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Effect of Carbonation on the Nitrogen BET Surface Area of Hardened Portland Cement Paste

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The progressive decrease in the nitrogen BET surface area of dried hydrated portland cement paste during storage in plastic vials was found to be caused by carbonation, a reaction between the C-S-H phase and carbon dioxide in the air. A strong correlation between the surface area and the amount of carbonation as measured by thermogravimetric analysis was found. Historically, nitrogen BET values of surface area have shown great variability and low reproducibility, which has limited the value of this useful technique. The results of this work suggest that carbonation may have contributed to this problem. ADVANCED CEMENT BASED MATERIALS 1996, 3, 76–80

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The high surface area of hydrated portland cement is primarily due to the microstructure of the main hydration product, CaO-SiO_2-H_2O (C-S-H).[1] The C-S-H in hardened cement paste (HCP) is an amorphous or poorly crystalline phase that does not have a fixed composition. Instead, it has a calcium:silicon ratio that varies from 1.2 to 1.8, and a water:silicon ratio that varies widely depending on the drying condition [1].

To measure the surface area by a gas sorption technique, the water stored in the pores must be removed. There are two general types of pores present in C-S-H, both of which can contain water. Capillary pores are larger pores that hold water in saturated conditions but lose their water on exposure to air. Gel pores are nanometer-sized pores. Water present in the gel pores is more strongly bonded than capillary water and can be removed only by drying the paste. The most common drying technique, called D-drying, consists of equilibrating the cement to a water vapor pressure of 5×10^{-4} torr by continuously pumping through a trap containing dry ice at −79°C. Powers and Brownyard [2] called the water removed from saturated C-S-H during D-drying the "gel water." Any water present after D-drying is chemically bound water within the interlayer spaces.

The most common method of measuring the surface area of a porous solid material with a high surface area is by the BET gas sorption technique using either nitrogen or water vapor as the sorptive gas. The application of the gas sorption technique to the measurement of cement surface area has been recently reviewed [3]. The surface area of hardened cement paste measured using water vapor, S_W, is about 200 m^2 per g of dried HCP and is relatively constant [4]. However, the surface area measured using nitrogen, S_N, has been found to vary from 10–200 $m^2\ g^{-1}$ depending on the drying technique used and on the water:cement ratio [5]. Differences between S_N and S_W have been attributed to the ability of the water vapor molecules to penetrate more of the C-S-H porosity than the larger nitrogen molecules [6,7]. However, another school of thought maintains that surface area measurements using water are inherently invalid because water is a fundamental part of the C-S-H structure [8,9]. No reasonable explanation for the wide variability of the nitrogen surface area values has been proposed, but it has been widely assumed that some drying techniques damage the structure of C-S-H more than others. Recently, a model for the structure of C-S-H has been proposed [4] that predicts the surface area as measured by nitrogen for D-dried samples. However, the model does not account for variability in S_N due to the drying technique.

Rarick et al. [10] recently found that widely varying values of S_N obtained using different D-drying times could be correlated to a single factor—the length of time

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[1] Cement chemistry notation is used: C = CaO, S = SiO_2, H = H_2O, A = Al_2O_3, F = Fe_2O_3.

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between removal from the D-drying apparatus and the surface area measurement (see Figure 1). The surface area was found to decrease significantly with the storage time and to be independent of the amount of D-drying. This result is quite significant, because the time elapsed between drying and the surface area measurement is not generally reported in the literature, and it could thus potentially explain much of the historical variation in the nitrogen BET surface area of HCP.

The carbonation of cement paste is a well-documented reaction between CO_2 dissolved in the pore liquid and the C-S-H. In steel-reinforced concrete structures carbonation is a detrimental process in which atmospheric CO_2 slowly lowers the pH of the pore fluid, allowing corrosion of the reinforcing steel to occur. In small laboratory samples carbonation can occur more quickly because of the higher outer surface:volume ratio, and care must be taken during studies of cement hydration to avoid contamination with CO_2 [1]. The effect of carbonation on the surface area of D-dried HCP has not been documented carefully, possibly because the lack of pore water was felt to eliminate the reaction route. However, this work demonstrates that the decrease in surface area reported by Rarick et al. [10] was due to carbonation of the dried HCP, even though the specimens were exposed only to small amounts of moisture and CO_2 during storage.

