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The use of nitrogen adsorption to assess the microstructure of cement paste

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Abstract

Surface area and porosity as measured by nitrogen are controversial and may not represent the real or entire surface of cement paste. However, when experimental variation is minimized, changes in nitrogen surface area and porosity due to chemistry and processing are observed that provide valuable insight into the elusive calcium silicate hydrate (C-S-H) microstructure. Understanding the causes of variation, both experimental and microstructural, is vital if nitrogen adsorption is to be a legitimate tool for studying cement pastes. Historical data on nitrogen BET surface area of cement pastes were examined and sources of variation identified. The following variables were determined to be among the most influential in altering surface area: drying method, age, water-to-cement ratio, curing temperature, and calcium chloride addition. These were addressed experimentally in order to clarify or confirm the effects seen in the literature. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

There is much controversy surrounding the use of nitrogen adsorption techniques to study the surface area of cement pastes and related systems [1]. In the literature there are frequently disclaimers that nitrogen adsorption methods are unreliable, inconsistent, or not measuring the "true" surface area. However, nitrogen adsorption, and the accompanying BET analysis are widely and effectively used for testing other colloidal and microporous materials [2]. Historically, the primary cause of the controversy with cement paste has been that the value measured with nitrogen is much less than that measured by water vapor adsorption. This was compounded by the fact that the reported values using nitrogen vary widely (5–250 m^2/g). These observations spurred countless arguments over how to measure surface area, i.e., which method measures the "true" surface area. Arguments against nitrogen include the "bottle-neck" theory: nitrogen molecules are bigger than water and are therefore excluded from pores with small openings [3–5]. Arguments against water vapor stem from the belief that water may be entering spaces within the layers of the calcium silicate hydrate (C-S-H) structure, analogous to "interlayer" spaces in clays, which should be excluded from surface area measurements [6–9].

Newer techniques for measuring surface area such as small angle X-ray and neutron scattering (SAXS and SANS), and nuclear magnetic resonance have been developed over the past 25 years [10]. The hope has been that results from these techniques would provide insight into the elusive "true" surface area of cement paste, thereby clearing up the controversies created by the gas adsorption techniques. Instead of answering questions, however, newer techniques have added to the confusion. The values from these techniques do not agree with those from water vapor or nitrogen adsorption, or even with each other. *No two techniques measure the same surface area for a given type of cement paste sample*. Consequently, even now, there is no consensus among cement researchers about what the surface area of cement really is and what factors affect it.

A better understanding of the surface area of cement paste (as measured by all techniques) would be invaluable,

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as it would provide insight into the nature of cement's primary hydration product, C-S-H. Since it is widely accepted that almost all of the surface area comes from C-S-H, the development of surface area in cementitious systems is directly related to the development of this highly porous phase. Although much is known about the structure and chemistry of C-S-H at the atomic level, many questions remain about its nanometer scale structure [11]. Rationalization of surface area measurements can contribute toward solving this puzzle. Furthermore, it is accepted that surface area is related to bulk properties such as shrinkage, creep, and permeability [12]. However, these relationships have yet to be quantified. A quantitative correlation between a microstructural feature such as surface area to one or more physical properties would be useful for the prediction of performance and engineering of new materials.

In order to advance our knowledge of cement paste microstructure, perhaps we should abandon the notion of a "true" surface area. Instead, we should focus on understanding which interfaces within the microstructure each technique measures. We can start by assuming that each technique evaluates a different fraction of the surface, thereby yielding different results. For example, techniques yielding lower values, such as nitrogen adsorption, may not reach all of the surfaces because of bottleneck pore entrances (or other unknown reasons). Techniques yielding very high values, such as SAXS, may be measuring surfaces within the C-S-H structure that are not meant to be considered part of the surface area (i.e., interlayer gel pores). If we can better understand the information from all sources, we can begin to build a complete picture of the cement paste and C-S-H microstructures.

An appropriate place to start a critical investigation of surface area measurements is with nitrogen adsorption. It is the cheapest, quickest, and most readily available method. Since we have decided to put aside differences in values between techniques for the time being, the greatest obstacle in understanding nitrogen surface area of cement paste is the great intrinsic variation in values. This variation is so large that values obtained by different researchers cannot be directly compared. The goal of this paper, therefore, is to identify the sources of variation in nitrogen surface area values in an attempt to make this technique more valuable for the study of cement pastes.

The intrinsic variation in nitrogen surface area values is often believed to detract from its merit as a technique for assessing the microstructure. We believe that, when better understood, this variation will become one of the most valuable characteristics of nitrogen adsorption. The first step toward understanding variation is to separate it into mutually independent categories: (1) units of data reporting, (2) sample preparation/experimental differences, and (3) microstructural differences (due to actual differences in the chemistry or quantity of C-S-H). If we can minimize the first two, the effects of the last will become clearer. In other words, our goal is to increase the "signal-to-noise ratio" in nitrogen adsorption measurements.

There are several discussions of the causes of variation in nitrogen surface area values, the most comprehensive of which being that of Lawrence [13]. It becomes clear upon examination that one of the largest contributors toward variations in values in the literature is simply the use of different units for reporting data. Conversion between units such as square meters per gram of ignited paste and per gram of dry paste is nearly impossible because papers often leave out the information necessary for such calculations (or omit the units entirely). There should be a standardized unit of reporting so as to minimize perceived variation, and facilitate sharing of information.

