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New insights into the effects of sugar on the hydration and microstructure of cement pastes

Maria C. Garci Juenger[a,1], Hamlin M. Jennings[a,b,*]

[a]Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA
[b]Department of Civil Engineering, Northwestern University, Evanston, IL 60208, USA

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Abstract

The effects of adding sugar to cement paste on hydration and microstructure were observed. While 1% sugar delayed hydration as expected, the delay period was shortened by increased curing temperature. When samples containing sugar began to react, hydration progressed very quickly and the degree of hydration soon surpassed that of control samples. Sugar addition increased the surface area and altered the pore size distribution, as measured by nitrogen, of cement pastes. Results indicate that sugar not only alters the rate of cement paste hydration, but the microstructure of calcium-silicate-hydrate (C-S-H) as well. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Hydration; Retardation; Calcium-silicate-hydrate (C-S-H); Surface area; Pore size distribution

1. Introduction

Many chemical admixtures alter the hydration of cement paste through mechanisms that are not generally understood. Sugar has long been known to retard hydration and set, a phenomenon that was discovered quite by accident when it was observed that cement stored in old sugar sacks failed to set properly [1]. Further problems were encountered historically when mixing water had been contaminated with traces of sugar as in the case of a concrete floor placed in a candy factory [2]. It is now recognized that many types of sugars and starches retard cement hydration and set, including some water-reducing agents containing lignosulfonates. While many types of sugars are retarders, some are more effective than others. Furthermore, increasing the amount of sugar increases the extent of retardation.

The mechanism of the curious interaction between sugar and cement is poorly understood. It is generally accepted that retardation occurs because sugar adsorbs to: (1) surfaces of the hydrating cement particles, and/or (2) surfaces of hydration products, thereby forming a temporary barrier to further hydration. The adsorption may take place through a process called chelation where the organic molecules form a complex with the metal ions in cement phases. Taplin [3] showed that the ability of a sugar to bond with a cement phase depends on the presence of the group, HO-C=O. A characteristic feature of this group is that the oxygen molecules can approach each other, a requisite condition for chelation. While many retarding sugars contain the chelating group, other effective retarding sugars do not. Bruere [4] demonstrated that many of the latter hydrolyze in the high pH environment of cement paste to form saccharinic acids, which do contain the HO-C-C=O group. While shedding some light on the mechanism of sugar adsorption, this information is insufficient, as it does not tell us onto which phases the sugars are adsorbing.

After reviewing the data available prior to 1972, Young [5] proposed the following theory for retardation. Sugar first bonds to the aluminate phases by complexing or chelating as described previously. This promotes the dissolution of ions from the hydrating calcium-silicate phases, resulting in a higher concentration of ions in solution. When precipitation of hydration products occurs, their growth is inhibited by the adsorption of sugar. Eventually,

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* Corresponding author. Tel.: +1-847-491-4858; fax: +1-847-491-5282.
E-mail address: h-jennings@northwestern.edu (H.M. Jennings).

[1] Present address: Department of Civil and Environmental Engineering, University of California, 721 Davis Hall, Berkeley, CA 94720, USA.

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the sugar is incorporated into the hydration products and further hydration proceeds. Young's theory incorporates the ideas of adsorption of sugar onto both hydrating particles and hydration products.

There has been some experimental evidence since the publication of Young's theory showing sugar adsorption onto hydrating phases and hydration products. Ramachandran et al. [6] reported that cements high in aluminates need a higher quantity of sugar to achieve the same retardation, suggesting that sugar adsorbs on aluminates. Singh and Ojha [7] and Yang et al. [8] showed that the zeta potential of hydrating cement is positive in the absence of sugar, but negative when a sugar is present. The difference in zeta potential can be explained by adsorption of the sugar onto hydrating particles, but no distinction can be made from this data as to whether the adsorption is on an aluminate or a calcium-silicate phase.

Thomas and Birchall [9–11] have shown strong evidence that complexation of sugar onto phases containing calcium is responsible for retardation. They studied the concentration of calcium, silicon, aluminum, iron, and hydroxide ions in solution. In neat cement pastes, the concentration of silicon, aluminum, and iron was very low and the Ca/Si ratio was 1000. In pastes containing 50 mM sucrose, the calcium and hydroxide ion concentrations were higher, and the silicon, aluminum, and iron concentrations were 500 times larger. After 2 h of hydration, the Ca/Si ratio in solution decreased to 6. They proposed that sugar was poisoning the surfaces of the hydration products, allowing ions to coexist in solution at much higher concentrations without causing precipitation. They showed that the stronger the retarder, the better it solubilized cement. They further showed that sugar does not form a complex with silicon, but it does with calcium. In broad agreement with Young [5], they proposed that sugars retard hydration by increasing the solubility of cement and then adsorbing onto calcium hydroxide (CH) and calcium-silicate-hydrate (C-S-H) thereby inhibiting their growth.

