

Adsorption of Organic Vapors in Relation to the Pore Structure of Hardened Portland Cement Pastes

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Investigations of hardened pastes of portland cement were performed similar to the investigations of the pore structures and surface areas by nitrogen adsorption (8).

Adsorption-desorption isotherms were determined using organic vapors of different molecular areas and polarities; the vapors used were cyclohexane, isopropanol and methanol. The surface areas and pore volumes accessible to each were obtained and compared to those obtained with nitrogen and water vapor.

The results obtained can be explained by visualizing the microstructure of the paste as consisting of aggregated masses of the basic structural units, mainly tobermorite gel sheets, with the masses separated by pores of an average size larger than the average size of pores within the aggregated masses. The pore system within these masses is designated the internal pore system, and between the masses the external pore system. The main conclusions were as follows:

1. Cyclohexane and isopropanol measure only the external pore system, whereas methanol and nitrogen can partly be admitted to the internal pore system. Water seems to measure the entire pore structure of the paste.

2. The external pore system contains both S (small) and L (large) pores. There is evidence that the internal pore system also contains both S and L pores. Cyclohexane and isopropanol are excluded from the internal pore system because the aggregated masses have narrow entry ways to the internal pore system.

3. Study of the hydraulic radii shows that the entry ways to the pores have a size distribution.

4. The size of the adsorbate molecule determines its ability to penetrate into small pores. Polarity of the molecules plays a minor role at low relative vapor pressures, but at high pressures it causes expansion of the pastes.

•IN A cement paste that has been cured and hardened for some time the major part of the hydrated mass consists of a cryptocrystalline of colloidal phase. Because of its similarity to the natural mineral tobermorite, and because of its gel-like properties, it is called tobermorite gel. Tobermorite gel plays a dominant role in the setting and hardening of portland cement paste and in determining the strength and dimensional stability of hardened paste and concrete. Thus, tobermorite gel is the most important constituent of concrete.

The cementing properties of materials are caused by the forces residing in the surfaces of these materials. The magnitudes of these surface forces depend on the nature and the extent of the surface. Thus composition and specific surface area are two of the most important properties of tobermorite gel (1). The specific surface of the gel

constitutes at least 80 percent of the specific surface area of fully hydrated portland cement.

Powers and Brownyard (2) were the first to measure the specific areas of hardened portland cement pastes using the BET (3) method with water vapor as the adsorbate. Practically all investigators who published specific surface area values for tobermorites used the BET method. Greenberg (4) used nitrogen adsorption, but nitrogen surface values for tobermorites are unreliable. Nitrogen adsorption, in almost every instance, leads to a smaller specific surface area than water vapor adsorption. Kalousek (5) used both nitrogen and water vapor, and believed that nitrogen measured only the external surfaces. He attributed the difference between the two to the layer structure of tobermorite gel, and to the ability of water and the inability of nitrogen to penetrate between the layers of the gel. However, later work has shown that water can not penetrate between the layers of strongly dried tobermorite gel, even when the gel is soaked in water (6). Thus, the difference between water and nitrogen adsorption may be a consequence of the pore structure of the gel. Water, because of its smaller size and strong dipole character, may be able to measure the specific surface area and pore volume of spaces which are inaccessible to nitrogen. There is evidence that water measures the total surface area and pore volume of the gel (7).

The pore structure of well-cured hardened portland cement pastes by nitrogen adsorption has been reported recently by Mikhail, Copeland and Brunauer (8). By comparing areas and porosities of nitrogen with those of water, it was shown that a wide range of pore sizes exists, and that nitrogen is excluded from a part of the pore system because some of the pores are too narrow while others have too narrow entrances to admit nitrogen molecules. Thus, the differences were attributed to the sizes of the molecules used as adsorbates.

The above results show that tobermorite gel, like other high area solids, exhibits dependence of the area measured by gas adsorption techniques on the gas used in the determination. It seemed interesting to estimate the relative importance of the effects of size and polarity on the pore structures of cement pastes by considering the adsorption of molecules of different sizes and polar natures. The present paper considers the adsorption of a nonpolar molecule measurably larger than nitrogen, cyclohexane, and two polar molecules, methanol and isopropanol. Comparative study of the behavior of these three molecules, as well as nitrogen and water (8) may lead to a better understanding of the microstructure of hardened portland cement pastes.

EXPERIMENTAL

The hardened cement pastes investigated are the same pastes used in a previous work on a study of the pore structure by nitrogen adsorption (8). The pastes were prepared with different initial weight ratios of water to cement W_0/C , covering the range 0.35 to 0.70. The combined water contents indicated percentage hydrations ranging from 90 percent for the paste with $W_0/C = 0.35$ to 98 percent for the paste with $W_0/C = 0.70$. Details of preparation and conditions of drying were discussed in the earlier work (8). Outgassing was continued for 24 hours at room temperature, using a mercury diffusion pump backed by a mechanical oil pump.