Even when data is reported in the same units, researchers rarely report similar values of nitrogen surface area. This is primarily due to inconsistencies in sample preparation. As shown in Table 1, methods of curing, drying, etc., affect the surface area. For example, exchanging pore water with methanol before drying can double the measured surface area [14]. In order to minimize this variation, a standard method must be chosen. This standard must be consistent, reliable, repeatable, and show sufficient variation when microstructural features are varied.

Several variables that are known to affect the quantity, chemistry, and microstructural characteristics of C-S-H as well as the nitrogen surface area are also shown in Table 1. This is the variation we are truly interested in examining; rather than being an artifact of experimental conditions, it is a reflection of microstructural change.

Several of the variables in Table 1 were chosen to be the basis of the present research. Upon examination of the literature, it was determined that, among sample preparation techniques, drying method had the most influential effect on the measured values. Three different methods of drying were examined, with the intention of finding the most

Table 1
Factors that have historically influenced the nitrogen surface area of cement pastes

Sample preparation variables	Microstructural variables
Curing: submerged, 100% relative humidity, sealed	Composition: C_3S, C_2S, Portland cement Age (degree of hydration)
Crushing: test as cylinders; test as particles, time of crushing (before or after drying), size of crushed particles	Curing temperature Water-to-cement ratio Chemical admixtures: calcium chloride Mineral admixtures: fly ash, slag, silica fume
Drying: temperature of drying, rate of drying, drying apparatus, solvent exchange	
Storage after drying: presence of moisture or carbon dioxide, length of storage time	

appropriate technique for use in examining microstructural changes. Optimum methods of curing, crushing, and storing were chosen based on the published information available [13,15,16].

Some of the variables known to influence surface area by microstructural means were also addressed experimentally. These were age, water-to-cement ratio, curing temperature, and calcium chloride additive (the only chemical admixture widely reported in the literature to have an effect on surface area). Clarification of the effects of these variables was necessary because much of the information in the literature is contradictory and incomplete. Pore size distribution as measured by nitrogen desorption was also determined for the variables of interest in order to gain even more quantitative information about the microstructure. The influence of mineral admixtures is addressed elsewhere [17].

2. Methods

The parameters used for each experimental series are shown in Table 2. Samples were made from ASTM Type I Portland cement with water-to-cement ratios (w/c) of 0.35, 0.45, and 0.55. Mixing was done by hand for 5 min with a small, stainless steel spatula. The small batch sizes that were used (20–200 g cement) necessitated hand mixing; this method was found to be comparable to mechanical mixing in efficacy and repeatability for small batches [18]. For specimens containing calcium chloride, 1% $CaCl_2 \cdot 2H_2O$ by weight of cement was dissolved in the water prior to mixing. Samples were cast in polystyrene vials (25 mm diameter, 50 mm height) and sealed in airtight polyethylene containers for the first 24 h. Lime–water was then placed in the sample containers, and they were resealed for the duration of the curing period, 1–270 days. Samples were cured in a 2°C refrigerator or in water baths at 20°C or 40°C.

After the specified hydration time, specimens were removed from the vials and ground to particle sizes in the range of 600 (#30 sieve) and 1180 μm (#16 sieve). Samples were then dried in one of three ways: (1) D-dried for 14 ± 1 days, (2) 105°C oven-dried for 1 day, and (3) immersed in methanol for 7 days + D-dried 14 ± 1 days. Samples were tested immediately after drying. The D-drying apparatus was set up according to the method of Copeland and Hayes [19], and consists of vacuum-drying to the vapor pressure of water at the temperature of dry ice (5×10^{-4} Torr). Equilibrium D-drying time was measured to be approximately 14 days. Complete methanol exchange was achieved by immersing 2–3 g of sample in 60–80 ml methanol, which was replaced daily for 7 days. Particles smaller than 600 μm were used for loss on ignition testing in order to determine degree of hydration (α).

Nitrogen adsorption and desorption were done using a Coulter Omnisorp 360 (Coulter, Hialeah, FL). Surface area was calculated using the BET [20] method of analysis, over a relative pressure range of 0.05–0.25 on the adsorption isotherm. Total pore volume available to nitrogen (1–40 nm pore radius range) and pore size distribution were calculated by the Barrett, Joyner, Hallenda [21] method using data from the desorption isotherm (relative pressure range of 0.99–0.38).

3. Results and discussion

3.1. Drying method

Because the method of drying had the strongest influence on surface area of the sample preparation techniques examined in the literature, the effects warrant further study. Three drying methods were chosen: oven-drying at 105°C, D-drying, and methanol exchange followed by D-drying. Nitrogen surface area results for samples prepared in these ways are shown in Fig. 1a. Each point displayed is the average value of three or more samples with error bars indicating the standard deviation (when the error was smaller than the size of the point marker, bars were omitted). It is clear from Fig. 1a that oven-drying at 105°C results in the lowest measurable nitrogen surface area while exchanging with methanol prior to D-drying results in the highest measurable surface area.

