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by G.G. Litvan

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VARIABILITY OF THE NITROGEN SURFACE AREA OF HYDRATED CEMENT PASTE

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ABSTRACT

The difference between the BET specific surface areas computed from water and nitrogen adsorption isotherms of bottle hydrated cement paste were found to vanish if special techniques for drying the samples were applied. Typical features of the methods were replacement of the pore water by methyl alcohol which in turn was substituted by pentane and final drying was achieved by distillation either in vacuo or above the critical temperature. The nitrogen and water surface areas of the specially dried paste are both approximately $200 \text{ m}^2/\text{g}$. It is suggested that the commonly observed discrepancy in surface areas is due not to deficiencies of the measuring method but to real differences evoked by the particular drying technique applied.

La différence entre les aires de surface spécifiques B.E.T. calculées à l'aide des isothermes d'adsorption d'eau et d'azote de la pâte de ciment hydratée dans une bouteille disparaît lorsque l'on utilise des techniques spéciales de séchage des échantillons. Ces méthodes comportent le remplacement de l'eau interstitielle par de l'alcool méthylique, lui-même remplacé par du pentane, et un séchage final par distillation sous vide ou bien au-dessus de la température critique. Les aires de surface de l'eau et de l'azote dans la pâte séchée de façon spéciale sont toutes deux d'environ $200 \text{ m}^2/\text{g}$. L'auteur estime que la divergence communément observée des aires de surface est le résultat non pas de quelque lacune de la méthode de mesure mais d'un écart réel dû à la technique de séchage utilisée.

The BET specific surface areas of hydrated Portland cement computed from the water adsorption isotherm (1,2) are much larger than those calculated from the nitrogen isotherm (3 - 6). The differences are quite substantial: although the nitrogen area values fall in the range between 13 and 84 m²/g (5) the water area is typically 200 m²/g (1,2). Values obtained from the adsorption of oxygen, argon (3) and organic vapors are in line with the nitrogen areas: approximately 50 m²/g for cyclohexane and isopropanol, and between 50 and 114 m²/g for methanol (7). The specific surface area values determined by small-angle x-ray scattering, an independent physical method, are similar to that of the water area for the dry material (8). The method makes it possible to determine the surface area of a solid also in the wet state.

The pertinent literature dealing with the reasons and theoretical implications of the discrepancy is extensive (9 - 12) and will not be discussed here.

Hunt, Tomes and Blaine showed that surface areas are affected not only by the nature of the absorptive but also by the length of the drying period, the degree of aggregation (13) and the rate of drying (14). These findings suggest that the discrepancies in surface areas are not so much due to the inadequacies of the measuring technique but rather to the variability of the surface area caused by changes in environmental conditions and the nature of the adsorbing vapor. Similarity appears to exist in this respect between cement and other hydrophilic adsorbents such as clays (15), casein (16), and bacterial spores (17). For the last-mentioned substance, Neihof, Thompson and Deitz developed a drying method known as solvent replacement which greatly increased the nitrogen surface areas although they were still only half as large as the area computed from the water adsorption isotherm (17).

The aim of the present work was to investigate if drying of cement paste by solvent replacement increased its nitrogen surface area. In addition, the effect of using the critical point drying method was explored. For this method, as the name implies, the solvent is removed at a temperature above its critical point, thus avoiding the collapse of the structure caused by the receding meniscus.

Experimental

The cement used in these tests was hydrated in a single batch for more than three years in a sealed polyethylene bottle under continuous rotation. The surface areas were determined in a high vacuum volumetric adsorption apparatus. Prior to measurement, pumping through a liquid nitrogen trap was continued until the residual pressure was less than 1×10^{-1} Pa (1 mm Hg). The surface area values are expressed in square metre per gram of ignited (1050 °C) cement.

The water surface area was determined by the 'desiccator method' (2) and a modification of it, which consisted of exposing the slurry to the approximate relative humidity and after a minimum of 133 days of equilibration time, 'D-drying' the conditioned sample.

Results

A summary of the surface area values and brief description of the sample preparation are given in Table I. Sample No. 1 was dried in a desiccator over Mg(ClO₄)₂ for 133 days followed by final pumping at room temperature. The nitrogen area was found to be 69.6 m²/g. Sample No. 2 was pumped continuously for 39 days at room temperature and the surface area was 105.0 m²/g. Pumping time was drastically reduced to 6.5 h when the temperature of sample (No. 3) was raised to 110 °C. The surface area was 121.8 m²/g.

TABLE I

Nitrogen surface area of samples prepared by various techniques.