The adsorption values for the three organic vapors, cyclohexane, isopropanol and methanol, were obtained by using a volumetric apparatus of conventional type. Between successive points—three hours in the case of cyclohexane and five hours for the other two—vapors were allowed for equilibration for both the adsorption and desorption points. In several cases several days were allowed, but still the same points were obtained. Surface areas were calculated by using a value of 39 \AA^2 , for the molecular area of cyclohexane, which assumes this molecule to lie flat on the surface (9); for isopropanol and methanol the values are 27.7 \AA^2 and 18.1 \AA^2 respectively. The latter two values were calculated by the equation given by Brunauer (10), assuming closest packing of spherically shaped molecules and that the density of the adsorbed phase is the same as the density of the liquid.

The porosities of the pastes were determined by extrapolation of the adsorption isotherms except for methanol adsorption. The adsorption isotherms of methanol

approach the saturation vapor pressure axis asymptotically, which makes the extrapolation extremely difficult. Therefore the pore volumes were determined by soaking weighed dried samples in methanol, then the liquid was decanted, and the pastes were superficially dried and weighed again; the increase in weight corresponds to the fraction of methanol absorbed into the pore structure.

RESULTS

Figure 1 shows the adsorption isotherms of cyclohexane at 35 C on two cement pastes of $W_o/C = 0.35$ and 0.7 . The isotherms obtained for the rest of the specimens are essentially similar in character. The adsorption of cyclohexane is physical, and outgassing at room temperature for at least five hours completely removes the adsorbate from the surface.

Two adsorption and two desorption isotherms were determined for each paste. In every instance an almost closed hysteresis loop was obtained. It is probable that if very long times would have been allowed for equilibration, the hysteresis loops would have closed completely. The shape of the hysteresis loop, its area and the pressure at which the loop tends to close, all seem to be functions of the water/cement ratio of the paste.

The adsorption of isopropanol at 35 C on the 0.35 and 0.7 pastes is shown in Figure 2; the isotherms shown can be considered as representative for all the pastes investigated.

Although the isotherms for the paste with $W_o/C = 0.70$ do not show it, in a subsequent run it was found that the amount adsorbed at higher relative pressure tended toward a saturation value, similar to type IV isotherms of the Brunauer classification (10). Curves A2 of Figure 2 represent the desorption isotherms, and in every instance a wide-open hysteresis loop is formed. This open hysteresis loop persists to the lowest pressures, which makes it difficult to interpret its existence in terms of capillary condensation alone. There is no doubt that capillary condensation plays a dominant role in the high pressure region, but it cannot account for the existence of the hysteresis observed at low pressures. It seems, therefore, that the adsorption of isopropanol itself causes a change in the pore structure. An expansion of the pore system is produced which is partly irreversible, and which may be the cause of hysteresis at low relative pressures. Similar effects, although to a much smaller extent, have been observed with nitrogen (8).

At a low pressure, a second adsorption isotherm was started, represented by curves A3. It always coincided with the low pressure portion of the first desorption isotherms, and formed a closed hysteresis loop with it. The second desorption always coincided with the first desorption. This means that after the first adsorption run, which causes an expansion in the pore system, the structure remains stable, as indicated by the closing of the hysteresis loop.

When the pastes were outgassed thoroughly at room temperature, incomplete removal of the adsorbate was effected and other adsorption isotherms were obtained which are markedly lower than the original isotherms (series B, Fig. 2). The isotherms obtained after outgassing at room temperature retain all the characteristic features of the original isotherms regarding shape, irreversibility and the nature of the hysteresis loop, but the amounts adsorbed are smaller.

Thus outgassing at room temperature is insufficient to clean the surface of adsorbed molecules, and it seems that a strong binding energy between isopropanol and the surface of cement paste exists. Successive outgassing at higher temperatures removes larger amount of the alcohol and the resulting isotherms are successively higher than those obtained after outgassing at room temperature, but even after outgassing at 100 C the resulting isotherm is lower than the original isotherm (curve C, Fig. 2). Outgassing at higher temperatures than 100 C could not be tested, for it brings some decomposition of the cement paste itself.

These results indicate that the binding energy of the alcohol molecule to the surface is larger than the binding energy of the nonpolar cyclohexane. The alcohol molecules are attached to the surface with variable binding energies, and so they require increasingly higher temperatures of outgassing for removal from the surface.