3.1.1. Oven-drying

Several studies have shown that changing the rate or mechanism of drying affects surface area as measured by nitrogen [13,14,22–25]. It is not surprising then that oven-drying and D-drying produce such different surface area values. While D-drying and oven-drying at 105°C are both generally assumed to remove all of the physically adsorbed water [11], they use different means of water removal. D-drying is a more common drying technique because it is more strictly defined. In this particular experiment, slightly more water is removed by oven-drying than by D-drying

Table 2
Experimental matrix

Factor examined	Drying method	Ages (days)	w/c	Curing temperature (°C)
Drying method	all	1–84	0.45	20
Age	D-dried	1–270	0.45	20
Water-to-cement ratio	D-dried	1–270	0.35, 0.45, 0.55	20
Curing temperature	D-dried	1–270	0.45	2, 20, 40
1% $CaCl_2$	D-dried	1–270	0.45	20

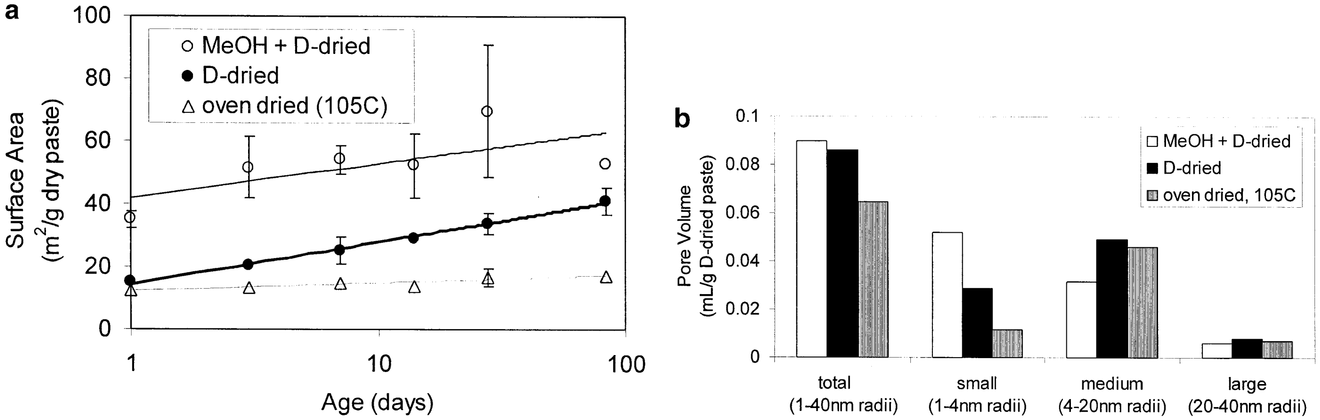

Fig. 1. (a) Effect of drying method on the surface area of cement paste. (b) Effect of drying method on the pore size distribution of cement paste (age = 7 days, $\alpha = 0.674$).

(Table 3). The loss of more water could result in the collapse of more pores and thus decrease the surface area.

It is interesting to note that the surface area of a 1-day-old oven-dried sample is almost equivalent to the surface area of a 1-day-old D-dried sample. At 1 day, the weight losses are almost equal under the two drying conditions, perhaps accounting for the equal surface areas. It cannot be assumed, however, that differences in weight loss account for all of the surface area differences. The differences in weight loss are slight in comparison to the differences in surface area, particularly at later ages. For example, both the 28-day-old D-dried sample and the 270-day-old oven-dried sample lose 17% of their weight on drying, but the surface areas are significantly different.

A close examination of the pore size distribution data in Fig. 1b sheds light on why the surface areas of oven-dried samples are so low. The data shown in Fig. 1b are from a single sample dried in all three ways; it is representative of several tests at various ages. The total pore volumes available to nitrogen (1–40 nm) of the oven-dried samples are consistently lower than those of comparable D-dried samples. The most striking difference in the pore size distribution data is that samples dried at 105°C have a much lower volume of small pores (1–4 nm radius) than the D-dried samples. Oven-drying must be harsher, meaning that there is an increased likelihood of pores collapsing due to capillary pressures on drying. The smallest pores are the most likely to collapse during drying because capillary pressure increases with decreasing pore size. The smallest pores also have the highest surface area per unit volume, thus explaining the significantly lower surface area values of these samples.

Table 3
Weight loss on D-drying and oven-drying (105°C) of cement pastes

Sample age (days)	D-dried		Oven-dried (105°C)	
	wt.% lost	surface area	wt.% lost	surface area
1	22.9 ± 1.2	15.29 ± 1.0	21.9 ± 1.0	12.49 ± 1.2
7	16.4 ± 0.9	25.24 ± 4.2	20.2 ± 1.35	14.95 ± 1.3
28	17.0 ± 0.9	33.87 ± 3.2	19.7 ± 0.6	16.77 ± 2.8
270[a]	15.4	56.99	17.1	20.56

[a] Values for 270-day-old samples are not averages; only one sample was tested.

3.1.2. Methanol exchange

The doubling of surface area achieved by methanol exchange, as seen in Fig. 1a, is already well documented [13,14,24–27]. The pore size distribution data in Fig. 1b are representative of several tests showing that methanol exchange does not significantly affect total pore volume available to nitrogen (1–40 nm) compared to D-drying alone. The increase in surface area is therefore not simply the result of increased total pore volume. The data in Fig. 1b do show a significant increase in the volume of the smallest pores (1–4 nm radius). The smallest pores have the highest surface area per unit volume, thus explaining why the methanol-treated samples have higher surface areas.

That the samples exchanged with methanol have a greater volume of small pores is evidence that the solvent acts to "preserve" the microstructure, or lessen the deleterious effects of drying [27]. Capillary pressures during drying are greatest in the smallest pores, rendering them most susceptible to collapse. Substituting the water in these pores for methanol, which has a lower surface tension, reduces capillary pressure and prevents pore collapse.