Experimental Procedure

The HCP used in this study is a 2.5-year-old portland cement paste with a water:cement ratio of 0.5. The primary components of the cement were determined by Bogue analysis to be 61.5% C_3S, 22.5% C_2S, 9.5% C_4AF, and 3.2% C_3A. After 24 hours of hydration in a constant temperature bath at 22°C, the cement paste was stored in lime water at room temperature. The degree of hydration of the cement was found to be 94% after 2 years, as measured by the loss-on-ignition technique. This is the same HCP used by Rarick et al. [10].

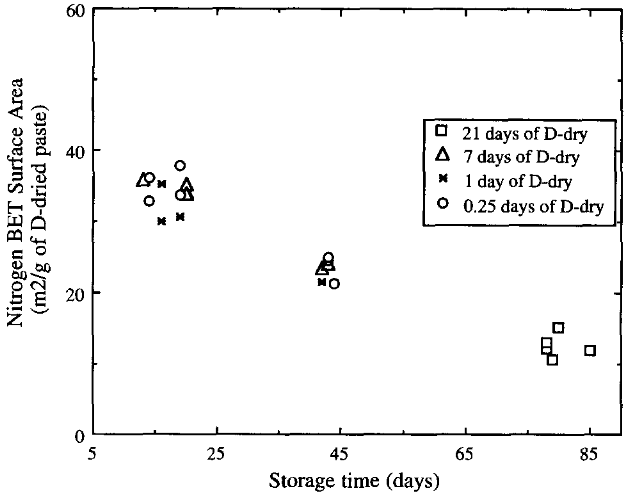

FIGURE 1. Nitrogen BET surface area of a portland hardened cement paste (HCP) stored in closed plastic vials as a function of the storage time between D-drying and the surface area measurement, after Rarick et al. [10].

Specimens for surface area testing were prepared by grinding the HCP in a mortar and pestle. Only cement that passed through a #16 sieve and was caught on a #30 sieve was used, giving a relatively uniform particle size of about 1 mm. The ground paste was immediately placed into a D-drying apparatus for a period of 7 days, which resulted in a paste with a maximum surface area of 70–75 $m^2\ g^{-1}$. After drying, the cement was removed and stored in plastic or glass vials under different conditions.

To create a dry environment, a plastic vial was placed into a desiccator containing a layer of desiccant material (anhydrous calcium sulfate). To create a CO_2-free environment, a glass vial (we have found that CO_2 penetrates the plastic vials) was placed into a desiccator that was evacuated and backfilled with high-purity nitrogen. Direct exposure to CO_2 was achieved by placing a plastic vial with a perforated lid into a sealed glass jar through which pure CO_2 flowed continuously. After exiting the jar, the CO_2 passed through an oil bubbler to keep air out of the jar. As with the desiccators, the glass jars contained a layer of either desiccant or water to create a dry or wet environment.

To measure the nitrogen BET surface area, small samples (0.25 g) of cement were periodically removed from the vials and immediately analyzed in the BET instrument (Omnisorp 360, Coulter Instrument Co., Hialeah, FL). The samples were weighed before and after the analysis. The nitrogen BET surface area values were calculated automatically by the system software and are reported as square meters per gram of dried HCP.

To test for carbonation directly, thermogravimetric analysis (TGA) was employed. Samples of conditioned cement for TGA were removed from the vials along with the surface area samples and were immediately analyzed using a TGA instrument (TGA-1500, Omnitherm Co., Mundelein, IL) at a heating rate of 10°C min^{-1}. The amount of carbonate present was determined from the weight loss between 650°C and 850°C as $CaCO_3$ decomposed to CaO and CO_2, and from the residual weight at 900°C, which was assumed to be the weight of cement originally present [11]. Although calculating the amount of carbonate present using TGA is somewhat inaccurate because of simultaneous weight loss from the cement paste, comparison of the values for different specimens provides a good indication of the relative degree of carbonation.

Results and Discussion

To determine if moisture or CO_2 in the air caused the surface area to decrease during storage, a 15-g sample of cement that was D-dried for 7 days was divided into three samples. One sample was placed into a plastic vial and left in the laboratory so that it was exposed to the air, to duplicate the conditions reported by Rarick et al. [10]. The other samples were stored in moisture-free and CO_2-free environments, as discussed earlier. The effect of storage time on the surface area of these specimens appears in Figure 2.

The elimination of either moisture or CO_2 in the atmosphere surrounding the vials allowed the surface area to remain constant at 70–75 m^2 g^{-1} for 41 days, while the surface area of the cement that was protected from the air only by the plastic vial dropped to 38 m^2 g^{-1} over the same time period. For comparison, the results of Rarick et al. [10] for 7 days of D-drying are also plotted in Figure 2. Those values are somewhat lower than the current values, but follow the same trend. These results are a strong indication that moisture, or CO_2, or both are able to penetrate into the plastic vials, either by an imperfect seal between the lid and the vial or by diffusing through the plastic. To test this assumption, another batch of D-dried ground HCP was stored in a glass vial with a thick, tight-fitting plastic lid. No decrease in surface area was observed in this sample after 47 days, indicating that the glass vials are impermeable to moisture and CO_2.

