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The BET-specific surface area of hydrated Portland cement and related materials

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Abstract

Factors that may affect the results in the determination of the BET-specific surface area of hydrated Portland cement and related materials are analyzed on the basis of available experimental data. In addition to factors brought about by starting mix composition and curing conditions, the obtained result is also influenced by sample preparation, especially by the way free water is removed from the pore system. The consistently lower BET_{N2} values, as compared to BET_{H_2O} results, are brought about by the extremely restricted ability of nitrogen molecules to penetrate small pore entrances under conditions used in the measurement and to enter a part of the overall pore space.

Keywords: Calcium silicate hydrate; Portland cement; Surface area; Adsorption

1. Introduction

The BET method is a widely used and established approach of determining the specific surface area of solid materials, especially such with distinct open porosity. In it, the amount of an adsorbate required to produce a hypothetic densely packed monomolecular layer at the surface of the sample is determined from the low partial pressure region of the obtained adsorption isotherm, using the equation suggested by Brunauer et al. [1]. From this value, the magnitude of the surface may be established if the area covered by a single adsorbate molecule is known.

For determining the specific surface area of hydrated cements, two adsorbates are almost exclusively used, namely, nitrogen and water vapor. One should expect that measurements with any of those two will yield identical results; however, practical experience indicates that in systems that contain the C-S-H phase as one of its constituents, the BET_{N2} values are consistently lower than those found by water vapor adsorption. Different interpretations have been suggested to explain this anomaly. However, the problem is still not definitely resolved and remains subject of discussion.

Some investigators believe that in measurements performed using water vapor, a fraction of water molecules taken up by the sample enters spaces between the C-S-H layers from which the original water was removed in the course of sample preparation rather than to be adsorbed on the existing surface. The consequence is an excessively high amount of H_2O bound by the material, which leads to erroneously high BET results. Contrary to that, N_2 molecules do not enter such interlayer spaces, remain only adsorbed at the surface, and thus the obtained BET_{N2} values reflect the true surface area of the material [2–8].

According to another view, molecules of N_2, unlike molecules of H_2O, are unable to penetrate the whole existing pore space; thus, the obtained BET_{N2} values indicate only the magnitude of that surface, which is located in pores accessible to this adsorbate [9–13].

Different interpretations were forwarded to explain this anomalous behavior of nitrogen: one possibility is the existence of very narrow pore entrances in the structure of the hydrated cement paste, which can be penetrated by smaller molecules of H_2O but not by larger N_2 molecules [8]. The fact that H_2O molecules possess a distinct dipole, whereas N_2 molecules do not, may also play a role [11]. It was also suggested that penetration of the adsorbate molecules into spaces accessible only through very narrow openings (called ink bottle pores) can take place only by activated diffusion, the rate of which—unlike that of normal

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diffusion—is highly temperature dependent. The greater permeability of H_2O molecules through pores of this kind is due to the fact that measurements with nitrogen are done at temperatures that are significantly lower than those made with water vapor [9,11,14]. Diamond [15] pointed to the large amount of crystalline calcium hydroxide in hardened Portland cement pastes that may engulf some C-S-H and may prevent penetration of N_2 but not H_2O into this phase. Jennings et al. [16–18] explained the existing discrepancy between the found BET_{N2} and BET_{H_2O} results by assuming the presence of two distinct types of C-S-H in hydrated cement pastes, one into which nitrogen can penetrate and another one into which it cannot.

In addition to C-S-H, Portland cement and some related binders in their hydrated state may contain calcium hydroxide (whose specific surface area is negligible) and variable but usually small amounts of ettringite ($C_6AS_3H_{32}$) and/or monosulfate (C_4ASH_{12}). The latter two phases decompose under D-drying conditions but barely retake any of the lost chemically bound water at low relative water vapor pressures as are used in BET determinations.

Within this study, factors that may influence the magnitude of the obtained BET values are analyzed. Also, are the available experimental data will be evaluated with the aim to clarify the reasons for the differences in BET results obtained by nitrogen and water vapor adsorption. The analysis is based on a review of data published by other authors as well as our own published and unpublished results.

2. Experimental

2.1. Sample preparation

Upon mixing with cement, a fraction of the added water is consumed in the hydration process and becomes a part of the hydrates formed. The rest of the water—unless it spontaneously evaporates—remains in the existing pores in the form of free water or water adsorbed to the surface of the existing solid phases. As the BET method is based on adsorption from the gaseous phase, the free and adsorbed water must be removed first to enable the migration of the adsorbate gas to the internal surface and its subsequent adsorption. A problem exists, however, in the limited possibility to quantitatively separate the water adsorbed to the surface of the existing pores without simultaneously removing some interlayer water present within the formed hydrates. This is due to the fact that even though the average binding energy of the combined water is greater than that of adsorbed water, both binding energies posses their own spectrum and both spectra strongly overlap. Thus, the most firmly bound part of adsorbed water has a higher binding energy than the most weakly bound part of combined water. To overcome this dilemma, the terms "evaporable water" and "nonevaporable water" were adopted by which the fraction of "total water" that escapes or remains bound under arbitrarily selected experimental conditions is identified.

