Nitrogen Sorption Measurements and Surface Areas Of Hardened Cement Pastes

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Surface area by nitrogen adsorption and nonevaporable water were determined on hardened cement pastes of four water-cement ratios, ranging from 0.251 to 0.501, and four ages, ranging from 1 day to 180 days.

Water-cement ratio made very little difference in the surface area of hardened pastes at 1 day, but with pastes at later ages, evidence suggests that surface area may reach a limiting value which is a function of the original water-cement ratio. The ratio of surface area by nitrogen adsorption to nonevaporable water was not constant but increased with increasing hydration in paste of water-cement ratio 0.501 and changed very little or even decreased slightly in paste of water-cement ratio 0.251.

The degree of subdivision of the paste during drying exerted a significant effect on the measured surface area except for specimens of high water-cement ratio measured early in the hydration process. In most cases pastes which were dried as cylinders, ½ in. in diameter and ½ in. long, had lower surface areas than specimens of the same pastes which were crushed to particle sizes less than 1 mm before drying. The sorption isotherm and calculated pore size distribution of a paste after different drying treatments were also determined.

•THE USE of low-temperature nitrogen adsorption measurements to determine surface areas of colloidal solids has become a common procedure since the development of the Brunauer-Emmett-Teller theory (1). Surface area measurements make it possible to demonstrate the presence of colloidal structure, to detect changes in this structure, and under some circumstances to estimate the dimensions of the submicroscopic structural units which comprise the solid. The surface area of a hydrated cement is essentially the surface of the colloidal hydration products since the surface of the original cement is comparatively small. Although surface areas by nitrogen adsorption have been reported for hardened cement pastes (2, 3) and hydrated calcium silicates (4), water vapor has been used more often than nitrogen as the adsorbate in surface area measurements of these materials. Some of the reasons for this practice have been summarized by Powers (5).

As Gleysteen and Kalousek (3) have observed, surface areas of hardened cement pastes determined by nitrogen adsorption are indicated to be smaller than those determined by water vapor adsorption. Somewhat similar behavior is also characteristic of montmorillonite, which is able to swell and accommodate water between the expanding layers of its lattice (6). However, according to the observations of Brunauer, Kantro and Copeland (7), a different explanation must be found for tobermorite gel, the principal constituent of hardened cement paste, because once the material has been dried, as in a surface area determination, the contraction of the layers is irreversible. Nevertheless it is obvious that water can be accommodated in the pore structure in some way that is not available to nitrogen. Mikhail, Copeland and Brunauer (8), in their study of the pore structure and surface area of hardened cement pastes, concluded that nitrogen can be excluded from the pores in hardened cement pastes by two

TABLE 1

CHEMICAL COMPOSITION OF CEMENT

Constituent	Percentage by Weight
CaO	64.1
SiO_2	22.3
Al_2O_3	5.0
Fe_2O_3	3.0
MgO	1.9
SO_3	2.0
Ignition loss	1.0
Insoluble residue	0.3

mechanisms. Either the pores can be too narrow to admit the nitrogen molecules or the pore entrances can be too narrow. This latter mechanism may be one of the reasons why surface areas by nitrogen adsorption undergo large decreases when partially dried pastes are stored in a closed system (10). Surface areas available to nitrogen are not only lower than those available to water vapor but are sometimes more responsive to the environmental history of the specimen after hydration has stopped.

The present paper reports the results of surface area measurements by nitrogen adsorption for hardened pastes of different ages and water-cement ratios as well as nonevaporable water determinations for the same specimens. Although such information is available for pastes 2 years old and older (8), it is not available for pastes in the earlier stages of hydration. This paper also considers some effects of sample preparation and drying procedure on the calculated surface areas as well as on the complete sorption isotherm of a hardened paste.

EXPERIMENTAL

The pastes used in these experiments were prepared from a type 1 cement (11) whose chemical analysis is given in Table 1.

Preparation of Specimens

Pastes were prepared by mixing water and cement in a rubber soil density balloon. The soil density balloons used for mixing pastes had a total volume of about 160 ml and a wall thickness of 0.4 to 0.5 mm. They were sufficiently strong to withstand the impacts used to mix the pastes. These balloons were obtained from the Rainhart Company of Austin, Texas.

