conditioned at 94 percent relative humidity in a closed container. The milligrams of water vapor taken up at this higher humidity per gram of dry sample are also given in Table 5, as well as the ratio between the surface areas obtained by water-vapor and by nitrogen sorption.

The surface areas of these specimens, as determined by water-vapor sorption, do not show as consistent a relationship with performance in the rapid freezing-and-thawing test as do the surface areas determined by

<sup>3</sup> T. C. Powers has pointed out that surface areas of hydrated cement pastes by water vapor sorption are in good agreement with surface areas calculated from water-permeability measurements.

nitrogen sorption. However, the weight of water vapor taken up at 94 percent relative humidity shows a little better correlation with this kind of durability. The number of determinations is small however, and further work would be desirable to establish the best way to use and interpret water-vapor sorption in predicting resistance to frost action.

In Table 6, surface areas by water-vapor sorption are given for a few of the limestones whose nitrogen surfaces are listed in Table 2. Again there is no very consistent relationship between these surface areas and the results of the freezing-and-thawing test.

TABLE 6  
WATER-VAPOR SORPTION BY LIMESTONES

Ref.	Surface	Surface H <sub>2</sub> O Surface N <sub>2</sub>
No.	sq. m. per g.	
8	0.29	1.5
14	0.89	1.6
34	0.43	1.3
57	0.37	1.0
91	0.85	1.5

TABLE 7  
WATER-VAPOR SORPTION BY  
CONCRETE AGGREGATES

Material	Surface	Surface H <sub>2</sub> O Surface N <sub>2</sub>
	sq. m. per g.	
<b>Chert A</b>		
Light fraction .....	2.6	1.2
Dark fraction .....	2.5	1.0
<b>Chert B</b>		
Light fraction .....	4.5	0.9
<b>Crushed limestone C</b>		
.....	0.4	1.5
<b>Crushed limestone D</b>		
.....	2.5	1.4

When the surface areas of some of the concrete aggregates, however, were measured by water-vapor sorption, the values were in agreement with performance records in concrete, as may be seen by comparing Tables 3 and 7.

The ratio between surface areas by water-vapor sorption and by nitrogen sorption are given in Tables 5, 6, and 7. These ratios may ultimately throw some light on the nature of the submicroscopic structure of these materials, but the importance of this ratio from the standpoint of durability is not fully understood. A typical ratio for hydrated cement paste is about 5 to 1. The ratio varies over a fairly wide range for different materials, but

varies over a much smaller range for similar materials.

All of the stones, bricks, and aggregates tested had much smaller surfaces by water-vapor sorption than the hydrated-cement paste.

#### SUMMARY AND CONCLUSIONS

Exploratory experiments on the application of Brunauer-Emmett-Teller surface-area measurements to freezing-and-thawing research have been carried out. Results to date have indicated that surface areas calculated from low-temperature nitrogen-sorption measurements were larger on the average for certain stones, bricks, and hydrated cement which failed in a few cycles of very rapid freezing and thawing than for materials which failed only after a large number of cycles of freezing and thawing. When surface areas of these materials were plotted against the number of cycles of freezing and thawing required for failure, a curve was obtained which had the general form expected from the hydraulic pressure hypothesis of frost action.

Surface-area measurements by water-vapor sorption on a few of the same materials did not show as consistent a relationship to durability as the nitrogen surface areas, but the matter should receive further study.

Certain concrete aggregates with poor service records had larger surface areas than aggregates with good service records.

The results of this study are consistent with the previously expressed idea that the weathering and frost resistance of a substance is related to the volume of micropores which it contains.

Hydrated-cement paste and mortar had much-larger surface areas than any of the other materials examined, by both water-vapor and nitrogen sorption. The presence of an air-entraining agent did not appear to make a significant difference in the surface areas of paste or mortar. This is significant, because it indicates that while surface measurements are valuable for detecting microstructure, they give no hint of the presence of protective air voids.

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## Alkali-Aggregate Phase of Chemical Reactivity in Concrete

J. A. HESTER, *Chief Chemist*, and O. F. SMITH  
*Alabama State Highway Department*

● THE action of potassium and sodium oxides on certain types of aggregate continues to be one of the primary topics in most publications concerning concrete reactions. The reality of this action has been recognized by a majority of the cement-research chemists; however, the theories explaining this action seem, in most cases, to be inadequate. This, among other reasons, has caused many investigators to treat this as a secondary reaction, or merely a vague possibility.

Many structural failures attributed to alkali-aggregate reaction may be the result of other chemical or physical action. Even when it is evident that alkali action is present, it is usually too late to prevent serious damage. A thorough knowledge of the individual concrete components, including the chemical analysis of the cement, water, and aggregate plus the petrographic analysis of the aggregate should certainly be required before designing the concrete mix. Several faulty structures in Alabama contain cements with high magnesia contents, as well as high alkali. In practically all instances, records of these structures contain little or no information concerning the petrographic or chemical content of the individual components. Many aggregates containing high sodium and potassium release the corresponding hydroxides by reaction with lime from hydrated cement. Some of the zeolites contain as much as 16 percent sodium oxide.

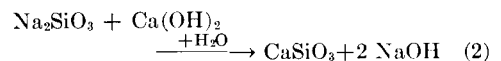
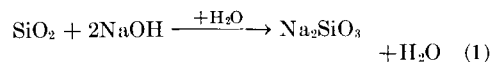
For alkali-aggregate reaction to progress, at least five major factors must exist: (1) sufficient alkali to react with the silica; (2) silica that is reactive with rather low concentrations

of alkali; (3) water available in amounts necessary to continue the reactions; (4) lime free to react with the alkali silicates, releasing the alkali back to solution, or enough alkali present to injure the concrete without regeneration; and (5) enough force to rupture the concrete after the damage by the alkali. It is evident that the last two factors contain the main controversial issues.

There is sufficient reason to doubt that the comparatively small amounts of alkali, derived from portland cement, could destroy enough aggregate or produce enough alkali silicate to be of great concern without some process of reviving the alkali hydroxides so as to continue the cycle. There is also evidence that the osmosis theory, as applied to the alkali silicates, has little or no application to the affected concrete samples examined in this department.

### ALKALI SILICA AND LIME

The basis for the following data and comments is shown very simply by the following equations:



The use of sodium and calcium metasilicate is for simplicity only. It will be noticed that the sodium and calcium silicates have a higher silica ratio when used with a hydrous form of silica in the following experiments, however, the reactions produce similar results.