The most commonly used procedure to remove evaporable water is the D-drying method developed by Copeland and Hayes [19] in which the sample is vacuum dried to the vapor pressure of water at the temperature of dry ice (5×10^{-4} Torr). It is believed that under these conditions, all adsorptively bound water is removed from the sample surface. A milder procedure is P-drying [20] in which the material is kept over magnesium perchlorate at a water vapor pressure of 8×10^{-3} Torr. The possibility also exists to apply oven drying at an elevated temperature, typically at 105 °C, or freeze drying. However, a direct comparison of different drying methods performed on identical samples revealed that the amount of water removed by different procedures is not identical [13]. It was also reported that exchanging pore water with a suitable organic solvent, such as methanol or pentane, before D-drying can increase the resultant BET_{N2} value significantly [13,21]. Another factor that may influence the BET results is the rate of drying. Generally, the found surface area tends to decline with prolonged drying time [13,22]. All these experimental data suggest that some collapse of the original C-S-H structure on the nanometer scale occurs in the course of drying whose form and extent depends on the drying approach employed.

Also, comminution to the required particle size may increase the found surface area. However, this factor will play only a minor role in high surface materials such as hydrated cement pastes.

2.2. Reversibility of the drying–resaturation process

The question arises whether the fraction of water leaving the interlayer spaces of C-S-H upon D-drying—if they remain unaffected by the drying procedure at all—can reenter these spaces upon resaturation. Brunauer et al. [11,23] reported data according to which D-dried samples did not soak up water even when completely immersed in water. Contrary to it, Feldman and Sereda [4] expressed the view that interlayer water can reenter D-dried material even at low humidity.

Parrot [24] reported a coarsening of the pore structure upon drying, resulting in a decline of the N_2-specific surface area from over 100 m^2/g at 90% rh to around 30 m^2/g at 10% rh.

Ludwig [25] determined adsorption–desorption isotherms of C-S-H starting with both an original nondried and a D-dried preparation. He found that they are not identical, indicating the absence of reversibility of the drying–resaturation process.

Odler and Koster [26] dried small discs of hydrated Portland cement pastes to D-dried conditions and resaturated them with D_2O-enriched H_2O. The obtained data show that drying and resaturation resulted in an increased perme-

Table 1
Effect of equilibration time on BET result

Sample	BET_{H_2O} (293 K) desiccator method (m^2/g)	BET_{H_2O} (293 K) voluminometric method (m^2/g)	BET_{N2} (77 K) voluminometric method (m^2/g)
C_3S, w/s = 0.33 hydrated 28 days at 20 °C	143	85	5.4
C_3S + 2.0% $CaCl_2$, w/s = 0.33 hydrated 28 days at 20 °C	171	88	38
C_3S, w/s = 0.33 hydrated 1 day at 100 °C	63	50	n.d.
C_3S, w/s = 0.33 hydrated 28 days at 100 °C	60	36	n.d.

Source: unpublished data; n.d.: not determined.

ability as well as an increase of pore volume into which migration of water may take place. The specific surface areas, as calculated from experimentally found porosity and permeability data, became smaller. All these results indicate that alterations of the structure brought about by drying are irreversible.

2.3. Effect of equilibration time

To obtain correct results in BET-specific surface area determinations, the required experimental data must be collected after equilibrium conditions in the studied system have been established. To do so, in practice, the amount of adsorbate adsorbed by the sample is determined in regular intervals whose length, for technical reasons, must have an upper limit (typically 15–60 min). An equilibrium is believed to be established when no additional adsorbate consumption is observed in repeated measurements. The amount of consumed adsorbate may be determined either gravimetrically, i.e., by determining the weight increase of the sample, or voluminometrically by determining the amount of still nonadsorbed sorbate on the basis of its pressure and volume in the measurement chamber. Both approaches are commonly employed in BET_{N2} determination of cementitious materials.

In the determination of the amount of adsorbed H_2O, the desiccator method may be also employed. Here, the studied sample is equilibrated in a desiccator over the saturated solution of an appropriate salt, which determines the relative water vapor pressure to which the sample is exposed. Such approach does not set limits to the time to be used for equilibration and is the method of choice in BET_{H_2O} determinations performed on hydrated cement samples. Equilibration times of several weeks are commonly employed.

To determine whether a very slow adsorption still continues after establishing an apparent equilibrium by the standard voluminometric procedure, in a series of experiments on identical samples, BET_{H_2O} determinations were performed both by the desiccator method, with an equilibration time of 4 weeks and by the voluminometric method. In the latter case, the amount of consumed adsorbate was determined in intervals of 30 min and the measurement was discontinued when no change was found in at least three rechecks. From Table 1, it is apparent that results obtained by the latter approach were significantly lower than those found by the desiccator method, even though they remained higher than the corresponding BET_{N2} values. Thus, it appears that in the studied samples, after a relatively fast initial adsorption, a subsequent significantly slower H_2O adsorption still took place.