The large variation in surface area values of methanol-exchanged samples can be attributed in part to sample preparation. If not all of the water in the gel pores is exchanged with methanol, the values may collapse down to the D-dried values. When the water is adequately exchanged, values are much higher.

Furthermore, there are inconsistencies in the D-drying process that appear to cause larger variations in samples with high surface areas. For example, it was observed that changing the temperature of the dry ice trap, placing very wet samples in the desiccator, drying for longer periods, or changing the type of vacuum pump altered the surface area measured for high surface samples. Since the methanol-exchanged samples have very high surface areas, these are particularly sensitive to such perturbations during drying.

3.1.3. D-drying

D-drying was chosen as the drying method for the remainder of variables examined because of its repeatability and sensitivity to increases in surface area with age (Fig. 1a). Oven-drying yielded results that were too low to see a clear change in surface area with age, and thus it is inadequate for examining variables whose effects may be even more subtle. Methanol exchange, although it produces higher surface areas, causes too much variation in the values obtained to see effects of other variables clearly. It is interesting to note that approximately the same slope is observed in surface area versus age in Fig. 1a for samples with and without methanol treatment; the methanol samples merely have higher values. This suggests that in order to study the effects of variables on the surface area it is not necessary to exchange the pore water with methanol. If only the relative effects of variables are required, equilibrium D-drying should be sufficient. In fact, it may be advantageous to omit the methanol step, as the D-dried samples have better repeatability. Furthermore, omission of methanol avoids the controversial possibility of a chemical reaction between calcium hydroxide and the solvent [28–30].

3.2. Age

Many researchers have demonstrated that nitrogen surface area increases with age [22,31–33]. Such a trend is expected, as cement paste surface area is primarily associated with the C-S-H phase. The quantity of C-S-H increases with age due to continuing hydration, increasing the volume of the gel pores in the system [12], which increases the surface area and pore volume measured by nitrogen. The degree of hydration (α) is a better reflection of the amount of C-S-H present than is sample age, and is thus a better independent variable to examine. Surface area is plotted versus degree of hydration in Fig. 2a. It is confirmed that surface area increases with degree of hydration for D-dried samples. Correspondingly, the total pore volume available to nitrogen (1–40 nm) increases with degree of hydration (Fig. 2b).

3.3. Water-to-cement ratio

The relationship between nitrogen surface area and w/c is not as clear in the literature as that for surface area and age. Historically, samples have been compared which have different w/c, but the same age. As demonstrated in Fig. 3a, this comparison is faulty; w/c strongly influences the degree of hydration of cement pastes, particularly at later ages (each point shown is the average of three or more samples; average standard deviation = 0.024). It is critical, therefore, that surface area be examined versus degree of hydration rather than age for older samples so as not to confound increases due to w/c with increases due to degree of hydration.

Surface area results are shown in Fig. 3b. It appears that w/c has little effect on surface area, as the values fall along the same curve. At late ages, however, the w/c = 0.35 samples may have slightly lower surface areas. More, older samples are necessary in order to confirm this observation. Acquiring such data is difficult because samples with low w/c take many years to achieve high degrees of hydration.

The total pore volume results (1–40 nm) are similar to the surface area results (Fig. 3c). At low degrees of hydration the total pore volume available to nitrogen is independent of w/c. At higher degrees of hydration the total pore volume appears to increase with w/c.

Similar results were reported by Hunt [31] for samples with w/c = 0.25–0.50, when surface areas were plotted versus percent nonevaporable water (for samples that were crushed before drying, as in the present study). Changes in surface area with w/c were more apparent at higher nonevaporable water contents (comparable to higher degree of hydration). Mikhail et al. [34,35] also saw a significant increase in surface area with w/c for samples with degrees

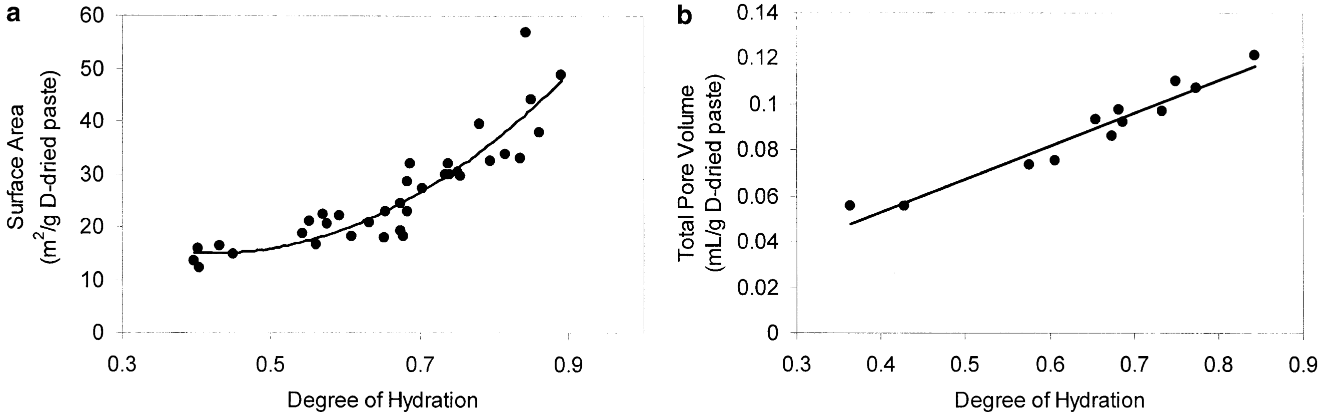

Fig. 2. (a) Effect of degree of hydration on the surface area of cement paste. (b) Effect of degree of hydration on the total pore volume available to nitrogen of cement paste, 1–40 nm pore radius range.