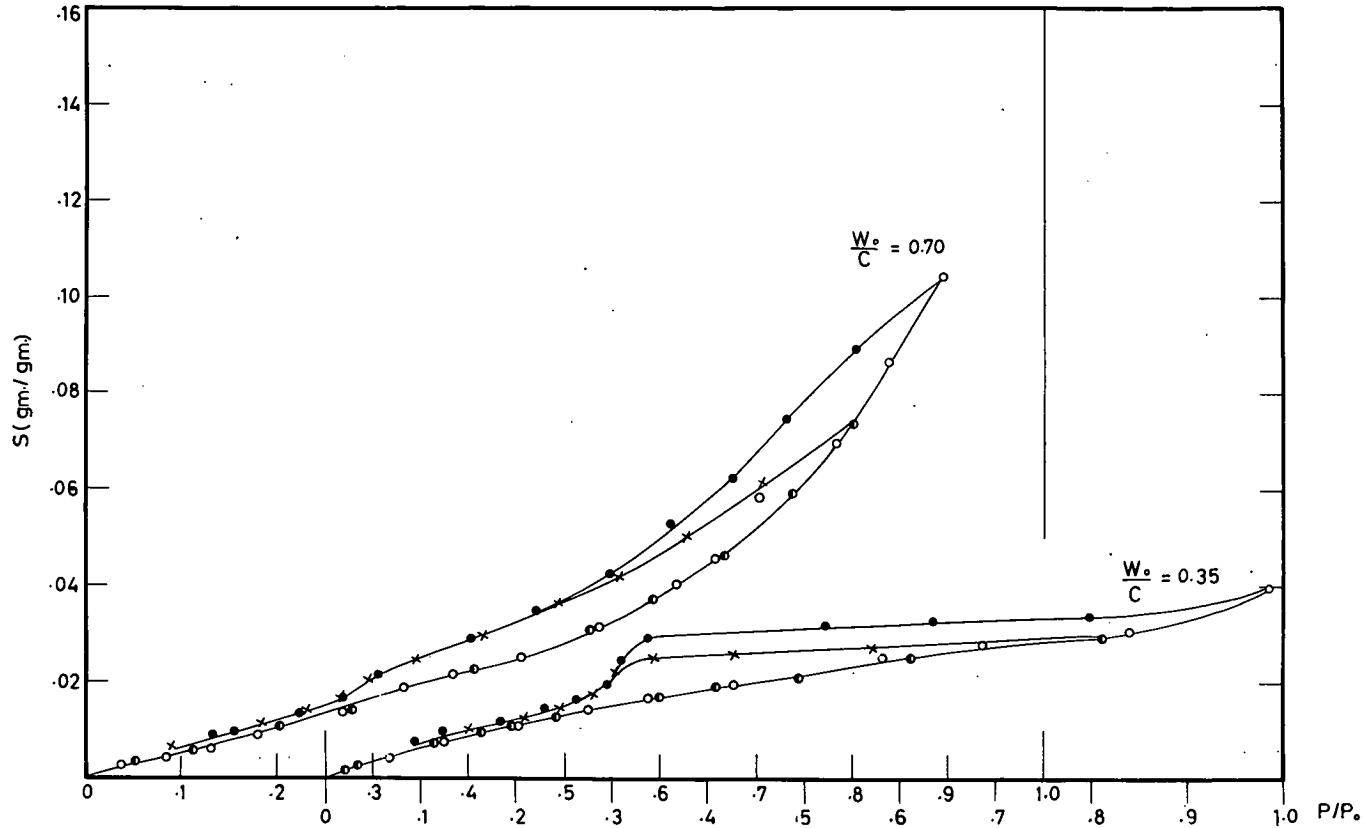


Figure 1. Isotherms of cyclohexane on the 0.35 and 0.7 cement pastes: o = first adsorption; ● = first desorption; ● = second adsorption; x = second desorption.