The pastes were cast in the form of cylindrical rods ½ in. in diameter. After 24 hr they were removed from the molds and cut into half-inch lengths, and, except for the 1-day specimens, were stored under water until time of test. After this curing treatment all pastes were dried for a week at about 21 C in a vacuum desiccator with a dry ice trap between the desiccator and the pump. This is a procedure similar to the one described by Copeland and Hayes (12). Since both solid pieces of paste and crushed paste have been used in the past for surface area determinations, in the present experiments half of the paste of each age and water-cement ratio was crushed to particle sizes 1 mm and finer with a mortar and pestle just prior to drying. The other half was dried in the form of half-inch cylinders.

Determination of Surface Area, Pore Size, Nonevaporable Water and Water-Cement Ratio

Nitrogen sorption measurements were made at -195 C on the dried specimens which were either in the form of crushed material or half-inch cylinders. An apparatus similar to the one described by Emmett (13) was used. This is a vacuum system in which gas is measured volumetrically. Prior to measurement each specimen was outgassed overnight on the apparatus at a temperature of 100-110 C, except where otherwise designated.

Surface areas were calculated by means of the BET equation

$$\frac{p}{v\,(p_o-p)} = \frac{1}{v_mC} + \frac{C-1}{v_mC}\,\frac{p}{p_o} \qquad (1)$$

TABLE 2

SURFACE AREA AND NONEVAPORABLE WATER CONTENT OF HARDENED PASTES DRIED AS HALF-INCH CYLINDERS

Time of Curing (days)	Water-Cement Ratio	Nonevaporable Water After Outgassing (g/g ignited cement)	Weight Loss During Outgassing (g/g ignited cement)	Surface Area, Duplicate Determination (m^2/g ignited cement)	
1	0.251	6.4	2.4	15.5	15.7
7	0.251	9.9	4.8	13.9	14.0
28	0.251	11.4	5.1	15.1	13.4
180	0.251	13.4	4.8	13.2	13.2
1	0.333	5.4	1.5	18.5	18.8
7	0.333	10.3	4.5	24.7	23.9
28	0.333	13.6	6.8	31.7	33.7
180	0.333	15.7	5.1	42.3	35.3
1	0.442	5.7	1.4	18.2	18.4
7	0.442	9.9	2.4	32.3	34.8
28	0.442	13.8	4.6	47.8	49.9
180	0.442	17.3*	7.6*	70.3*	71.1*
1	0.501	5.5	1.4	20.7	20.6
7	0.501	9.1	2.3	31.4	34.1
28	0.501	12.0	5.0	52.5	53.3
180	0.501	16.8	4.4	81.6	84.4

*These specimens subjected to rehumidification during drying when dry ice around vacuum trap evaporated.

where p is the pressure of gas in equilibrium with the sample, p_0 is saturation pressure, v is the amount of gas adsorbed, C is a constant, and v_m is the amount of gas required for monolayer coverage of the specimen. Surface areas were obtained from v_m assuming an area of coverage of 16.2 Å^2 for the nitrogen molecule.

The method of Innes (14) was used to calculate the pore size distribution of two specimens. This method is based on the Kelvin equation corrected for multilayer adsorption and treats the adsorbent as a system of parallel plates. It considers only that part of the pore system with wall separations between about 15 Å and 225 Å. As with all methods based on the Kelvin equation, it requires an estimate of the amount of gas adsorbed at p/p_0 values ranging from 0 to 1. In other words, it is based on the complete sorption isotherm.

Nonevaporable water was based on the ignition loss of the dried specimens corrected for carbon dioxide content. After surface area measurements on duplicate specimens, ignition loss at 1050 C was determined on one specimen and carbon dioxide on the companion specimen. Nonevaporable water (Wn) determined after outgassing at 100-110 C was less than that obtained after a week of vacuum drying at room temperature, a procedure similar to that described by Copeland and Hayes (12). However, weight losses during outgassing were determined so that nonevaporable water could be estimated on either basis.

Water-cement ratio was obtained from the ignition loss and carbon dioxide content of undried specimens taken directly from the mold 24 hours after casting.