2.4. Effect of temperature

Due to differences in the vaporization characteristics of nitrogen and water, the adsorption data needed for BET_{N2} and BET_{H2O} determinations have to be collected at different temperatures, typically at the boiling temperature of liquid nitrogen (77 K) for BET_{N2} and at ambient temperature for BET_{H_2O}. To see, whether and to what extent, the differences in temperature at which the measurement is made may affect the results, the BET_{N2} value was determined on a series of C-S-H-based samples both at 77 and 90 K using liquid oxygen as coolant. From the results shown in Table 2, it is apparent that an increase of the temperature of adsorption consistently increased the resultant BET_{N2} value. Nevertheless, both values stayed significantly below those found by H_2O adsorption. In an independent study, an anomalous increase of adsorption of nitrogen by coals with increasing temperature was observed by Maggs [27]. This phenomenon was attributed by the author to a reduced accessibility of the internal surface of coal to N_2 at low temperatures.

2.5. Cross-sectional area

To determine the BET-specific surface of a sample, the cross-sectional area, i.e., the area occupied by a single molecule of the adsorbate on the surface of the sample at

Table 2
BET_{N2} and BET_{H_2O} values of selected samples determined at different temperatures

Sample	BET_{N2} 77 K (m^2/g)	BET_{N2} 90 K (m^2/g)	BET_{H_2O} 77 K (m^2/g)
C_3S, w/s = 0.33 hydrated 28 days at 20 °C	5.4	8.0	143
C_2S, w/s = 0.33 hydrated 35 days at 20 °C	14.1	19.7	65
OPC, w/s = 0.30 hydrated 28 days at 20 °C	8.3	12.6	95
Tobermorite (synthetic)	64	84	135

Source: unpublished data.

the temperature of measurement, must be known. If one assumes a spherical or nearly spherical shape of the molecule, the cross-sectional area may be calculated from the molecular mass and density of the adsorbate in liquid form at the temperature of adsorption. This way, a cross-sectional area of 0.162 nm^2 may be determined for N_2 at 77 K and this value is commonly used in BET_{N2} determinations.

In some adsorbates, the cross-sectional area may deviate from the value determined by the previously described method due to the shape of the molecule, dipole moment, or other factors and may even vary with different sorbents. This has to be taken into account in the estimation of the BET surface. In the determination of BET_{H_2O}, cross-sectional areas ranging between 0.105 and 0.125 nm^2 were employed by different investigators (in all our own work the value 0.114 nm^2 was used).

2.6. Adsorption–desorption isotherms and pore volumes accessible to N_2 and H_2O

Bodor et al. [10] published complete adsorption–desorption isotherms for a series of hydrated samples using N_2 at 77 K. All were typical type 2 isotherms with a relatively small hysteresis loop closing at about $p/p_s = 0.35$, indicating the presence of pores with narrow entrances commonly called “ink bottle pores.”

Adsorption–desorption isotherms of the same samples determined with water vapor were published by Hagymassy et al. [14]. These were very similar to those found by nitrogen with the sole difference of the “final uptake,” i.e., amount of adsorbate taken up at the relative partial pressure of $p/p_s = 1.00$. These values were significantly higher when water vapor rather than nitrogen was used. As the final uptake corresponds to the whole pore volume accessible to the given adsorbate, it is obvious that nitrogen was able to fill only a fraction of the pore space, even at its saturation partial pressure. From Table 3, it may be seen that the volume accessible to nitrogen amounted only to about 60% of that accessible to water vapor, and the assumption is justified that an incomplete filling will take place even at lower partial pressures.

Table 3
Porosity accessible to water vapor at 20 °C and to nitrogen at 77 K in mature C_2S, C_3S and Portland cement pastes

Sample	w/s	P_{H_2O} (ml/g)	P_{N2} (ml/g)	$P_{H_2O}-P_{N2}$ (ml/g)	P_{N2}/P_{H_2O}
C_2S	0.45	0.271	0.161	0.110	0.594
	0.57	0.330	0.197	0.133	0.597
	0.70	0.411	0.219	0.192	0.533
C_3S	0.45	0.229	0.147	0.082	0.642
	0.57	0.271	0.189	0.082	0.699
	0.70	–	0.190	–	–
PC	0.40	0.184	0.118	0.066	0.641
	0.45	0.225	0.136	0.089	0.604
	0.70	0.385	–	–	–

Sources: Refs. [10,14].