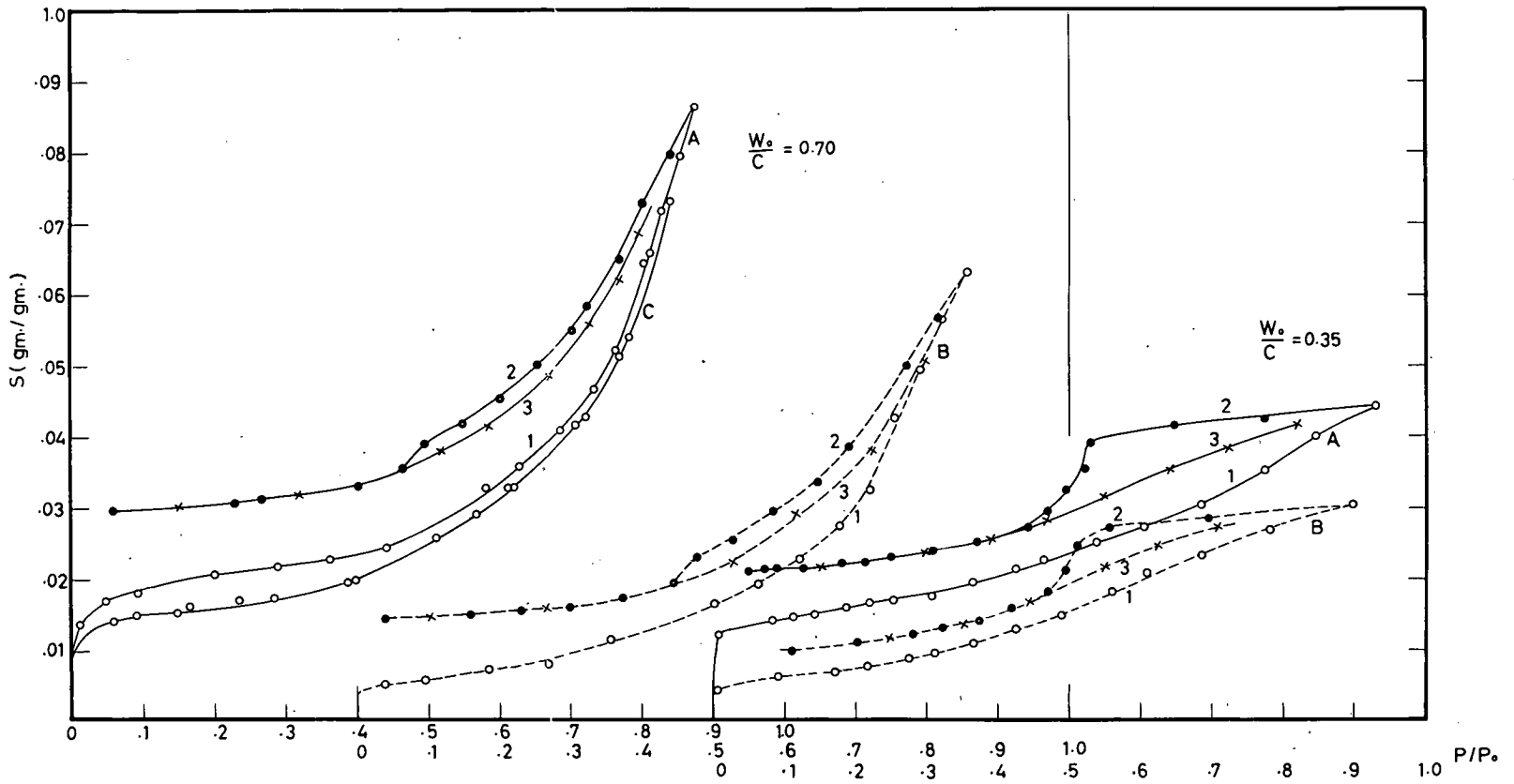


Figure 2. Isotherms of isopropanol on the 0.35 and 0.7 cement pastes.

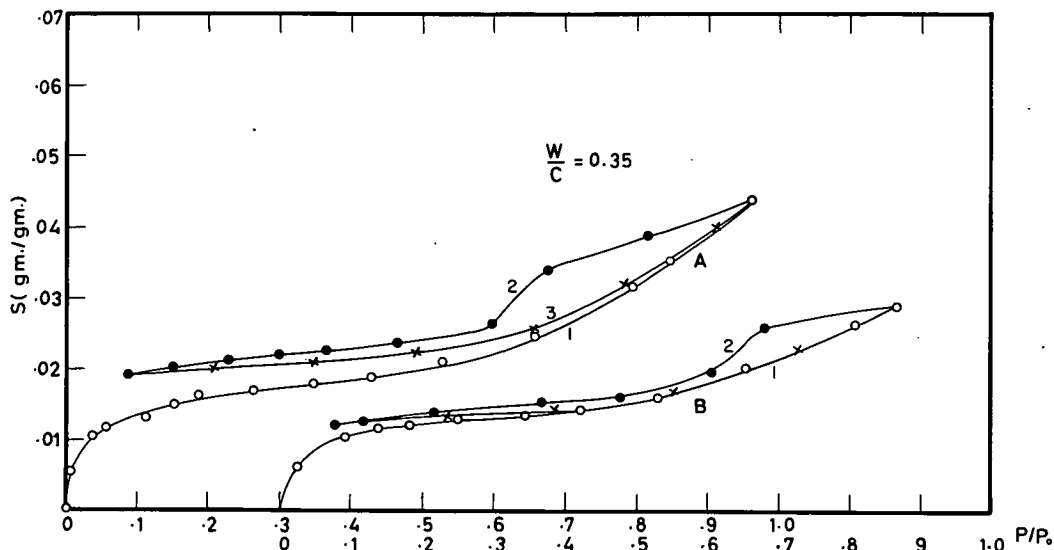


Figure 3. Isotherms of methanol on the 0.35 cement paste: o = adsorption; ● = desorption; x = resorption.

The behavior of methanol on the surface of cement paste is essentially similar to the behavior of isopropanol. A typical isotherm is shown in Figure 3, which shows the adsorption on the 0.35 paste. Outgassing at room temperature does not clean the surface of adsorbate, and the second runs of adsorption isotherms are appreciably lower than the original isotherms (series A and B, Fig. 3). The binding strength of the methanol molecule to the surface is also variable, for continuous raising of the temperature of outgassing removes the adsorbate gradually from the surface.

The two readily available quantities from these isotherms are the specific surface area and the pore volume obtained from the amount taken at the saturation pressure of the vapor. For methanol, the pore volumes were obtained by an independent method as stated earlier. In calculating the pore volumes the assumption was made that the densities of adsorbed vapors were the same as those of the corresponding liquids. If some error is introduced by this approximation, it cannot affect any of the conclusions reached in this paper.