RESULTS AND DISCUSSION

Surface areas available to nitrogen, together with weight losses during outgassing and nonevaporable water contents, are summarized in Tables 2 and 3. Table 2 presents data for specimens dried as half-inch cylinders and Table 3 for crushed specimens. In comparing corresponding values in Tables 2 and 3 it may be noted that different values are usually obtained for each hydrated paste, depending on the form in which it is dried. This makes it clear that these surface areas represent comparative rather than absolute values. Where there is a difference, the crushed paste usually

TABLE 3

SURFACE AREA AND NONEVAPORABLE WATER CONTENT OF HARDENED PASTES WHICH WERE CRUSHED BEFORE DRYING

Time of Curing (days)	Water-Cement Ratio	Nonevaporable Water After Outgassing (g/g ignited cement)	Weight Loss During Outgassing (g/g ignited cement)	Surface Area, Duplication Determination (m^2/g ignited cement)	
1	0.251	5.7	0.8	30.5	30.8
7	0.251	8.6	2.2	24.4	23.9
28	0.251	10.5	2.0	23.5	25.0
180	0.251	12.3	2.2	27.4	17.9
1	0.333	5.3	1.1	25.7	23.7
7	0.333	9.4	1.4	37.7	36.1
28	0.333	11.8	2.6	53.7	53.9
180	0.333	15.3	2.8	41.8	61.6
1	0.442	5.6	0.9	20.3	20.7
7	0.442	9.5	2.1	35.9	41.3
28	0.442	12.7	2.2	75.1	70.1
180	0.442	16.2*	3.6*	75.8*	68.7*
1	0.501	5.4	1.5	20.3	19.4
7	0.501	9.0	1.7	34.8	35.0
28	0.501	12.8	2.1	68.9	74.9
180	0.501	15.9	2.7	112.2	124.2

*These specimens subjected to rehumidification during drying when dry ice around vacuum trap evaporated.

has a higher surface area. The most obvious explanation for this difference is that crushing opens blind pores previously inaccessible to nitrogen. However, this is not a satisfactory explanation, for it has been found that crushing the paste, once it is dried, does not usually result in an increase in surface. In fact slight decreases have been observed.

The difference is probably a manifestation of what Powers (5) has referred to as the instability of cement paste. It was previously shown (8) that the surface area of a particular crushed paste, vacuum dried at room temperature, ranged from 43 to 70 m^2/g depending on the rate of drying. Slower drying of the paste allows more time for colloidal changes to take place resulting in lower surface area. In fact, incidental or unintentional interruptions or variations in drying procedure at certain critical stages of the process can sometimes lead to significant differences in measured surface area. Comparing Tables 2 and 3 it may be seen that the difference between crushed specimens and their uncrushed counterparts is negligible at 1 day or even 1 week in hardened paste of water-cement ratio 0.501, but is significant at 28 and 180 days. In the dense paste of water-cement ratio 0.251 the difference is measurable at all ages. Apparently a hardened paste of high water-cement ratio and early age dries in vacuum with sufficient rapidity that difference in drying rate between a crushed and uncrushed specimen is not a controlling factor in determining surface area, but with older pastes and pastes of low water-cement ratio, crushing of the specimen before drying has a measurable effect.

Effect of Water-Cement Ratio

Figure 1A shows surface area as a function of water-cement ratio for half-inch cylinders of hardened paste which were hydrated for periods ranging from 1 to 180 days. Figure 1B shows similar data for crushed specimens. In order to observe intrinsic differences due to age and water-cement ratio it is necessary to base comparisons on pastes of the same form and dried in the same way. Surface area by nitrogen adsorption, unlike surface area by water vapor (9), is extremely dependent on the water-cement ratio of the paste. Differences due to difference in water-cement