Table 4
Specific surface area of selected samples as determined by different methods

Material	w/s	BET_{H_2O} (m^2/g)	BET_{N2} (m^2/g)	S_t (m^2/g)	S_{cum} (m^2/g)	S_{Hg} (m^2/g)
C_3S, 24 months at 20 °C	0.45	128	36.3	37.2	38.7	22.6
	0.50	129	48.7	46.3	38.4	21.0
	0.60	131	56.0	52.2	57.8	31.2
	0.70	138	57.8	58.9	66.8	37.3
	1.00	142	65.0	66.0	67.2	39.9
OPC, 24 months at 20 °C	0.30	105	4.4	4.8	5.8	5.9
	0.40	101	7.3	8.3	10.8	11.4
	0.50	109	9.5	11.0	18.9	20.0
	0.70	113	18.8	17.9	21.7	27.4
	1.00	114	–	–	23.5	33.4
OPC, 2 months at 90 °C	0.70	87	8.4	8.6	6.6	23.5
	1.00	83	9.5	9.1	6.2	26.0

S_t: Specific surface area as determined by the T-method of Lippens and deBoer [28]; S_{cum}: cumulative pore surface area of pores in which capillary condensation takes place calculated from the adsorption branch of the N_2 isotherm, assuming a cylindrical geometry of the pores; S_{Hg}: cumulative pore surface area of pores accessible to mercury at pressures up to 2000 bar calculated under the assumption of a cylindrical pore geometry.
Source: Ref. [26].

2.7. Specific surface area of D-dried samples as determined by various methods

Table 4 shows the specific surface area of selected samples as determined by several methods:

In the T-method suggested by Lippens and deBoer [28], the experimentally found adsorption isotherm is compared with a suitable *t* curve, i.e., an isotherm that had been determined on a nonporous material with a known surface area. Under these conditions, a proportionality between the amount of adsorbed vapor and surface area exists for the low partial pressure range of these isotherms.

The cumulative surface area is calculated from the amount of adsorbate, which becomes bound within the remaining empty volume of the pores by capillary condensation, after the surface of the material, including the internal walls of the pores, had became covered by adsorption. As capillary condensation takes place only in pores possessing a minimal cross section, the surface area determined this way does not include the surface located in very fine pores, i.e., those with radii below about 2–4 nm.

In addition to results determined on the basis of the adsorption data, Table 4 also includes the specific surface areas determined by mercury porosimetry, assuming a cylindrical pore cross section. Obviously, the method enables to determine only the surface of those pores into which mercury had penetrated and this depends on the maximum pressure employed in the measurement. The values shown in Table 4 exclude the surface area located in pores with radii below about 4 nm.

The most important conclusion from the obtained results is the observation that the BET_{N2} surface areas were very similar to results found by methods in which the surface located in fine pores is not registered. In an independent

Table 5

BET-specific surface are of selected samples determined using N_2, H_2O, NH_3, and O_2 as adsorbates

Sample	BET_{N2} (m^2/g)	BET_{H_2O}/d (m^2/g)	BET_{H_2O}/v (m^2/g)	BET_{NH3} (m^2/g)	BET_{O2} (m^2/g)
OPC, w/s = 0.45 cured 7 years at 20 °C	89	191	107	98	95
OPC, w/s = 0.70 cured 2 years at 20 °C	76	200	135	121	91
C_3S, w/s = 0.33 cured 28 days at 20 °C	7.1	143	85	20	8.0
C_3S + 2% $CaCl_2$, w/s = 0.33 cured 28 days at 20 °C	38	171	88	16	33

BET_{N2}: voluminometric method, 77 K; BET_{H_2O}/d: desiccator method, 293 K; BET_{H_2O}/v: voluminometric method 293 K; $BET_{NH3:}$ voluminometric method, 240 K; BET_{O2}: voluminometric method, 90 K.

Source: unpublished data.

study, an equality of the BET_{N2} results and the cumulative surface area was also found by Bentur [29].

2.8. Effect of cement mix composition and curing

Even though it is rarely possible to directly compare BET results obtained by different investigators due to differences in the exact measuring procedure, some general observations emerged as to the effect of sample preparation and curing on the resultant BET values. They can be summarized as follows:

The BET_{N2} and BET_{H_2O} surfaces of different binders, if compared at equal degrees of hydration, may differ just as the mutual ratio of these two values [14,30].

For a given hydrated binder that contains the C-S-H phase as one of its main constituents, the BET_{H_2O} value increases linearly in proportion to the degree of hydration, indicating a constant-specific surface area of the hydration products formed at different stages of hydration [30–34]. Thus, the possibility exists to determine the amount of C-S-H present in a hydrated paste from the amount of water vapor adsorbed [35]. The BET_{N2} values increase with progressive hydration as well, at least in the initial stages of hydration, though not necessary linearly [13,16–18,36–39]. It tends to level off as the hydration progresses [16–18,36] or may even decline after reaching a maximum value [33,34,38,39].

At the same degrees of hydration, the specific surface area declines with increasing curing temperature [13,40–42].

In mature pastes, the BET_{H_2O} value is independent of the initial water–cement ratio, whereas the BET_{N2} value increases [9,10,14].

The addition of calcium chloride to the starting C_3S or Portland cement mix significantly increases the BET_{N2} value without noticeably affecting the BET_{H_2O} results [13,31,32,41–43].

