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TECHNICAL NOTES

Deterioration of the Nitrogen BET Surface Area of Dried Cement Paste with Storage Time

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Gas sorption surface area measurements have been important for developing microstructural models for the structure of calcium-silicate-hydrate (C-S-H), the major hydration product of portland cement. However, surface area measurements using the nitrogen BET method have historically had high variability and have not always been reproducible. In this study, the variability of the nitrogen BET surface area of hardened cement paste (HCP) was investigated by varying the D-drying time and by storing the dried cement for various times before the BET measurement. The surface area of the samples was found to decrease with increasing storage time, and the surface area values became independent of the initial D-drying time after about 2 weeks. The storage time accounted for most of the observed variation in the data. ADVANCED CEMENT BASED MATERIALS 1996, 3, 72–75

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Hardened portland cement paste (HCP) has a large specific surface area, which is primarily associated with the calcium-silicate-hydrate (C-S-H)[1] gel phase. The specific surface area of HCP is usually measured using the gas sorption technique developed by Brunauer, Emmett, and Teller, commonly known as the BET method [1]. A good general discussion of this technique can be found in the book by Gregg and Sing [2].

When measured with water vapor at room temperature using the gravimetric BET technique, HCP has a specific surface area of about 200 m^2 per gram of dried paste [3,4]. However, as measured by nitrogen at 77 K using the volumetric BET technique, the surface areas reported in the literature range from 10 m^2/g to 200 m^2/g, with the value depending upon the method used to dry the paste [5–7]. The nitrogen BET surface area also depends on the water:cement ratio (w:c), whereas the water vapor surface area has only a slight dependence on w:c [4]. Several theories have been proposed to explain the differences between the water and nitrogen BET surface areas, including the Powers-Brunauer model [8,9], the Feldman-Sereda model [10], the Munich model [11], and the Jennings and Tennis model [12]. More details concerning the application of gas sorption surface area techniques to the cement paste system can be found in a recent critical literature review [13].

Cement specimens for BET surface area measurements need to be conditioned before analysis to remove adsorbed water. The sample is typically exposed to vacuum drying or to solvent replacement followed by vacuum distillation. The most common drying technique, called D-drying, involves equilibrating the cement to the vapor pressure of water at the temperature of dry ice (–79°C). Litvan [7] has shown that nitrogen surface areas are dependent on the method of conditioning. It is also difficult to draw conclusions from the literature because of inconsistencies in the way results are reported. Surface area values have been calculated per gram of dried paste, per gram of ignited paste, or per gram of C-S-H, and it is often unclear which measurement unit was reported [13]. All surface area values in this paper are reported in square meters per gram of dried paste.

In this study, a series of experiments was undertaken to analyze the variability of the nitrogen BET surface area. The primary variable to be investigated when the experimental matrix was designed was the drying tech-

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[1] Cement chemistry notation is used: C = CaO, S = SiO_2, H = H_2O.

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nique used, particularly the length of D-drying time. It should be noted that storage of the dried paste in dry air was not considered to have an effect on the surface area until well into the experimental matrix. However, during analysis of the results, this variable was found to be a major source of variability.

Experimental Procedure

The composition of the portland cement used in these experiments was determined by Bogue analysis to be 61.5% C_3S, 22.5% C_2S, 3.2% C_3A, and 9.5% C_4AF. A cement paste with w:c = 0.5 was prepared under a nitrogen atmosphere. The paste was then poured into small plastic vials and tapped several times to remove entrapped gas, then sealed. The sealed vials were slowly rotated in a water bath at 22°C for the first 24 hours of hydration to preserve the homogeneity of the samples. The first 12 hours of hydration were monitored using a calorimeter to assure that hydration was occurring normally. After 24 hours of hydration, the samples were removed from the vials and cured in saturated lime water at room temperature for 2 years. During the 2-year curing time, samples were taken for loss-on-ignition testing. After 2 years, the degree of hydration of the cement was determined to be 94%, assuming a factor of 0.24 g of bound H_2O per gram of ignited paste at complete hydration.