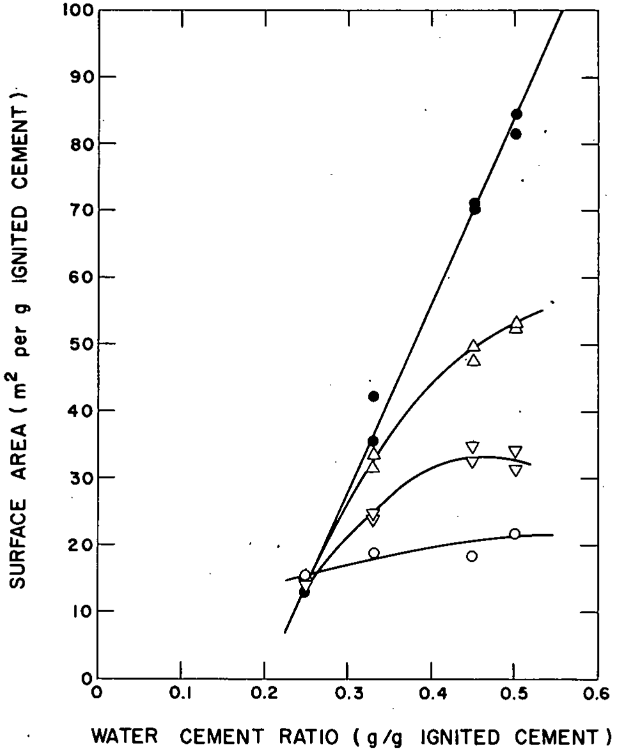

Figure 1A. Surface area as a function of water-cement ratio for hardened pastes dried as half-inch cylinders: ○ 1-day, ▽ 7-day, △ 28-day, ● 180-day-old paste.

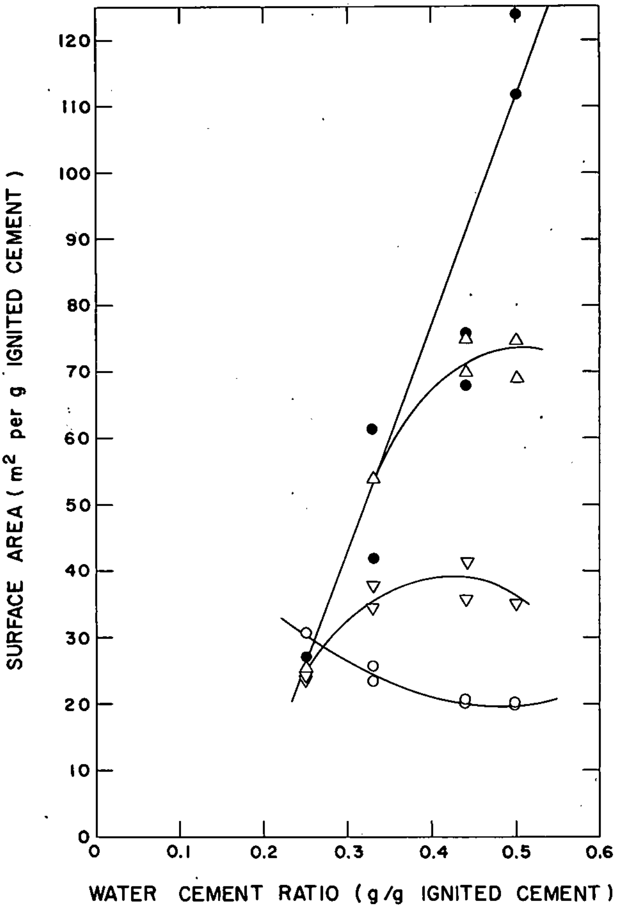

Figure 1B. Surface area as a function of water-cement ratio for hardened pastes crushed before drying: ○ 1-day, ▽ 7-day, △ 28-day, ● 180-day-old paste.

ratio are small at 1 day but become very large as hydration proceeds. The data suggest that the surface area accessible to nitrogen may reach a limiting value which is a function of the original water-cement ratio; this limiting value may be a linear function of the original water-cement ratio. This trend is shown particularly by the 180-day specimens in Figure 1A, but the data of Mikhail, Copeland and Brunauer (8) for pastes of water-cement ratio 0.35, 0.40, 0.45 and 0.57, and the data of Blaine and Valis (2) for pastes of water-cement ratio 0.25, 0.40 and 0.55 also suggest a possible linear relationship between surface area and water-cement ratio for pastes which have hydrated for a long time.