2.9. The BET-specific surface area determined with other adsorbates than N_2 and H_2O

Vidick [44] compared BET_{N2}-specific surface areas with values obtained with argon and krypton. For anhydrous cement samples, the results were very similar; however, in hydrated samples, the BET_{N2} values were 4–5 times higher. He attributed this discrepancy to the differences in the size of the different molecules as well to the presence of a quadruple moment in the N_2 molecule.

Several investigators determined the BET surface area with vapors of various organic compounds [21,45,46]. They found values ranging between about 50 m^2/g for cyclohexane and isopropanol and 114 m^2/g for methanol. A difficulty in comparing these results with BET_{N2} values lies in the fact that different adsorption temperatures have to be used for different adsorbates.

To explore the role of a molecular dipole in the capability of a molecule to penetrate the pore space, data obtained by N_2 and H_2O adsorption were compared with those fond with NH_3. Ammonia was selected, as its dipole moment is high and not too different from that of water (H_2O: $\mu = 1.85 \times 10^{-18}$ esu; NH_3: $\mu = 1.47 \times 10^{-18}$ esu) and the sizes of both molecules is similar. The results are summarized in Table 5. For better comparison, the table contains results found volumetrically, in addition to BET_{H_2O} values obtained by the desiccator method. Also included are pertinent BET_{O2} results. In the two analyzed Portland cement pastes, but not in the studied C_3S paste, the BET_{NH3} values were similar to BET_{H_2O} results found with the voluminometric method. Just as in BET_{N2} measurements, a significant increase of the

Table 6

BET_{N2}- and BET_{H_2O}-specific surface areas of selected samples

Sample		BET_{N2} (m^2/g)	BET_{H_2O} (m^2/g)	Source
Dicalcium silicate, hydrated for 7 years	w/s = 0.45	39	209	Ref. [14]
	w/s = 0.57	46	204	
	w/s = 0.70	56	213	
Tricalcium silicate, hydrated for 4 years	w/s = 0.45	84	147	Ref. [14]
	w/s = 0.57	96	206	
Portland cement, hydrated for 7 years	w/s = 0.45	89	191	Ref. [14]
Portland cement mortar		5	35	Ref. [46]
Gypsum–lime mortar		6	2	Ref. [46]
Gypsum board		11	5	Ref. [46]
Synthetic tobermorite		57	125	
Autoclaved lime–silica bricks	d = 1.76 g/ml	14.8	11.3	Ref. [47]
	d = 1.84 g/ml	13.5	13.5	
	d = 1.93 g/ml	13.7	13.9	
	d = 2.00 g/ml	14.7	16.0	
Silica gel		273	116	Ref. [48]
		399	206	
		793	826	
		396	385	
		658	597	
Basalt–acid treated		173	170	Ref. [46]
Active carbon		59	0	Ref. [46]
		240	0	

specific surface area of hydrated C_3S, due to $CaCl_2$ addition, was also observed when O_2 was used as adsorbate. Contrary to it, such increase was not observed with NH_3 and in this respect NH_3 behaved similarly to H_2O. In assessing the results in Table 5, one has keep in mind that—for technical reasons—the measurements with different adsorbates were performed at different temperatures, which also influenced the obtained values.

2.10. The BET-specific surface area of different materials

Table 6 summarizes BET values determined by N_2 and H_2O adsorption for a series of selected materials. The BET_{N2} value was below that of BET_{H_2O} in some but not all instances. Some materials yielded practically identical or even higher BET_{N2} values.

3. Discussion

A serious limitation of the BET method is the fact that it can only be applied in porous samples only if these posses an open porosity, if their pore system is empty, and if no strange molecules are already adsorbed on the walls of the existing pores. Alternatively, new techniques have been developed in recent years, such as small angle X-ray scattering (SAXS), small angle neutron scattering (SANS), or nuclear magnetic resonance (NMR) [13,16,17,49–51], but the obtained values neither agree with each other nor with BET results [13].

It is also important that the BET results in cementitious materials may be greatly affected by the preparation of the sample, particularly by the drying procedure. Apparently, changes in the texture of the solid phase (C-S-H) at the nanometer scale take place under these conditions and these are not reversible even under renewed exposure to 100% rh or complete resaturation with liquid water. Consequently, the BET results are valid only for a particular drying method and do not have general validity. Also, limitations exist as to the possibility to assess the surface area of the original wet material.

In assessing whether the BET_{N2} or BET_{H_2O} reflects the true surface of the studied hydrated cementitious material, the following facts have to be taken into consideration:

(i.) A significant fraction of the overall pore space in samples containing C-S-H as product of hydration appears inaccessible to nitrogen even at a partial pressure of $p/p_s = 1.00$. Consequently, one can assume that these pores will be inaccessible to N_2 even at $p/p_s < 0.35$, which is the range of partial pressures used in BET determinations.

(ii.) BET-specific surface areas determined with nitrogen as the adsorbate are similar to the cumulative surface area and the surface area calculated from mercury porosimetry data, even though the latter two results do not include the surface area located in pores below a threshold size. Thus, the assumption is justified that the BET_{N2} results do not reflect the total surface area of the pores either but rather only of a fraction of it.