The specific surface areas obtained are summarized in Table 1. The values for water and nitrogen were obtained and discussed in an earlier publication (8), but are inserted in Table 1 for comparison. Several interesting comparisons can be made by examining the data of Table 1. Water gives a measure of the total surface area of the paste (7); therefore it is expected to record the biggest values in Table 1. These values are independent of the water/cement ratio of the paste.

Columns 3 and 4 of Table 1 show the specific areas obtained from nitrogen and methanol adsorption respectively. The values in both columns show essentially the same trend. There is an increase in the area measured by both molecules with increase in the water/cement ratio of the paste. It has been shown (8) that nitrogen is excluded from parts of the pore structure, and therefore does not measure the total area of the paste. As the pores get wider with rise in the water/cement ratio of the paste, the areas measured by nitrogen also show such an increase. The behavior of methanol is essentially the same. The slightly lower areas measured by methanol may be attributed to the slightly larger size of the methanol molecule.

The specific surface area values obtained from isopropanol and cyclohexane adsorption are shown in columns 5 and 6 of Table 1. The two vapors gave almost the same values, which are much smaller than the total areas of the pastes measured by water, ranging between 20 and 25 percent of the values given by water. Also, it should be noted that the values given by isopropanol and cyclohexane are almost independent of the water/cement ratio of the paste.

TABLE 1
SPECIFIC SURFACE AREAS OF HARDENED PASTES
(m² per g)

1	2	3	4	5	6
W_o/C	S_{H_2O}	S_{N_2}	S_{CH_3OH}	$S_{C_3H_7OH}$	$S_{C_6H_{12}}$
0.35	208.0	56.7	50.0	41.7	41.2
0.40	202.6	79.4	62.5	45.0	44.5
0.50	194.6	97.3	88.5	49.0	48.0
0.57	193.8	132.2	107.0	49.5	49.0
0.70	199.6	139.6	114.0	51.4	49.0

TABLE 2
PORE VOLUMES OF HARDENED PASTES
(ml per g)

1	2	3	4	5	6
W_o/C	V_{H_2O}	V_{N_2}	V_{CH_3OH}	$V_{C_3H_7OH}$	$V_{C_6H_{12}}$
0.35	.1264	.0748	.0695	.0576	.0552
0.40	.1776	.1059	.0991	.0880	.0840
0.50	.2615	.1792	.1703	.1533	.1477
0.57	.3110	.2493	.2310	.1710	.1680
0.70	.4008	.2758	.2645	.1793	.1759

The values obtained for methanol and isopropanol were calculated from the original isotherms. As mentioned before, expansion of the pore system occurs at high relative vapor pressures, and larger surface areas are obtained if the resorption isotherms are used in the calculations (curve A3, Figs. 2 and 3).

The pore volumes obtained are shown in Table 2, which also includes the pore volumes measured by water (total pore volume of the paste) and by nitrogen (8).

It is interesting to note that for the pore volumes, just as for the surface areas, the values obtained by methanol are close to those obtained by nitrogen, and the values for isopropyl alcohol and cyclohexane are also very close to each other. Even more interesting is the observation that the values recorded in columns 5 and 6 of Table 2 represent about 50 percent of the total pore volume of the paste shown in column 2. This 50 percent is a mean value; for isopropyl alcohol the lowest value is 44 percent and the highest is 59 percent; for cyclohexane the range is 44 to 56 percent. Evidently, isopropanol and cyclohexane occupy the same pore space, which represents roughly 50 percent of the total pore volume. The area within this space is 20 to 25 percent of the total area of the paste.

DISCUSSION

The results of the present work confirm all conclusions reached in the earlier paper (8) and, in addition, lead to new and interesting conclusions.

The first new conclusion concerns the influence of dipole moment on the ability of a molecule to penetrate into small pores. In Figure 4, curve I represents the specific surface areas measured by water vapor and curve II the areas measured by nitrogen for the five pastes. These curves were taken from the earlier paper (8). The fact that water always measured larger areas was attributed to its ability to penetrate into smaller pores than nitrogen, partly because of its smaller size, partly because of its dipole moment. It was supposed that the attraction between an ionic surface, like that of tobermorite gel, and the dipole moment of the water enables water to penetrate into pores where a nonpolar molecule of equal size would be unable to penetrate.