Groves et al. [11] found that a few hours of exposure to pure CO_2 caused a degree of carbonation in C_3S paste equivalent to 60 days of exposure to air at the same relative humidity, so a similar increase in the rate of surface area deterioration would be expected. To determine if carbonation was causing the observed surface area decrease, the next set of experiments involved exposure of the cement to pure CO_2. Another sample of cement was ground and D-dried for 7 days, and then two 5-g samples were removed and exposed to either moist or dry CO_2 as described earlier. The surface area of these specimens was measured immediately after D-drying, and after 1 day and 4 days of exposure to CO_2 (see Figure 3). The surface area of the cement decreased significantly during the first 24 hours of exposure, after which it remained constant over the next 3 days. The surface area of the cement exposed to dry CO_2 decreased to about 40 m^2 g^{-1}, while the surface area of the cement exposed to moist CO_2 dropped to about 14 m^2 g^{-1}. To determine if any of this surface area decrease was recoverable, both samples were returned to the D-dryer for 1 day and then the surface area was measured again. No increase was observed.

To determine the rate at which the surface area decreases during exposure to CO_2, the experiment was repeated using shorter exposure times. As shown in Figure 4, almost all of the change in surface area in dry CO_2 occurred over a period of 1–2 hours, while the decrease in moist CO_2 occurred in about 30 minutes. The faster decrease and lower minimum surface area value observed in the presence of moisture are consistent with CO_2 first dissolving in the pore water and then reacting with the C-S-H. However, the significant surface area decrease observed in dry CO_2 suggests that some type of carbonation reaction may also occur with gaseous CO_2.

The specimens exposed to CO_2 were also analyzed using TGA. A good correlation was found between the amount of carbonate and the surface area of the HCP, with the surface area decreasing linearly with the weight percent of carbonate in the cement (see Figure

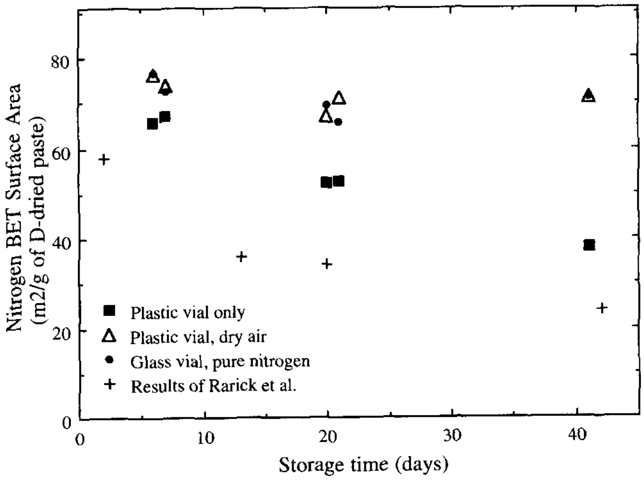

FIGURE 2. Nitrogen BET surface area as a function of the time between D-drying and measurement, for different storage conditions.

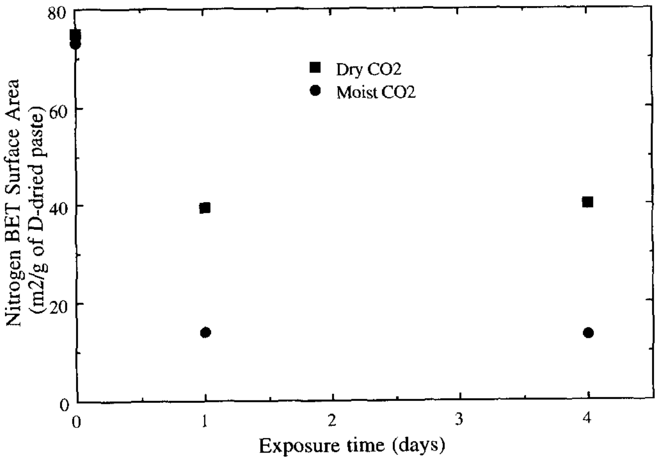

FIGURE 3. Nitrogen BET surface area after exposure to flowing CO_2 under dry and moist conditions.