(iii.) In pastes hydrated to different degrees under identical conditions, the BET_{H_2O} value is approximately proportional to the degree of hydration and thus to the amount of hydrates formed. This observation is in line with the assumption that hydrate phases formed at different stages of the hydration process possess the same surface area per weight unit. The initially relative and for some samples in later stages of hydration, even absolute decline of the BET_{N2} value may be interpreted as follows: In the initial stage of hydration, the network of the formed hydrates is rather open and thus—after drying—N_2 can penetrate into the entire pore space; the BET_{N2} value increases proportionally to the amount of hydrates formed. As the hydration progresses and free water is consumed, the overall pore space becomes smaller and the network of hydrates becomes more interwoven. Under these conditions, an increasing number of regions developes, which are separated from the rest of the pore system by narrow openings that are either totally or partially impermeable to N_2 molecules. At this stage, a linear proportionality between the amount of hydrates formed and the resultant BET_{N2} value ceases to exist, as a part of the surface will not be covered by adsorbed N_2 molecules anymore. After reaching a critical point, the fraction of the pore system inaccessible to nitrogen may increase so fast that even the overall BET_{N2} surface area of the paste declines, even though additional hydrates are formed.

(iv.) Brunauer et al. [23] determined the surface energy of a series of “tobermorite gel” preparations from their BET_{N2} and BET_{H_2O} values and heats of dissolution. Whereas a value of 386 erg/cm^2 was found using the BET_{H_2O} results, values derived from BET_{N2} results yielded negative surface energies in some instances, which is an absurdity. Therefore, one must conclude that only parts of the total surface were determined in the samples by BET_{N2} measurements.

(v.) It can be calculated that the volume of the pore space inaccessible to N_2, yet accessible to water vapor, in a sample of 1.1 nm tobermorite is significantly greater than the volume of water needed to enter the existing interlayer spaces and to convert the material completely to its 1.4 nm form. Thus, the existence of at least some adsorption of H_2O molecules in pore spaces not accessible to nitrogen must be postulated. Similar results are obtained if one assumes a hypothetical penetration of H_2O into interlayer spaces of D-dried hydrated C_3S samples.

All these facts indicate that the BET_{N2} values do not represent the total surface area of C-S-H-based materials and the BET_{H_2O} values appear to be more correct in this respect.

An explanation for the apparent inaccessibility of N_2 to a part of the pore system offers the experimentally found increase of the BET_{N2} value achieved if the temperature of adsorption is even moderately elevated. Such behavior is typical for activated diffusion and indicates the presence of narrow inkbottle pores, which separate a fraction of the pore system from the rest within the microtexture of the hydrated material. Consequently, upon exposure to the sorbate, the pore system initially fills by "normal" diffusion, which is relatively fast and barely temperature dependent, followed by "activated diffusion," which proceeds much more slowly and is highly temperature dependent. Thus, it appears that the lower BET_{N2} results are mainly due to low temperature and too short equilibration time employed, which allow to achieve equilibrium conditions to occur in pore spaces accessible by normal but not by activated diffusion. It was estimated that because of differences in the employed temperature of adsorption, water should pass over the energy barrier about 50 times more rapidly; thus, it would take nitrogen several years to equilibrate [11]. The presence of a dipole and a smaller H_2O molecule size may also contribute to faster equilibration if water vapor is employed as an adsorbate.

As to the size of pores not filled with N_2, their hydraulic radii indicate that their average diameter several times exceeds the diameter of the nitrogen molecule even in cement pastes with very low starting water–solid ratios. Thus, the missing N_2 could easily be accommodated in such pores.

The assumption that lower BET values are due to the presence of a C-S-H phase, which nitrogen cannot penetrate in addition to one readily accessible to N_2, is contradicted by the finding of temperature dependence of the BET_{N2} value; it cannot be assumed that the mutual ratio of these two forms of C-S-H in the hardened material will shift merely by altering the temperature at which N_2 adsorption takes place.

Finally, it has to be stressed that the difference between BET_{N2} and BET_{H_2O} values is not a general feature of the BET method and is confined to materials with a particular microtexture. In most materials, both values tend to be similar or BET_{N2} may even exceed BET_{H_2O}, especially in materials with highly hydrophobic surfaces.

4. Conclusions

1. Preparation of the sample, in particular removal of free water from the pore system, causes irreversible alterations in the microtexture of hydrated cementitious materials, which affect the magnitude of the resultant BET surface area.
2. In hydrated cementitious materials, the BET_{N2}-specific surface area is consistently lower than BET_{H_2O}. This is due to the presence of porous regions that are separated from the rest by very narrow entrances (inkbottle pores) and appear inaccessible to N_2 under commonly employed experimental conditions.
3. The apparent impermeability of narrow inkbottle pores to N_2 is mainly due to the fact that these are permeable only by activated diffusion, which is highly temperature dependent and significantly slower than normal diffusion. Whereas in determination of BET_{H_2O} made by the desiccator method, performed at ambient temperature and with equilibration times of several weeks, equilibrium conditions can be attained under conditions employed, in BET_{N2} measurements performed at significantly lower temperatures and shorter equilibration times, the equilibration remains incomplete.