Surface by Nitrogen Adsorption as a Function of Nonevaporable Water

In Figures 2A and 2B surface area obtained by nitrogen adsorption is plotted against the nonevaporable water content of the paste. It is clearly not a linear function of nonevaporable water as Powers and Brownyard found for surface area determined by water vapor adsorption (9). At the highest water-cement ratio, surface area is observed to increase with an increasing slope as hydration proceeds, while at the lowest water-cement ratio the change is small, and may even decrease slightly. At intermediate water-cement ratios another difference is observed depending on whether the test specimen was dried as a half-inch cylinder or crushed before drying. For crushed pastes the surface area appears to reach a limiting value and does not increase much more with further hydration. However, this effect is not observed in the case of half-inch cylinders, and it might possibly represent some artifact arising from the drying conditions. Powers and Brownyard (9) have suggested that "if a given cement produces the same kind of hydration products at all stages of its hydration, the ratio of surface area to nonevaporable water should be constant for any given cement under fixed curing conditions." Such a constant ratio has been observed for many hardened cement pastes when surface area is determined by water vapor adsorption. However, surface area determination by nitrogen leads to different results. At the highest water-cement ratio represented in Figures 2A and 2B the ratio of surface area to nonevaporable water becomes larger as hydration proceeds. This increase in ratio would be consistent with a situation where the apparent sizes of the particles accessible to nitrogen, which represent structure formed later in the hydration process, are smaller than those formed during earlier hydration. The opposite effect is observed in the specimens of the lowest water-cement ratio where the surface area changes very little while the nonevaporable water increases.

Considered from the standpoint of pore structure, if the pore volume accessible to nitrogen remains constant, or decreases with hydration as total pore space does, surface area can increase only if the new hydration products contain many new pores. The ratio of the volume of the pores to pore surface, which is the hydraulic radius of the pore system, becomes smaller as paste of high water-cement ratio hydrates. At the lowest water-cement ratio, either no new pores are formed as hydration continues or older pores become inaccessible, since surface area remains nearly constant or even decreases slightly as the nonevaporable water, and presumably also the amount of hydration products, approximately double.

The Sorption Isotherm and Pore Size Distribution

Complete sorption isotherms of a paste were determined in order to examine the effect of differences in drying and sorption history on parts of the isotherm not used in the BET calculation of surface area. A nine-month-old paste of water-cement ratio 0.501 was selected for the purpose. In Figure 3A the amount of gas adsorbed is plotted as a function of relative pressure for a specimen which was initially vacuum-dried for a week as a half-inch cylinder. The first isotherm was obtained after outgassing at 21 C, the second isotherm after re-outgassing at 100-110 C and the third isotherm after crushing the specimen and again outgassing at 100-110 C. The respective BET surface areas, calculated from the lower part of the adsorption branches of the three cycles were 95, 95, and 94 square meters per gram of ignited cement.

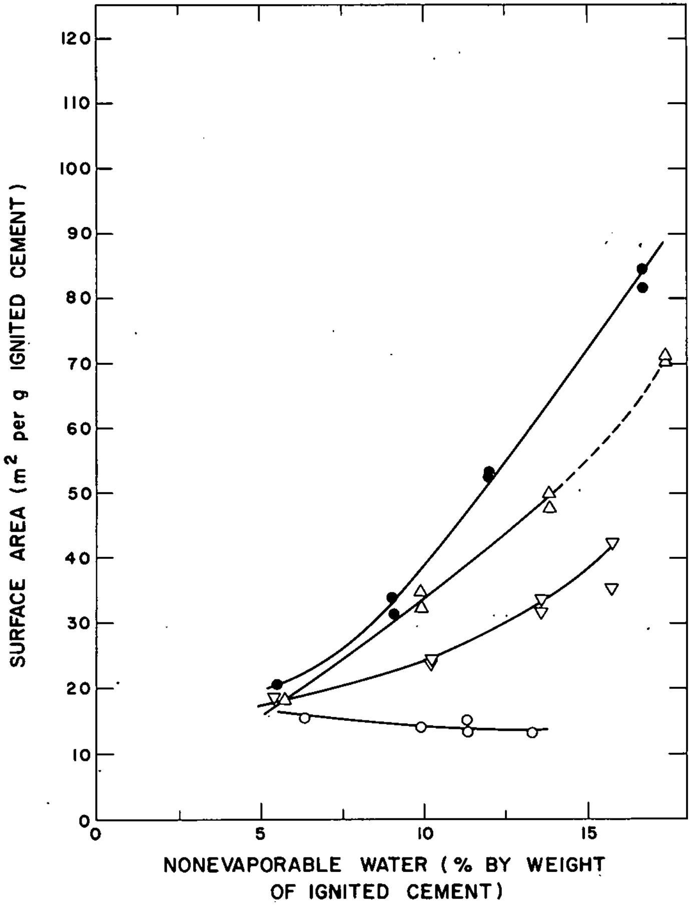

Figure 2A. Surface area as a function of nonevaporable water content for hardened pastes dried as half-inch cylinders, with water-cement ratios: O = 0.251, ∇ = 0.333, Δ = 0.442, ● = 0.501.