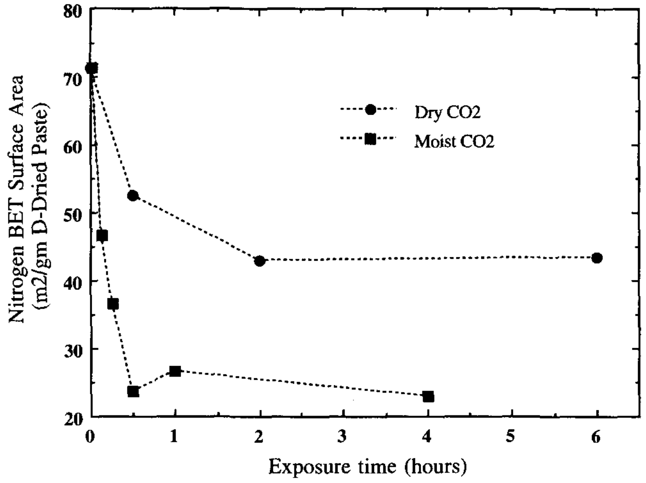

FIGURE 4. Nitrogen BET surface area as a function of the time exposed to flowing CO_2 under dry and moist conditions.

5). The weight loss values were normalized by assuming that no carbonation was present in the cement after D-drying. The carbonation values in Figure 5 therefore represent the amount of carbonate formed during the controlled exposure to pure CO_2. The results presented earlier clearly demonstrate that carbonation of hardened cement paste specimens causes a decrease in the nitrogen BET surface area, even if the dried HCP is stored in closed plastic vials.

Much of the historical variability in the nitrogen BET surface area has been attributed to differences in the sample preparation methods, particularly the drying technique. Litvan [5] has shown that drying tends to damage the C-S-H microstructure and that some drying techniques are better than others at preserving the surface area. However, the possibility that carbonation is responsible for at least some of the reported variability in nitrogen BET surface area values must also be considered in light of the present results, which show that carbonation of dried HCP occurred during storage in standard plastic laboratory vials. As noted by Rarick et al. [10], it is standard procedure to process samples in batches to reduce variability. Because a BET analysis takes a few hours (each of the BET runs conducted for this work took 3 hours), some samples wait much longer for analysis than others. Therefore, extreme care must be taken to avoid exposure to air and moisture. The influence of drying technique in light of these results is the subject of ongoing research.

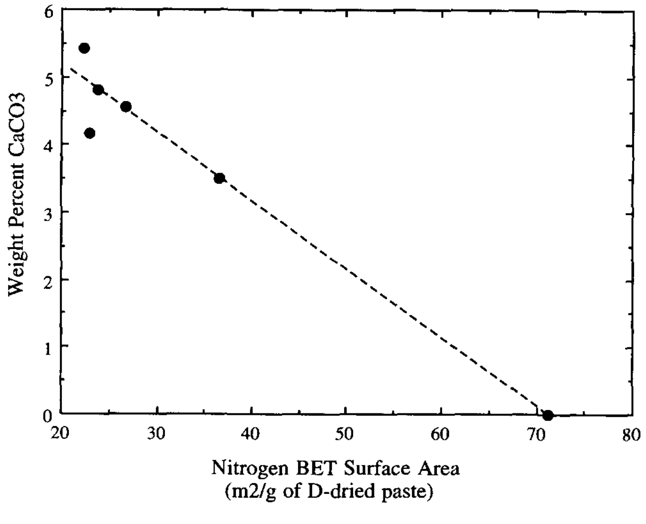

FIGURE 5. Amount of $CaCO_3$ in the cement as calculated from TGA, plotted against the nitrogen BET surface area.

Summary

Carbonation was found to have a strong effect on the nitrogen BET surface area of dried portland cement paste. The surface area of HCP exposed to small amounts of moisture and CO_2 that penetrated into closed plastic vials decreased progressively over a period of weeks, while the surface area of HCP exposed to pure CO_2 decreased to a constant minimum value in about an hour. The decrease in the surface area during exposure to moisture and CO_2 was more rapid than for CO_2 only, and the minimum surface area was lower. A strong correlation was found between the surface area and the amount of $CaCO_3$ in the cement as calculated from TGA.

It seems possible that some of the historical variability in the nitrogen BET surface area of cement was due to varying amounts of carbonation in the specimens. However, carbonation is easily avoided by preventing any contact between the dried cement and moist air. No decrease in surface area was observed after 6 weeks when the dried paste was stored in a plastic vial that was placed into a sealed desiccator to avoid moisture, or when the paste was stored in a glass vial.

Acknowledgments

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