References

[1] S. Brunauer, P.H. Emmet, E. Teller, Adsorption of gases in multimolecular layes, J. Am. Chem. Soc. 60 (1938) 309–319.
[2] R.F. Feldman, P.J. Sereda, A model for hydrated Portland cement as deduced from sorption-length changes and mechanical properties, Materiaux de Construction 1 (6) (1968) 509–520.
[3] R.F. Feldman, P.J. Sereda, A new model for hydrated Portland cement and its practical implications, Eng. J. Can. 53 (1970) 53–59.
[4] R.F. Feldman, P.J. Sereda, Discussion of the paper "The new model of hardened Portland cement paste" by S. Brunauer, I. Odler, M. Yudenfreund, Highw. Res. Rec. 326 (1970) 101–106.
[5] R.F. Feldman, P.J. Sereda, Separation of interlayer and adsorbed water in hydrated Portland cement using thermal analysis, Cem. Concr. Res. 1 (1971) 607–620.
[6] R.F. Feldman, V.S. Ramachandran, Investigations on the state of water and the stoichiometry of suspension-hydrated Ca_3SiO_5, Cem. Concr. Res. 4 (1974) 155–166.
[7] H.F.W. Taylor, Cement Chemistry, 2nd ed., Thomas Telford Publishing, London, 1997.
[8] F.W. Locher, Zement—Grundlagen der Herstellung und Verwendung (Cement—Fundamentals of Manufacturing and Use), Verlag Bau + Technik, Dusseldorf, 2000.
[9] R.Sh. Mikhail, L.E. Copeland, S. Brunauer, Pore structure and specific surface area of hardened Portland cement pastes as determined by nitrogen adsorption, Can. J. Chem. 42 (1964) 436–438.
[10] E.E. Bodor, J. Skalny, J. Hagymassy, M. Yudenfreund, Pore structure of hydrated calcium silicates and Portland cement determined by nitrogen adsorption, J. Colloid Interface Sci. 34 (1970) 560–568.
[11] S. Brunauer, I. Odler, M. Yudenfreund, The new model of hardened Portland cement paste, Highw. Res. Rec. 326 (1970) 89–101.
[12] A. Bentur, Pore structure of hardened cementitious compounds of different chemical composition, J. Am. Ceram. Soc. 63 (1980) 381–384.
[13] M.C.G. Juenger, H.M. Jennings, The use of nitrogen adsorption to assess the microstructure of cement paste, Cem. Concr. Res. 31 (2001) 883–892.
[14] J. Hagymassy, I. Odler, M. Yudenfreund, J. Skalny, S. Brunauer, Pore structure analysis by water adsorption III. Analysis of hardened calcium silicates and Portland cements, J. Colloid Interface Sci. 38 (1972) 20–34.
[15] S. Diamond, A critical comparison of mercury porosimetry and capillary pore size distributions of Portland cement pastes, Cem. Concr. Res. 1 (1971) 531–546.
[16] H.M. Jennings, P.D. Tennis, Model for the developing microstructure of Portland cement pastes, J. Am. Ceram. Soc. 77 (1994) 3161–3172.
[17] H.M. Jennings, A model for the microstructure of calcium silicate hydrate in cement paste, Cem. Concr. Res. 30 (2000) 101–116.
[18] P.D. Tennis, H.M. Jennings, A model for two types of calcium silicate hydrate in the microstructure of Portland cement pastes, Cem. Concr. Res. 30 (2000) 855–864.

[19] L.E. Copeland, J.C. Hayes, Determination of non-evaporable water in Portland cement pastes, ASTM Bull. 194 (1953) 70–74.

[20] T.C. Powers, T.L. Brownyard, Investigations on the physical properties of hardened Portland cement pastes, Res. Dept. Bull. 22, Portland Cement Association, Skokie, IL, (1947).

[21] G.G. Litvan, Variability of the nitrogen surface area of hydrated cement pastes, Cem. Concr. Res. 6 (1976) 139–144.

[22] C.D. Lawrence, An examination of possible errors in the determination of nitrogen isotherms on hydrated cements, Tech. Report 520, Cement and Concrete Assoc., Slough, UK, (1978).

[23] S. Brunauer, D.L. Kantro, C.H. Weise, The surface energy of tobermorite, Can. J. Chem. 27 (1959) 647–655.

[24] L.J. Parrot, W. Hansen, R.L. Berger, Effect of first drying on the pore structure of hydrated alite pastes, Cem. Concr. Res. 10 (5) (1980) 647–656.

[25] H. Ludwig, Binding of water and volume changes in cement stone (in German), PhD thesis, Technical University Clausthal (1985).

[26] I. Odler, H. Koster, Investigations on the structure of fully hydrated Portland cement and tricalcium silicate pastes III. Specific surface area and permeability, Cem. Concr. Res. 21 (1991) 975–982.