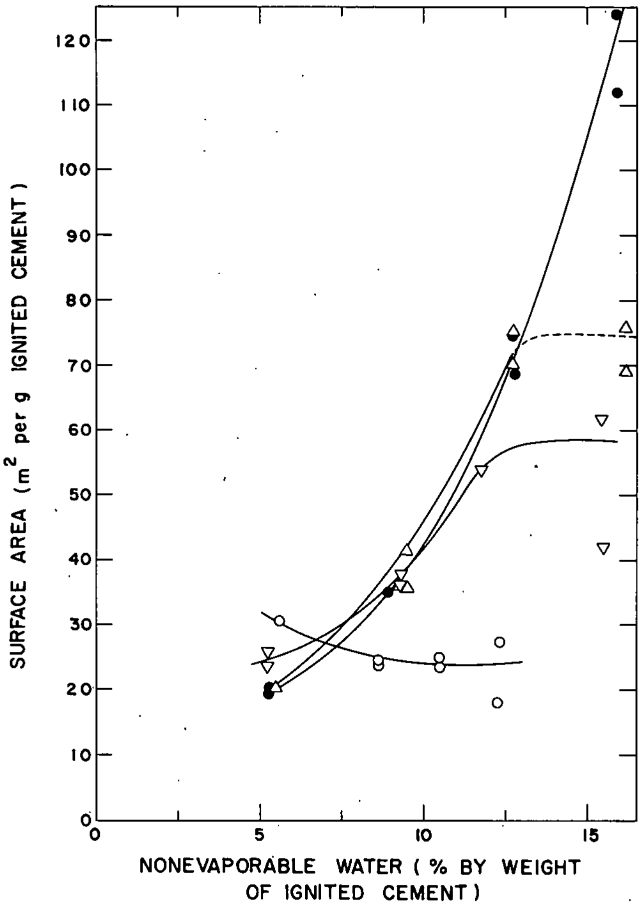

Figure 2B. Surface area as a function of nonevaporable water content for hardened pastes crushed before drying, with water-cement ratios: O = 0.251, ∇ = 0.333, Δ = 0.442, ● = 0.501.