Sample No.	Storage Time, days		Drying Mode	Final D-Drying		Area, m ² /g
	in Methyl Alcohol	in Pentane		hours	t, °C	
1	--	--	Mg(ClO ₄) ₂ 133d	24	20	69.6
2	--	--	D-drying 39d	40	20	105.0
3	--	--		65	110	121.8
4	8	--	Vac. dist.	20	50	196.3
5	108	--	Vac. dist.	20	40	194.0
6	8	6	Vac. dist.	20	50	209.5
7	1	3	Vac. dist.	20	50	219.9
8	0.8*	0.3*	Vac. dist.	20	40	228.1
9	69	2	Evap. 20 °C	20	110	208.9
10	8	6	Crit. point	20	40	188.2
11	1	3	Crit. point	20	40	219.2
12	44	0.8*	Vac. dist.	20	50	249.4

* refluxed

Sample No. 4 was prepared by centrifuging the aqueous slurry for 1 h at 1300 rpm, the water decanted and the solid washed five times with methyl alcohol during the subsequent eight-day period. Finally, the alcohol was vacuum distilled. The surface area was 196.3 m²/g. Sample No. 5 was dried in a similar manner except that it had been kept under methyl alcohol for 108 days, during which the liquid was renewed eight times. No significant change in surface area resulted (194.0 m²/g).

Samples Nos. 6 and 7 were dried under similar conditions except that, in the second stage, methyl alcohol was replaced by n-pentane. The surface areas were 209.5 and 219.9 m²/g respectively. A further moderate increase of the area to 228.1 m²/g occurred when the above procedure included refluxing of the solvents (sample No. 8).

Sample No. 9 was stored in methyl alcohol for 60 days after which the solvent was replaced by n-pentane. Finally, the solvent was left to evaporate at room temperature. The surface area was 208.9 m²/g.

Samples Nos. 10 and 11 were companion to Nos. 6 and 7. The final drying step, however, was not by vacuum distillation in these cases but by evaporation above the critical pressure and temperature (205 °C) of pentane. The nitrogen surface area of the samples were 188.2 and 219.2 m²/g, respectively.

The highest surface area value to date, 249.4 m²/g, was obtained with sample No. 12 which was stored in methyl alcohol for 47 days, refluxed with pentane for 16 h and dried by vacuum distillation.

The water surface area from the desorption branch of the isotherm is $286 \text{ m}^2/\text{g}$; from the adsorption branch it is $182 \text{ m}^2/\text{g}$.

Discussion

The nitrogen surface areas of 'D-dried' samples of the same cement paste were found to range from 69.6 to $249.4 \text{ m}^2/\text{g}$. In view of this extremely large variation, extreme caution must be exercised in the utilization of area values in theoretical considerations. Admittedly the discrepancy was created by the diversity of the drying procedure but the effect of the mode of drying as opposed to the final state is not generally realized in the literature; details of sample preparation are seldom given. Even if the drying procedure were standardized the obtained values could be more characteristic of the preparative procedure than of the paste itself.

Hunt, Tomes and Blaine reported (14) that a rapidly dried paste has a larger nitrogen surface area than a slowly dried one. This observation may explain the present results. Solvent replacement with the highly volatile n-pentane and critical-point drying methods provide practical means for achieving very high drying rates. The effectiveness of these methods appears to depend primarily on the completeness of the first water-replacing phase which can be promoted by elevating the temperature and extending the storage period. Very probably area values higher than $250 \text{ m}^2/\text{g}$ can be achieved by further improvements of the procedure.

The results presented in this paper indicate that the nitrogen surface area dried by special technique became comparable to the water area of conventionally dried cement samples. In run No. 13, cement was prepared in a manner similar to that followed with sample No. 8 and the water and nitrogen areas were determined using separate portions. The values obtained were 201 and $214 \text{ m}^2/\text{g}$ respectively, indicating that the difference between the two areas vanishes if the sample is dried by solvent replacement.

The nitrogen areas of several samples exceeded the water surface area value, in contrast to normal experience. Differences in surface areas obtained with different adsorbates is usually attributed to the inability of the adsorbing molecule to reach the entire surface, which is of constant magnitude. It may well be, however, that the adsorbate has a direct effect on the area inasmuch as adsorption of different molecules induce different response of the solid. Essentially there are two alternatives: 1) a real surface area does exist, which is constant and its value can be determined to a different degree of accuracy by the adsorption of molecules, or 2) the surface area of the solid is variable, a function of various parameters and each adsorbate measures more or less accurately the effective area. Although the first alternative has been accepted generally, the second appears to be a distinct possibility.

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SURFACE AREA, BET, NITROGEN, VARIABILITY

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