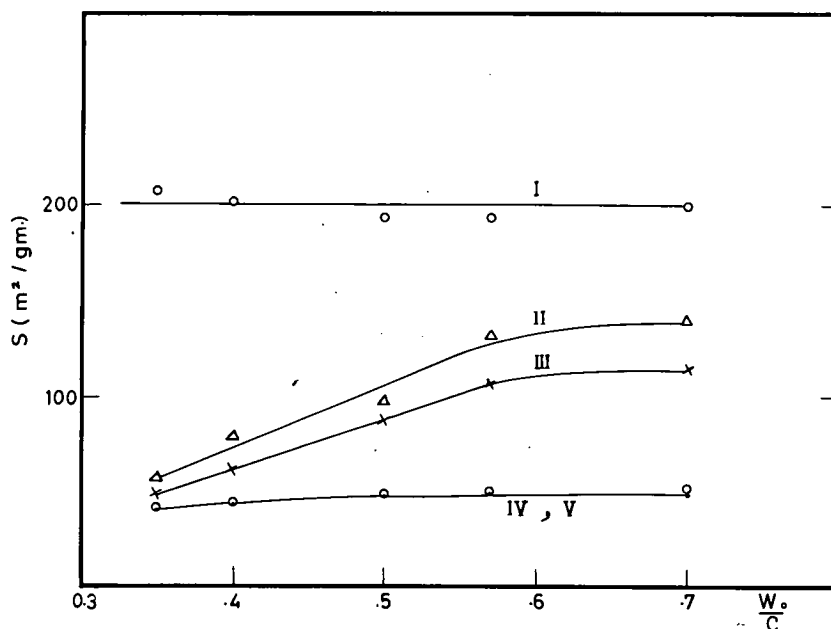


Figure 4. Variation with water/cement ratio of specific surface area available to the different adsorbates: I = water; II = nitrogen; III = methanol; IV = isopropanol; V = cyclohexane.

This supposition is refuted by the present experiments. The methanol molecule is only slightly larger than the nitrogen molecule (the molecular areas of methanol and nitrogen are 18.1 and 16.2 Å², respectively). If the dipole of methanol would have a sufficient effect, it might compensate for the small difference in size or even over-compensate for it, and methanol might be able to penetrate into the same pores or even smaller pores than nitrogen. However, this is not the case. As Table 1 and curve III in Figure 4 show, methanol measures a smaller surface, and as Table 2 shows, methanol measures a smaller pore volume for every paste than nitrogen measures. It appears, therefore, that the dipole has no appreciable effect, and the ability to penetrate into pores depends solely on the size of the molecule. This conclusion is probably of general validity and is not restricted to the particular adsorbent-adsorbate system investigated.

The second interesting new result is that isopropanol and cyclohexane measure the same surface, as seen in Table 1 and in curves IV and V in Figure 4. They also measure the same pore volume, as Table 2 shows. These molecules differ greatly in size (the molecular area of isopropanol is 27.7 and of cyclohexane 39 Å²). The areas measured by these two vapors represent 25 percent of the total surface area and the pore volumes are approximately half the total pore volume measured by water. The conclusion which can be drawn from such a result is that the structure of the paste is not continuous, and some sort of an "intermediate structure" exists. This intermediate structure is formed by the grouping or aggregation of the gel particles to form bundles or aggregates which are intermediate in size between the tobermorite gel particles and the size of the cement paste granules. Cyclohexane and isopropanol appear to measure the outer surfaces of these aggregates. Because of their size, these molecules have no access to the pore system within the aggregates; they only measure the pore volume external to the aggregates. Methanol and nitrogen can naturally penetrate into the same pore system, but in addition they have access to a part of the pore system within the aggregates themselves. In the densest pastes, the lower limit of the surface measured by both methanol and nitrogen will be the same as that measured by cyclohexane and isopropanol, namely, the outer surface of these

aggregates. In the literature, the nitrogen surface values published range between 21 and 100 percent of the water surface values, and it is interesting to note that the lowest limit of the nitrogen surface values is very close to the fraction of surface measured by cyclohexane or isopropanol in the present investigations.

Evidence for the existence of the intermediate structure was obtained by Copeland and Bragg (11) during their measurements of light scattering by portland cement pastes, and more direct evidence was recently obtained by Copeland and Chang (12) in their stereoscopic replica electron micrographs.

The pore system within the aggregated masses will be designated the internal pore system, and the pore system between the aggregates will be designated the external pore system.

As mentioned, the external pore system contains about 25 percent of the total surface area of the paste and about half its pore volume. It is totally measured by cyclohexane and isopropanol. Because the adsorption of cyclohexane brings no expansion of the pore structure and because it is purely physical in nature, the pore size distribution could be obtained from the hysteresis loops associated with its isotherms.

By applying the Kelvin equation to the desorption isotherms, the radii of pores of different sizes could be evaluated as a function of the volume of liquid they contain. In applying such an equation, it is assumed that the adsorbate is held by two mechanisms: (a) physical adsorption on the pore walls, and (b) capillary condensation in the inner capillary volume. The Kelvin equation evaluates the radius uncorrected for physical adsorption on the pore walls. To correct for this a t -curve for cyclohexane was constructed for a completely sintered oxide surface, which can be considered as a plane surface. The surface properties of this oxide will be discussed elsewhere (13). The t -curve represents a plot of the thickness of the adsorbed layer on a plane surface against the corresponding relative vapor pressure. The thickness of the adsorbed layer on a plane surface should be added to the radius obtained from the Kelvin equation.

The results of this analysis are shown in Figure 5 for the 0.35 and the 0.7 paste. The curves are plots of $dv/dr \times 10^2$ against the pore diameter D in Å. They represent differentiated structure curves or pore frequency curves for the desorption branches of cyclohexane.

It should be noted that for the 0.35 paste, there is only one maximum at 45 Å, which represents the most frequent diameter of the pores of the external pore system. The distribution is rather narrow and the greatest number of pores, or nearly all pores, have a diameter less than 75 Å. For nitrogen, the maximum was at 22.5 Å (8).