[27] F.A.P. Maggs, Anomalous adsorption of nitrogen at 90°K, Nature 169 (1952) 793–794.

[28] R.C. Lippens, J.H. deBoer, J. Catal. 4 (1965) 319.

[29] A. Bentur, The pore structure of hydrated cementitious compound of different chemical composition, J. Am. Chem. Soc. 63 (1980) 381–386.

[30] J. Skalny, I. Odler, Pore structure of calcium silicate hydrates, Cem. Concr. Res. 2 (1972) 387–400.

[31] J. Skalny, I. Odler, J. Hagymassy, Pore structure of hydrated calcium silicates I. Influence of calcium chloride on the pore structure of hydrated tricalcium silicate, J. Colloid Interface Sci. 35 (1971) 434–440.

[32] I. Odler, J. Skalny, Influence of calcium chloride on paste hydration of tricalcium silicate, J. Am. Ceram. Soc. 54 (1971) 362–363.

[33] I. Odler, J. Hagymassy, M. Yudenfreund, K. Hanna, S. Brunauer, Pore structure analysis by water vapor adsorption IV. Analysis of hydrated Portland cement pastes of low porosity, J. Colloid Interface Sci. 38 (1972) 265–276.

[34] I. Odler, J. Hagymassy, E.E. Bodor, M. Yudenfreund, S. Brunauer, Hardened Portland cement pastes of low porosity IV. Surface area and pore structure, Cem. Concr. Res. 2 (1972) 577–589.

[35] R.A. Olson, H.M. Jennings, Estimation of C-S-H content in blended cement paste using water adsorption, Cem. Concr. Res. 31 (2001) 351–356.

[36] G.M. Hunt, Nitrogen sorption measurements and surface areas of hardened cement pastes, Highw. Res. Board 90 (1966) 112–122 (special report).

[37] I. Odler, M. Rossler, Investigations on the relationship between pore structure and strength of hydrated Portland cement pastes II. Effect of pore structure and degree of hydration, Cem. Concr. Res. 15 (1985) 401–410.

[38] Q. Zhou, J.J. Beaudoin, Effect of applied hydrostatic stress on the hydration of Portland cement and C_3S, Adv. Cem. Res. 15 (2003) 9–16.

[39] J. Skalny, I. Odler, Pore structure of hydrated calcium silicates III. Influence of temperature on the pore structure of hydrated tricalcium silicate, J. Colloid Interface Sci. 40 (1972) 199–205.

[40] I. Odler, J. Skalny, Hydration of tricalcium silicate at elevated temperature, J. Appl. Chem. Biotechnol. 23 (1973) 661–667.

[41] V. Aluno-Rosetti, G. Chioccio, M. Collepardi, Low pressure steam hydration of tricalcium silicate, Cem. Concr. Res. 4 (1974) 279–288.

[42] A. Celani, M. Collepardi, A. Rio, The influence of gypsum and $CaCl_2$ on the hydration of C_3S, Ind. Ital. Cem. 36 (1966) 669–679.

[43] M. Collepardi, G. Rossi, G. Usai, The paste and ball mill hydration of tricalcium silicate in the presence of calcium chloride, Ind. Ital. Cem. 38 (1968) 657–663.

[44] B. Vidick, Determination of the specific surface area by gas adsorption. Effect of the adsorbate, Cem. Concr. Res. 17 (1987) 845–847.

[45] C.D. Lawrence, F.G.R. Gimblett, K.S.W. Sing, Sorption of N_2 and n-$C_4H_{10}O$ on hydrated cements, Proceedings of the 7th Symposium on Chemical Cement, Paris, vol. III (VI), 1981, pp. 141–146.

[46] R.Sh. Mikhail, S.A. Kelim, Adsorption of organic vapors in relation to pore structure of hardened Portland cement pastes, Highw. Res. Board 90 (1966) 123–134 (special report).

[47] I. Odler, H.B. Barthold, Investigations on the water vapor permeability of cementitious materials, Mater. Res. Soc. Sym. Proc. 137 (1989) 215–222.

[48] I. Odler, H.B. Barthold, The surface area and pore properties of calcium silicate phases formed in the autoclave hydration of lime–silica bricks, Proceedings at the International Symposium on the Relationship Between Properties of Lime–Silica Bricks and the Structure of the Binder, Karlsruhe, May 10–11, 1978.

[49] R. Gerhardt, A review of conventional and non-conventional pore characterization techniques, Mater. Res. Soc. Symp. Proc. 137 (1989) 75–82.

[50] J.J. Thomas, H.M. Jennings, A.J. Allen, The surface area of cement paste as measured by neutron scattering. Evidence for two C-S-H morphologies, Cem. Concr. Res. 28 (1998) 897–905.

[51] J.J. Thomas, H.M. Jennings, A.J. Allen, The surface area of hardened cement paste as measured by various techniques, Concr. Sci. Eng. 1 (1999) 45–64.