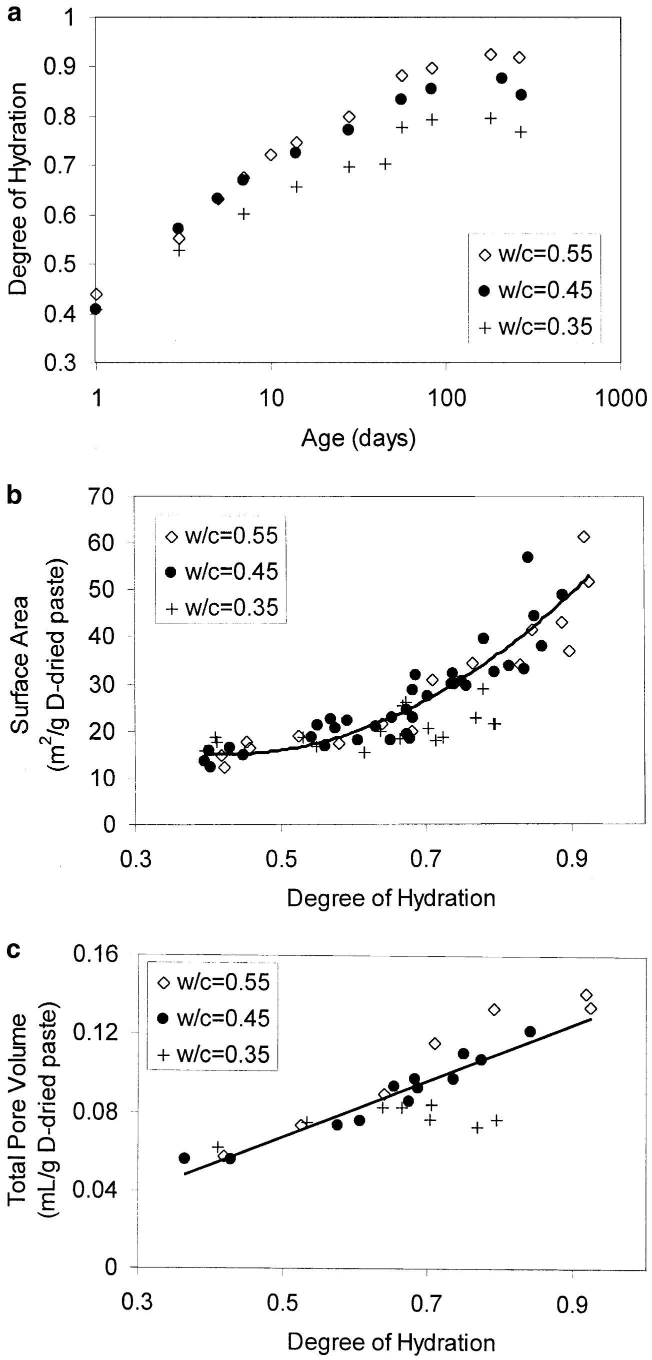

Fig. 3. (a) Effect of water-to-cement ratio on the degree of hydration of cement paste. (b) Effect of water-to-cement ratio on the surface area of cement paste (line is fit to w/c = 0.45 data). (c) Effect of water-to-cement ratio on the total pore volume available to nitrogen of cement paste, 1–40 nm pore radius range (line is fit to 20°C data).

of hydration from 90–98%. Hunt [31] proposed that the surface area approaches a limiting value with age. The age at which this limiting value is reached decreases with initial w/c. For example, Hunt's samples with w/c ≤ 0.30 reached their highest possible surface area after 1 day; i.e., the surface area for these samples was constant with age. Other researchers who have studied samples with very low w/c show similar results [22,33,36].

It is likely that the "limiting value" of surface area for samples with low w/c is the result of space limitations. When the w/c is low, there is less volume in which C-S-H can grow. At some point, new C-S-H that is forming cannot grow expansively, and the surface area will cease to increase. All pastes, regardless of w/c, will reach a point at which all the available space is consumed; samples with low w/c simply reach this state sooner because of the lower available volume.

3.4. Curing temperature

Curing at higher temperatures causes a higher degree of hydration at a given day (Fig. 4a; points shown are averages; average standard deviation = 0.019). The effect becomes negligible, however, for 40°C compared to 20°C samples after 7 days. The 2°C samples reach the same degree of hydration as the 20°C samples after 84 days. Therefore, like w/c, the effects of curing temperature on surface area should most certainly be examined versus degree of hydration rather than age.

There are conflicting data in the literature regarding the effects of curing temperature on nitrogen surface area. Blaine and Valis [22] showed no change with curing temperature (5°C, 21°C, and 38°C) for samples with ages of 1 and 84 days. At intermediate ages, however, surface area increased with curing temperature. Since the samples were compared on the basis of age rather than degree of hydration, it is impossible to isolate whether any of the differences were due to curing temperature. At 84 days, samples cured at all of the temperatures would have similar degrees of hydration, and were shown to also have the same surface area.