For the 0.7 paste, the maximum is still at 45 Å, and there is a smaller maximum at 65 Å. The distribution beyond that is very broad, as shown by the broad shoulder which covers all the range up to 300 Å. It should be noted that most of the pores possess a diameter less than 140 Å. Beyond this value a gradual dip is observed in the distribution curve. For nitrogen, the maximum for the 0.7 paste is at 32.5 Å.

The pore system was divided by Mikhail, Copeland and Brunauer (8) into two parts: a system of small pores, designated as S pore system, and a system of large pores, designated as L pore system. From the nitrogen distribution curves (8), an arbitrary but useful division between the pore systems could be made around 40 Å for the 0.35 paste and somewhere between 60 and 80 Å for the 0.7 paste. The pore size distribution curves of Figure 5 are continuous. They show that the external pore system contains both small and large pores, but the large pores constitute a greater fraction than the small pores. Because the maxima of the distribution curves of cyclohexane are shifted to higher values than recorded by the nitrogen curves (8), and because even nitrogen does not enter all of the pores, especially the small ones, it is concluded that the differences in the sizes of pores of the external and of the internal pore systems are great, the former having much larger pores than the latter.

The curves of Figure 5 represent only the pores accessible to cyclohexane. Evidently there is an increase in the size of all types of pores present with increasing water/cement ratio of the paste. There is another way of demonstrating such an increase, as was done in the earlier paper (8).

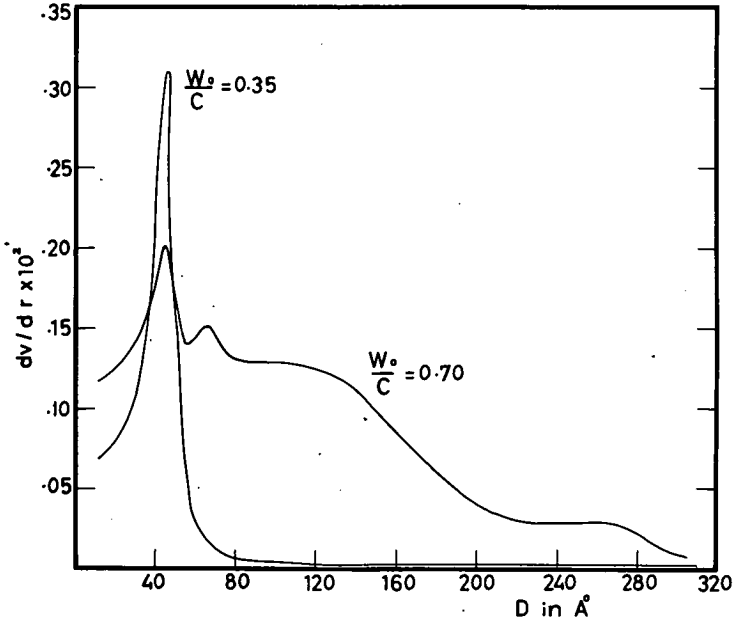


Figure 5. Pore size distribution curves of hardened portland cement pastes, as obtained from the adsorption of cyclohexane.

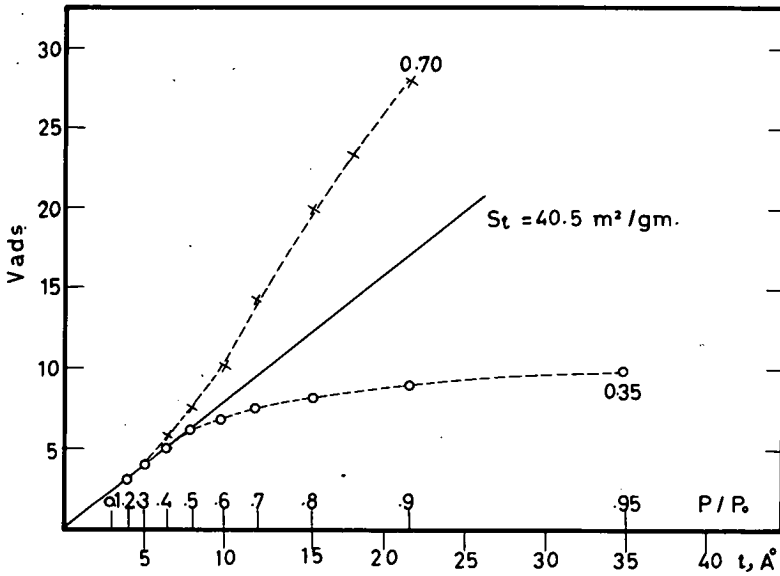


Figure 6. Plots of V_{ads} vs t for cyclohexane adsorption on hardened portland cement pastes.