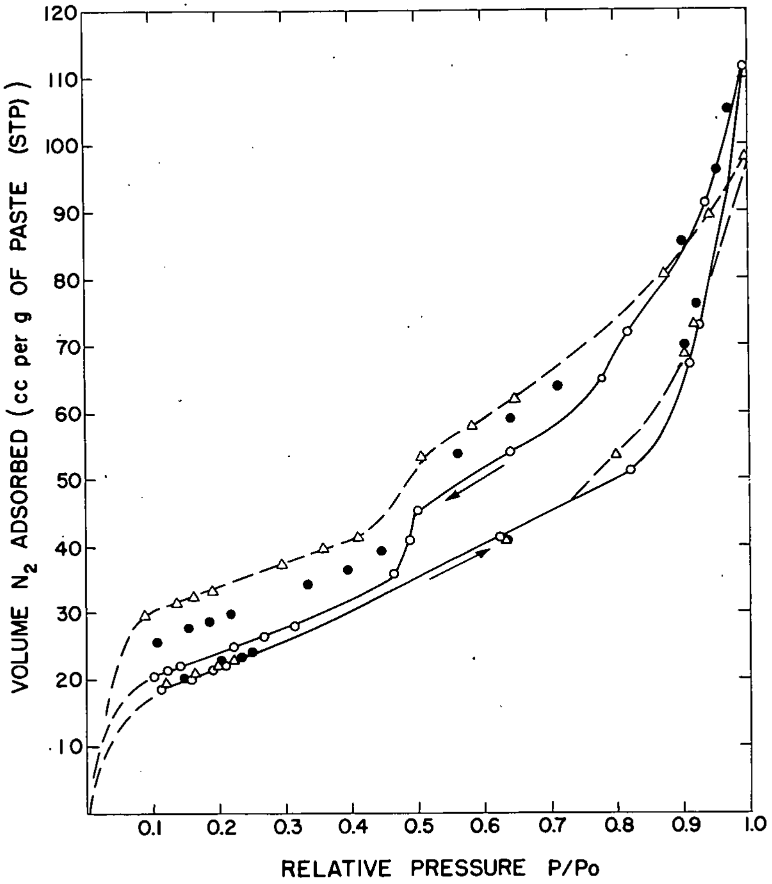

Figure 3A. Nitrogen sorption isotherms of hardened paste initially dried as half-inch cylinder: ○ = initial isotherm after outgassing at 21 C; Δ= second isotherm after outgassing at 100-110 C; ● = third isotherm after crushing and re-outgassing at 100-110 C.

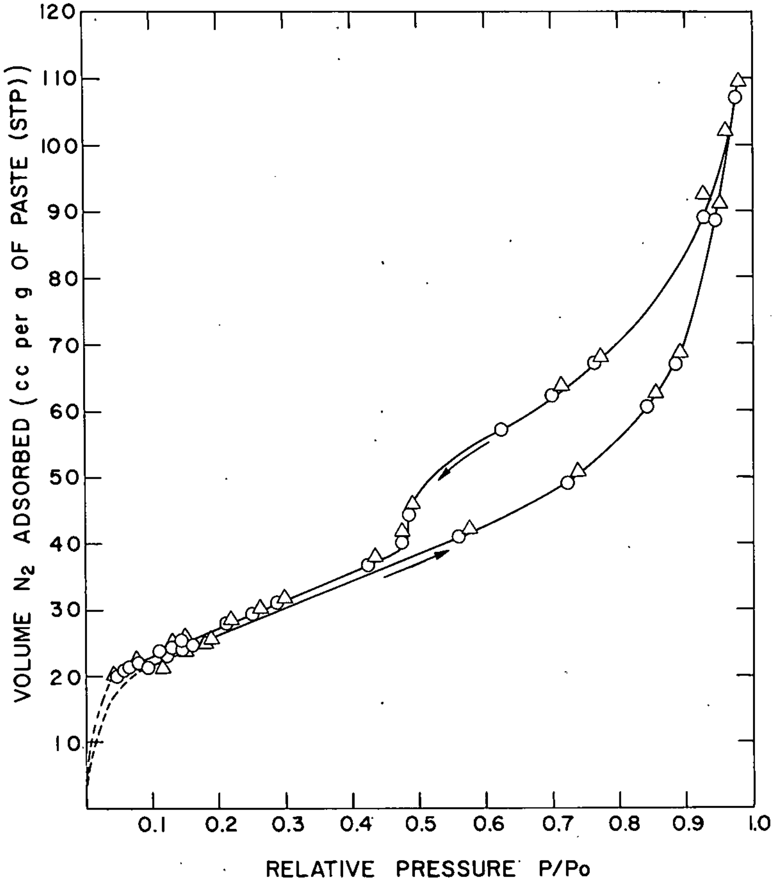

Figure 3B. Nitrogen sorption isotherms of hardened paste which was crushed before intial drying: ○ = initial isotherm after outgassing at 21 C; Δ = second isotherm after outgassing at 100-110 C.