Alunno-Rosetti et al. [37] showed that surface area and curing temperature were inversely related for 1-day-old tricalcium silicate (C_3S) pastes cured at temperatures of 25°C, 40°C, 60°C, and 90°C. This study does not explicitly state the units used for surface area reporting, but it appears that they may have been using units of square meters per gram of hydrated C_3S, effectively normalizing the data for degree of hydration. The work of Odler and Rössler [38] confirms this inverse relationship between temperature and surface area, with cement pastes 1–180 days old, cured at 0–100°C. These data were examined on the basis of age rather than degree of hydration, and units were not reported.

The results from the present study are shown in Fig. 4b. Increasing the curing temperature to 40°C has no appreciable effect on surface area (points shown are averages; average standard deviation = 2.77). Low temperature curing (2°C), on the other hand, clearly increases the surface area at a given degree of hydration.

Surprisingly, there is no clear relationship between curing temperature and total pore volume measurable by nitrogen (Fig. 4c). Curing temperature does, on the other hand, influence the pore size distribution (Fig. 4d). The data in Fig. 4d are for samples with degrees of hydration of 0.55.

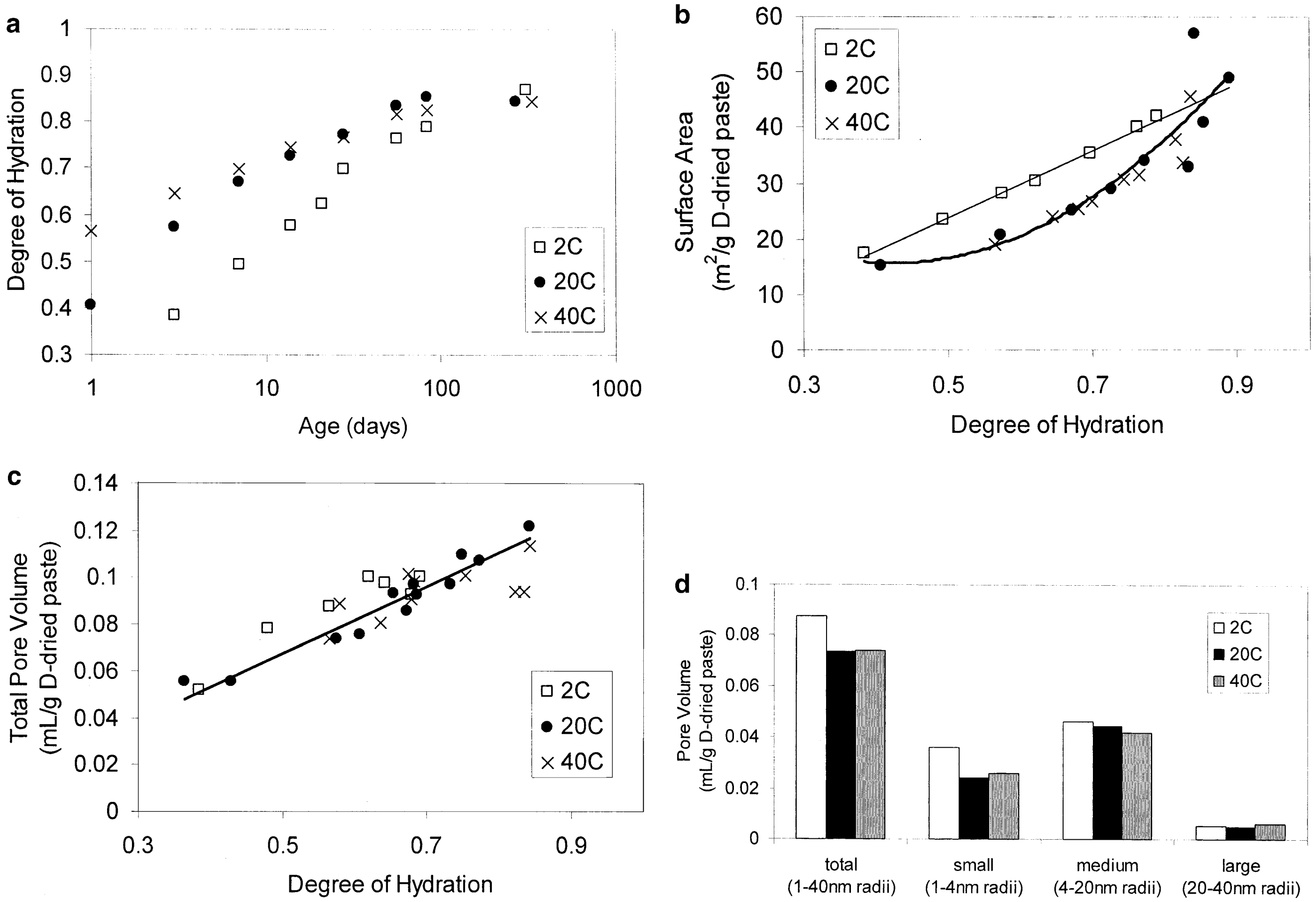

Fig. 4. (a) Effect of curing temperature on the degree of hydration of cement paste. (b) Effect of curing temperature on the nitrogen surface area of cement paste (lines are fit to 2°C and 20°C data). (c) Effect of curing temperature on the total pore volume available to nitrogen of cement paste, 1–40 nm pore radius range (line is fit to 20°C data). (d) Effect of curing temperature on the pore size distribution of cement paste ($\alpha \cong 0.55$, 2°C sample = 14 days old, 20°C sample = 3 days old, 40°C sample = 1 day old).