The statistical thickness of the adsorbed film of cyclohexane on a plane surface can be defined as the volume of the adsorbed film divided by the surface area of the adsorbent. For cyclohexane the equation is

$$t = 49.1 (V_{ads}/S_t) \tag{1}$$

TABLE 3
HYDRAULIC RADII OF PORES, Å

1	2	3	4	5
W_0/C	Total pore system r_1	Pores inaccessible to N_2 r_2	Pores inaccessible to C_6H_{12} r_3	Pores accessible to C_6H_{12} r_4
0.34	6.1	3.4	4.3	13.4
0.40	8.8	5.8	5.9	18.9
0.50	13.4	8.5	7.8	30.8
0.57	16.0	10.0	9.9	34.3
0.70	20.1	20.8	14.9	35.7

A plot of the volume adsorbed, expressed in cc at S.T.P. (V_{ads}), against t , the thickness in Å, is a straight line with a slope of $49.1/S_t$, where S_t is the surface in m^2 per g. S_t is expected to be very close to, but not necessarily exactly the same as, the BET surface area.

The plot is a straight line at low pressures even for the porous bodies. At high pressure the plot deviates for one of two reasons: (a) the building of layers is interrupted because some of the narrow pores become filled by multilayer adsorption, and in this case the plot drops below the straight line, or (b) capillary condensation starts in certain pores in addition to multilayer adsorption, in which case the plot deviates above the straight line.

Figure 6 shows such V_{ads} vs t plots for the two extreme cases, the 0.35 and 0.7 pastes. The values of V_{ads} were taken from the adsorption branches of the isotherms of Figure 1, and the values of t were taken from the t -curve constructed in this laboratory (13), by reading the value of t corresponding to the relative pressure of the particular isotherm point.

At small values of relative pressure a good single straight line was obtained for both samples. From the slope of this straight line a value of S_t was calculated to be $40.5 m^2$ per gram. The agreement between S_t obtained in this way and the BET surface area is reasonable. This means that our t -curve gives a good representation of the average thickness of the cyclohexane film adsorbed at low pressures on cement pastes.

The curve for the 0.35 paste deviates negatively from the straight line at a thickness of 8 Å, evidently because an appreciable fraction of pores with hydraulic radii of 8 Å and smaller are filled with adsorbate. On the other hand the 0.7 paste does not show any sign of pore blocking in this region. Instead it clearly shows indications of capillary condensation at P/P_0 values above 0.4.

Figure 6 demonstrates in an excellent way the increase in the sizes of pores with increasing water/cement ratio, while the area measured remains essentially the same.

A possible way to visualize a pore system in which the surface area remains constant while the pore volume increases with W_0/C is to postulate that such volume is confined between slit-shaped capillaries. Variation in the distance between the walls of the slit does not alter the area measured but leads to variation in the volume. However, the evidence collected from adsorption data regarding the shapes of capillaries is not by itself conclusive unless supported by independent experiments, such as electron-microscopy (14).

Although there is some evidence to believe that many of the pores present are slit shaped, there is probably no solid which contains only pores of a single shape.

For pores of any shape, an average radius, called hydraulic radius, can be calculated by dividing the volume of the pore system by its surface area. The hydraulic radii from cyclohexane adsorption are given in Table 3. The values in columns 2, 3, 4 and 5 designated as r_1 , r_2 , r_3 and r_4 are V_{H_2O}/S_{H_2O} , $(V_{H_2O} - V_{N_2})/(S_{H_2O} - S_{N_2})$, $(V_{H_2O} - V_{C_6H_{12}})/(S_{H_2O} - S_{C_6H_{12}})$, and $V_{C_6H_{12}}/S_{C_6H_{12}}$ respectively (8).

Comparison of the values of columns 3 and 4 in Table 3 leads to a third new and interesting conclusion besides the other two conclusions already considered. Among the

five pastes investigated, four show nearly the same hydraulic radii for pores inaccessible to nitrogen and cyclohexane. When two different adsorbents give the same hydraulic radii by two different molecules, no definite conclusion can be drawn from the result, but when one and the same adsorbent gives the same hydraulic radii by two different molecules which are very different in their molecular sizes, then one can conclude that the size distribution of the pores inaccessible to the two molecules, in this case to nitrogen and cyclohexane, is the same. The fact that nitrogen can penetrate into a greater part of this common pore system indicates that there is a size distribution of the entry ways, the narrower entrances preventing cyclohexane from entering into some of the pores.

The fact that the values of column 4 are considerably smaller than the values of column 5 for all cases investigated clearly shows that in each paste there is a sizable fraction of pores into which cyclohexane cannot enter partly because of the small sizes of the pores, partly because of too narrow entry ways to larger pores. The exclusion of cyclohexane from a part of the pore system due to narrow entry ways seems to be predominant for pastes of high water/cement ratio. This has also been shown by nitrogen adsorption (8).

The hydraulic radii shown in columns 2, 4 and 5 show approximately a threefold increase in value in passing from the 0.35 paste to the 0.7 paste. For columns 2 and 4 the increase is slightly more than threefold, for column 5 it is slightly less than threefold. Both the external and internal pore system contain both S and L pores, and their distribution is broad with an average which is greater for the external than the internal pore system. The external system, which acts as a filter for large sized molecules, definitely does not contain only narrow pores.

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