After curing, samples of the cement were removed from the saturated lime water and ground in a mechanical grinder. A 1–2 g sample of cement paste that was caught between #16 and #30 sieves was placed into a 25-ml plastic vial with large holes in the lid and then D-dried for a specific period of time (0.25 day, 1 day, 7 days, or 21 days). The D-drying apparatus consisted of a sealed glass container attached to a mechanical pump through a cold trap cooled by a mixture of solid CO_2 and alcohol, following the technique first developed by Copeland and Hayes [14]. The equilibrium water vapor pressure within the D-dry apparatus is 5×10^{-4} torr, the vapor pressure of H_2O at −79°C. After removal from the D-drying apparatus, the sample was immediately sealed in the plastic vial with a nonperforated lid. The D-dried samples were then labeled and stored until the BET instrument became available. The storage time varied greatly, from 1 day to more than 80 days.

A preliminary study of the precision of the analyzer (Omnisorp 360, Coulter Instrument Co., Hialeah, FL) using a silica/alumina reference material indicated the standard deviation of the analyzer to be ± 2 m^2/g for nitrogen BET surface area measurements. For the HCP surface area measurements, a 0.25-g sample was placed into a sample tube, connected to the analyzer, and evacuated. Nitrogen adsorption and desorption isotherms at 77 K were obtained. The samples were weighed before and after analysis to ensure that no material was lost during the analysis. Nitrogen BET surface areas were calculated automatically by the system software.

Results and Discussion

The original experimental matrix was designed to establish the effects of D-drying time and other drying techniques, such as methanol exchange and freeze drying, on the nitrogen BET surface area. However, before the experiments involving D-drying of the ground cement for different times were completed, it became clear there was a large amount of scatter in the data that could not be accounted for. The only other factor that had varied significantly from sample to sample was the length of time between drying and the surface area measurement, referred to as the storage time. This was not a planned variable in the study but was simply the result of waiting for the BET analyzer to become available.

When the storage time was included in the data as a variable, two significant trends were seen that resolved almost all of the scatter in the data. When the BET measurement was conducted within 1 day of D-drying, the surface area was a function of the D-drying time, as shown in Figure 1. The surface area increased rapidly up to about 7 days of drying, reaching a maximum value of 70–75 m^2 g^{-1}. After 7 days of D-drying, the surface area values remained constant out to 46 days of D-drying. The value of 90 m^2 g^{-1} at 21 days is an obvi-

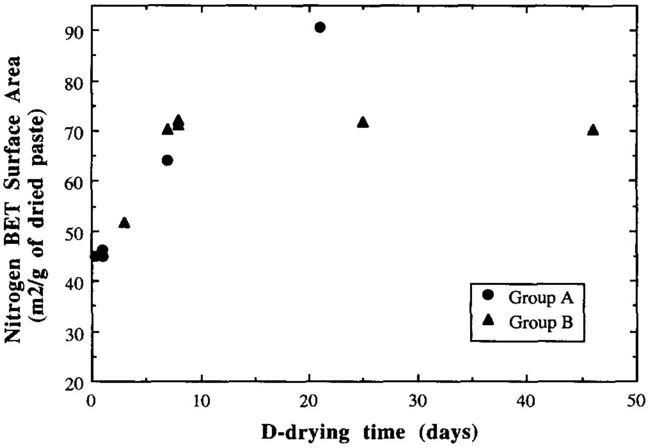

FIGURE 1. Nitrogen BET surface area as a function of D-drying time for specimens that were analyzed within 1 day of drying. Group A represents data from the original experimental matrix, and group B represents a later series of experiments.

ous outlier. The group A measurements were part of the original experimental matrix, while the group B measurements were conducted later to verify the effect of D-drying after no storage time.

In general, the time required to reach an equilibrium with the D-dry pressure would be expected to vary with the cement particle size, the degree of hydration of the cement, and other factors. The trend shown in Figure 1 is consistent with the results of Copeland and Hayes [14], who found that 4 days of D-drying was sufficient to bring their ground cement specimens acceptably close to equilibrium, which they defined as less than 1 mg of weight loss per gram of paste per day of drying. It should be noted that a constant nitrogen BET surface area does not necessarily indicate that the specimens were in complete equilibrium at the D-dry pressure.