These data are representative of those for several samples tested across a range of $\alpha = 0.4-0.8$. It is clear that samples cured at 20°C and 40°C have similar distributions of pore volume. For this particular set of samples, the one cured at 2°C has higher total porosity and small pore (1–4 nm) volume than the others. In order to prove that the total pore volume difference is significant, more testing is needed, as witnessed by Fig. 4c. However, all 2°C samples tested had higher small pore volumes than the 20°C samples. A small increase in the volume of these pores leads to a large increase in surface area (high surface-to-volume ratio).

A theory developed by Verbeck and Helmuth [39] can be used to explain why low temperature curing increases cement paste surface area. They noted that, in general, the rate of chemical reactions is much more temperature dependent than the rate of diffusion of ions. Therefore, during cement hydration at high temperatures, ions are reacting faster than they can diffuse, resulting in denser hydration products around the hydrating particle. This phenomenon would have two effects: (1) the dense rim would retard hydration in later stages (when it is diffusion controlled) as it would be more difficult for ions to diffuse, and (2) the distribution of hydration products would be less uniform because there would be regions of very high and very low density. It has been confirmed by several sources that hydration slows at late ages for samples cured at very high temperatures so that those cured at cooler temperatures actually have a higher degree of reaction at later ages [40]. Microscopy and porosity studies confirm higher capillary porosity and less uniformity of hydration products with higher temperatures [41–43].

A further confirmation of Verbeck and Helmuth's theory [39] comes from backscattered electron microscopy studies examining the rim of "inner product." Kjellsen et al. [44] saw denser shells of hydration products in samples cured at 50°C compared to those cured at 5°C. Scrivener [45] cured samples at 80°C for a short time, followed by extended curing at 20°C. She saw two-toned "hydration shells." The outer part of the rim was brighter (more dense) as it was formed during the 80°C curing period. The inner portion of the shell, formed during the 20°C curing, was darker (less dense). X-ray microanalysis of the areas showed no significant composition differences between the two zones. These results were confirmed by subsequent studies [46,47].

In the present study, only curing at lower than room temperature resulted in any noticeable microstructural changes. Using Verbeck and Helmuth's theory [39], a lower curing temperature decreases the reaction rate more than it decreases the diffusion rate and the ions diffuse farther from the hydrating particle before reacting. The hydration products are thus formed in open spaces, allowing them to form less densely and thus with higher nitrogen-accessible surface area. Perhaps curing at 40°C does not affect surface area because it does not alter the reaction/diffusion relationship enough to significantly change the microstructure. A higher curing temperature (60–80°C) may be required in order to see any significant differences in surface area.

3.5. Calcium chloride

It is well known that the addition of 1–2% calcium chloride to cement pastes accelerates hydration. However, the addition of 1% $CaCl_2$ does not significantly increase the degree of hydration of cement paste after 1 day (Fig. 5a; points shown are averages of three or more samples; average standard deviation = 0.020). The accelerative effects are only significant in the first few hours of hydration; after 24 h, the control pastes "catch up." Although surface areas could be presented effectively versus age, they will be presented versus degree of hydration for consistency with other results presented in this paper.

Several studies have shown that the addition of 2% $CaCl_2$ to C_3S pastes increases surface area [48–52]. The effects of 1% $CaCl_2$ on the surface area of cement paste cured at 20°C are shown in Fig. 5b (points shown are averages; average standard deviation = 3.21). It is clear that $CaCl_2$ increases the surface area of samples with degrees of hydration less than 0.8. Calcium chloride also increases the total pore volume available to nitrogen (1–40 nm; Fig. 5c). Representative pore size distributions are shown in Fig. 5d. Calcium chloride increases the volume of pores in all size ranges available to nitrogen.

At degrees of hydration greater than 0.8, the difference in surface area becomes negligible. It is possible that this is the result of space limitations similar to those discussed with regard to w/c. The highest surface area within a given w/c is limited. It may be impossible to see surface area values for D-dried samples of w/c = 0.45 higher than 60–70 m^2/g D-