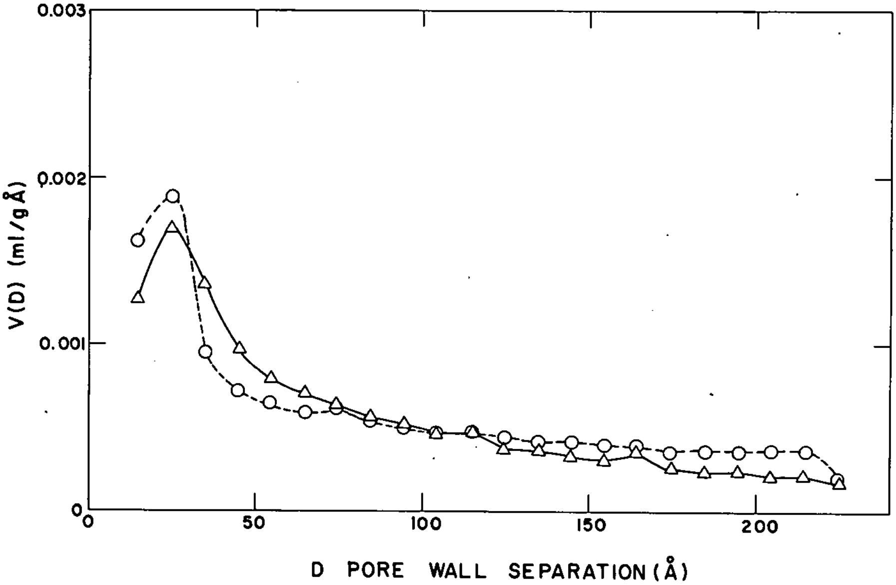

Figure 4. Incremental pore volume, V (D), as a function of pore size: Δ = paste dried as half-inch cylinder; O = paste crushed before drying.

The total pore space accessible to nitrogen, estimated by extrapolating each desorption isotherm to saturation pressure, decreased on the second cycle but increased on the third cycle.

The difference between the adsorption and desorption branches of the hysteresis loop increased in the second cycle, particularly at relative pressures below 0.45; and was still comparatively large after crushing the specimen and repeating the cycle. Mikhail, Copeland and Brunauer (8) also reported hysteresis loops with nitrogen which did not close at relative pressures between 0.1 and 0.45. They attributed this to expansion of the paste which was not completely reversible. However, they found that second adsorption isotherms started from some low relative pressure, without re-outgassing or applying heat, retraced the lower portion of the desorption isotherm. The lower part of the desorption loop was the most repeatable part of the isotherm. In Figure 3A, which represents a specimen which was outgassed before each cycle, this is one of the least repeatable parts of the isotherm. No similar variations between successive cycles were obtained with the specimen which was crushed before initial drying, as shown in Figure 3B. Thus, in addition to differences in surface area, differences in other parts of the isotherm also may depend upon the history of the specimen before measurement.

Pore size distributions of these two specimens are shown in Figure 4. These were calculated from the second isotherms in Figures 3A and 3B, which were both obtained after outgassing at 100-110 C. The adsorption branch of the isotherm was used in the calculations, although there is some disagreement as to whether adsorption or desorption data should be used for the purpose (14, 17). Analysis of pore size distribution from the desorption branch of the loop leads to higher and sharper peaks than those shown in Figure 4 and reflects irreversible swelling of the pore structure during the cycle. The principle peak in Figure 4 occurs at a wall separation of about 25 Å. This is a smaller value than would be obtained with a cylindrical pore model (16, 18). The curves for a specimen dried as a half-inch cylinder and a specimen crushed before drying do not coincide, but the differences are small compared to the differences obtained by Mikhail, Copeland and Brunauer (8) for hardened cement pastes of different water-cement ratios.

SUMMARY

Surface areas of hardened cement pastes of different age and water-cement ratio have been determined by nitrogen adsorption in order to compare them with the already well-known results of water vapor adsorption measurements (5, 9). In addition to lower surface areas obtained with nitrogen there are other important differences. Surface areas by nitrogen adsorption become more and more dependent upon the original water-cement ratio as hydration proceeds. There is some evidence that the surface area of highly hydrated cements may be a linear function of the original water-cement ratio. This is in contrast to surface area by water vapor which is almost independent of water-cement ratio. Furthermore, there is no constant v_m/w_n ratio when v_m is determined with nitrogen. All surface area measurements, regardless of the gas or vapor used, are usually performed on dried specimens. The manner of drying may make a measurable difference in the surface area obtained by nitrogen sorption. Specimens which were crushed with a mortar and pestle before drying usually had higher measured surface areas than specimens which were not crushed before drying. Crushing of the specimen also resulted in differences in the sorption isotherm, and in the calculated pore size distribution of the hardened paste. However, the difference in pore size distribution so produced was small compared with the differences obtained with pastes of different water-cement ratios (8).

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