Figure 2 shows the surface area of all of the specimens from the original experimental matrix plotted against the storage time. When the storage time was longer than a few days, the surface area decreased significantly with storage time. Also, the surface area values became virtually independent of the D-drying time as the storage time increased beyond about 14 days. The mechanism for the observed decrease in the nitrogen surface area of dried HCP is not understood.

A similar effect was observed by Hunt et al. [15], who noted relatively small decreases in the nitrogen surface area of D-dried cement over storage times of several months. They found that the amount of surface area deterioration was greater when the cement was D-dried for shorter times before storage, with virtually no deterioration occurring in specimens that had been D-dried long enough to remove all of the evaporable water. They attributed the loss of surface area to an interaction between the evaporable water and the C-S-H gel phase of the cement but did not propose a specific mechanism for this effect.

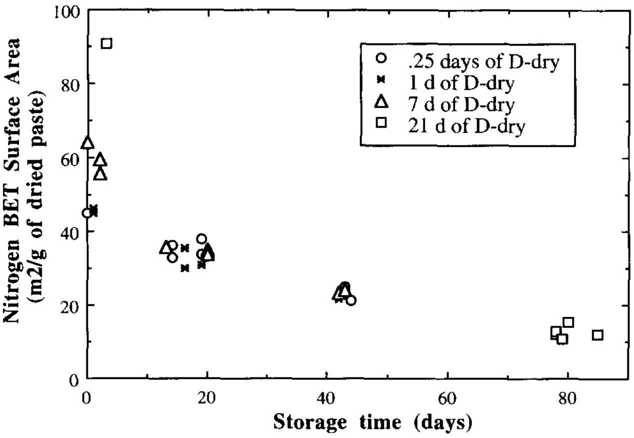

FIGURE 2. Nitrogen BET surface area as a function of the storage time between D-drying and analysis, for all of the specimens from the original experimental matrix.

In contrast to the results of Hunt et al. [15], the results shown in Figure 2 indicate that the total decrease in surface area over the first 20 days of storage was greater for specimens that were D-dried for longer times and therefore had less evaporable water. In general, the measured BET surface area of cement paste increases with decreasing evaporable water content because more of the C-S-H gel pores are empty and thus able to admit the sorptive gas molecules. The observation that the surface area values became independent of D-drying time after several days of storage is a strong indication that the smaller gel pores that are opened up by extended D-drying were affected so as to prevent their being accessed by the nitrogen molecules during the BET measurement. One possibility currently being investigated is that the cement underwent a small amount of carbonation during storage that reduced the size of the openings into the smallest pores. Although this would seem to contradict the traditional belief that carbonation does not occur in dried cement, it provides a good explanation for both the decrease in surface area and the lack of dependence on D-drying time. The results of this investigation are reported in a companion paper [16].

In light of these findings, certain measures can be suggested to reduce the variability of the nitrogen BET surface area of HCP. Samples are typically conditioned in batches to minimize experimental variability. However, the BET surface area measurement is rather time-consuming, so this approach tends to cause some specimens to wait longer than others for analysis. The results of this paper suggest that samples should be conditioned in smaller batches so that they can be analyzed immediately. If CO_2 is found to be the mechanism for the observed surface area deterioration of dried HCP specimens, then the variability in the surface area values could be significantly reduced by minimizing exposure to carbon dioxide.

Summary

The surface area of conditioned HCP samples as measured by nitrogen BET was found to decrease with the amount of storage time between initial D-drying and the surface area measurement. Furthermore, the surface area values became virtually independent of the D-drying time after about 14 days of storage. The storage time accounted for most of the variability in the surface area values from this investigation. The mechanism for the observed decrease in surface area is not understood, but a carbonation reaction that reduces the size of the openings into the smallest gel pores is a strong possibility. The deterioration of the surface area of dried cement paste during storage has not been well documented and has, therefore, probably contributed to the high variability and low reproducibility of the nitrogen BET surface area values reported in the literature.

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