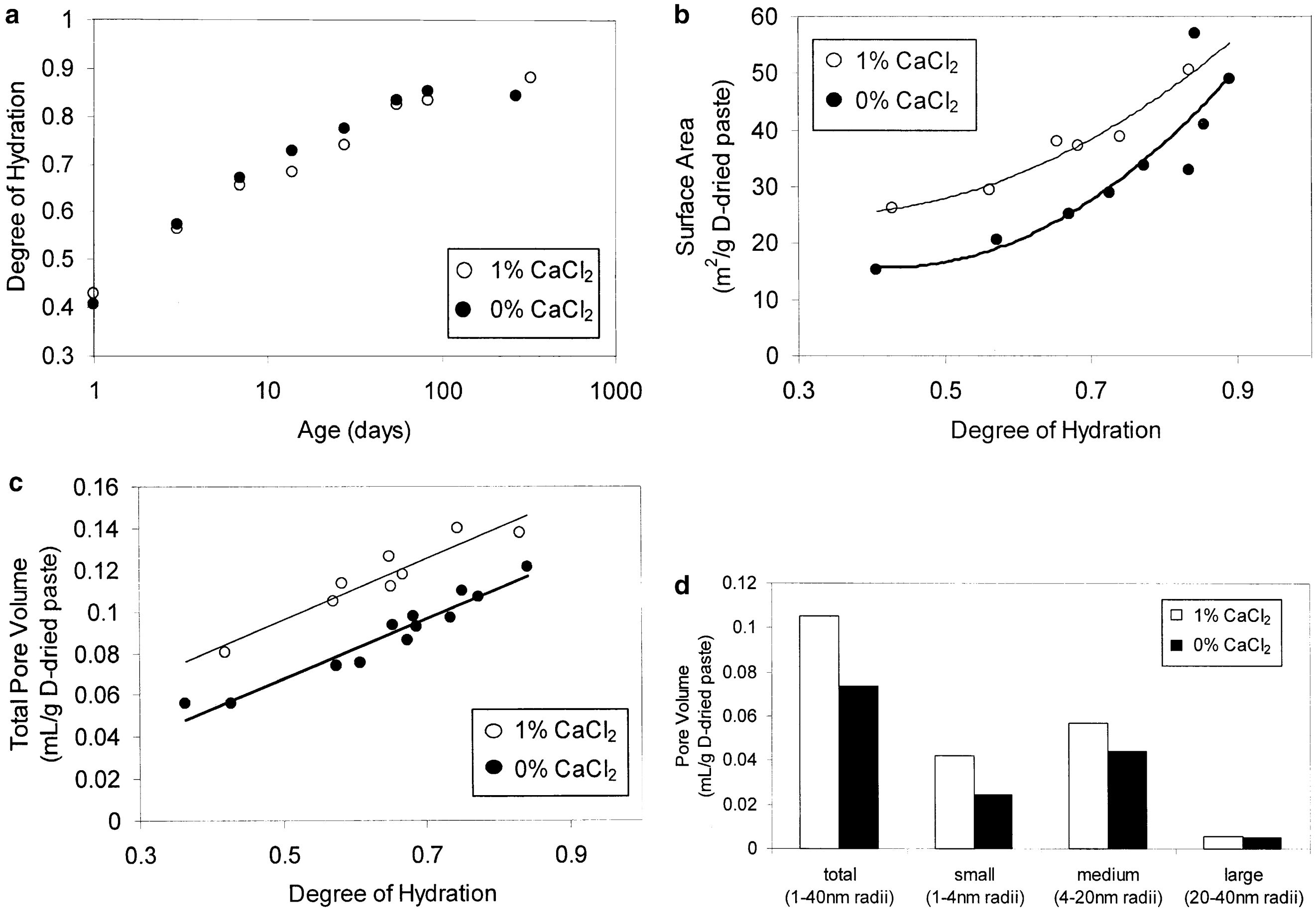

Fig. 5. (a) Effect of 1% $CaCl_2$ on the degree of hydration of cement paste. (b) Effect of 1% $CaCl_2$ on the surface area of cement paste. (c) Effect of 1% $CaCl_2$ on the total pore volume available to nitrogen of cement paste, 1–40 nm pore radius range. (d) Effect of 1% $CaCl_2$ on the pore size distribution of cement paste (age = 3 days, $\alpha \cong 0.55$).

dried paste. The reason why $CaCl_2$ encourages the formation of a higher surface area C-S-H is not clear, as the mechanisms for acceleration have not been adequately explained [11].

4. Conclusions

Table 4 summarizes the effects of the variables examined in this paper on the nitrogen surface area of cement pastes. Given a consistent and effective sample preparation protocol, changes in surface area and porosity corresponding to changes in composition and curing environment become clear. D-drying was shown to give more consistent and reliable results compared to oven-drying at 105°C or methanol exchange prior to D-drying. Oven-dried samples do not give adequate information on microstructural changes and methanol exchange causes too much variation in the measured values. The measurement of porosity in addition to surface area is valuable because it adds additional quantitative information, often clarifying inconsistencies in surface area results.

Even when degree of hydration is constant, the surface area and porosity of cement paste can be manipulated as seen in the cases of curing temperature and calcium chloride. Therefore, it can be concluded that the surface area of C-S-H itself is variable, a result that can be exploited further in attempts to model the microstructure and understand future surface area data.

Nitrogen adsorption data for cement paste and hydrated calcium silicates is typically viewed as an inadequate measure of the surface area of C-S-H. In the absence of an "ideal" technique of surface area measurement for cement-based materials, it is preferable to attempt to better understand this technique, its shortcomings, and advantages rather than discounting it altogether.

There are two vital points that one must consider when examining nitrogen adsorption data. The first is that variations in sample preparation strongly affect the measurable nitrogen surface area. Therefore, one must always use consistent experimental methods and report full details of those methods — in addition to disclosing the units used for data reporting. Although this may seem obvious, it is too frequently overlooked. Along the same line, because drying method has such a large effect on the values measured for surface area and porosity, it is more important to examine the relative effects of variables rather than absolute values.

The second important point is that we must interpret nitrogen surface area data as measuring a subset of the C-S-H surface rather than the entire surface. When the data is examined with this in mind, focus can be placed on how this subset changes with the chemistry of the system. Combining nitrogen surface area data with results from other methods will lead us to a better understanding of the C-S-H microstructure as a whole and how it can be manipulated.

Table 4
Summary of results

Variable	Effect on nitrogen surface area	Notes
Drying method:		
oven-drying, 105°C	↓	compared to D-drying
MeOH + D-drying	↑	
↑ Age	↑	D-dried
↑ Water-to-cement ratio	↑	D-dried, late ages only
↑ Curing temperature	↓	D-dried, not confirmed for 40°C
1% calcium chloride	↑	D-dried, $\alpha \leq 0.8$

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