More evidence for the increase in cement solubility in the presence of sucrose was presented recently by Mitchell et al. [12]. They used atomic force microscopy to study the surface of hydrating cement. The surfaces of the hydrating particles treated with sucrose appeared etched after 105 min. After 17 h, they appeared much smoother and more rounded. These observations indicate congruent dissolution of the hydrating phases.

The mechanism for retardation of cement hydration by sugars is, therefore, only partly understood. This paper seeks to further explore the effects of sugar on cement through an examination of its effects on hydration as measured by calorimetry and loss on ignition, and microstructure as characterized by nitrogen adsorption. Furthermore, the interaction of sugar addition and curing temperature was explored, as heat is yet another variable that influences the rate of cement hydration.

2. Experimental methods

ASTM Type I Portland cement pastes examined in this study had a water-to-cement ratio (w/c) of 0.45. In those samples containing sugar, table sugar (U.S. Sugar), 1% by weight of cement, was dissolved in the water prior to mixing.

Isothermal calorimetry was used to examine the rate of heat evolution over time at temperatures of 20 and 40 °C. Pastes were mixed by hand in 10 g (cement weight) batches for 3 min and experiments were done on 1 g (paste weight) samples using a differential scanning calorimeter (Hart Scientific, model 5008A). While all other experiments presented in this paper were done with Cement A (Table 1), Cements A and B were used for the calorimetry studies. Cement B was used because of difficulty distinguishing between the peaks for calcium aluminate and calcium silicates in the neat pastes made with Cement A.

Nitrogen adsorption and desorption were used to determine surface area and pore volume. Batches were small (10–200 g cement), and mixing was done by hand for 5 min with a stainless-steel spatula. Samples were cast in polystyrene vials (25 mm diameter, 50 mm height), sealed in airtight polyethylene containers (100 ml), and placed in 20, 30, and 40 °C waterbaths for the first 24 h. The sample containers were then filled with limewater, sealed, and returned to the baths for the duration of the curing period, 1–270 days.

After the specified hydration time, specimens were removed from the vials and ground to particle sizes in the range of 600 μm (#30 sieve) to 1180 μm (#16 sieve). These samples were then D-dried for 14 ± 1 days. The D-drying apparatus was set up according to the method of Copeland and Hayes [13], 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; samples were tested immediately

Table 1
Properties of Type I Portland cement

Phase	Cement A (wt.%)	Cement B (wt.%)
SiO_2	20.79	21.4
Al_2O_3	5.31	4.6
Fe_2O_3	2.25	2.7
CaO	63.54	65.8
MgO	3.72	1.7
SO_3	2.84	2.4
C_3S	54	64
C_2S	19	–
C_3A	10	8
C_4AF	7	–
Properties		
Loss on ignition	1.09	1.2
Insoluble residue	0.1	0.35
Free lime	–	0.92
Sodium equivalent of alkalis	0.51	0.48
Blaine fineness (m^2/kg)	368	372

after drying. Particles smaller than 600 μm were used for loss-on-ignition testing, in order to determine degree of hydration (α) for each sample.

Nitrogen adsorption and desorption tests were done using a Coulter Omnisorp 360 (Coulter, Hialeah, FL). Surface area was calculated using the Brunauer, Emmett, and Teller (BET) method of analysis [14], over a relative pressure range of 0.05–0.25 on the adsorption isotherm. Total pore volume and pore size distribution were calculated by the Barrett, Joyner, and Hallenda (BJH) method [15] using data from the desorption isotherm. This technique only measures pores with radii between 1 and 40 nm.

X-ray diffraction was used to determine the phases present in selected samples. Specimens were ground to particle sizes of less than 300 μm (#50 sieve) and D-dried. Samples were then mixed with an internal standard, anatase (TiO_2), in a ratio of 5:1 by weight, using a mortar and pestle. The testing parameters were 40 kV, 15 mA, Cu-Kα radiation (0.1542 nm), 0.05° 2θ step size, with 3 s per step (Phillips diffractometer).

3. Results and discussion

3.1. Hydration

Addition of 1% sugar to cement pastes cured at 20 °C retards hydration for more than 3 months (Fig. 1). Increasing the temperature of curing greatly shortens the retardation period. It is interesting to note that the shapes of the curves are similar for the different curing temperatures. Most of the samples discussed in this paper, both control and sugar-containing pastes, were cured at 40 °C in order to facilitate testing.

A comparison of the progression of degree of hydration with time for samples cured at 40 °C is shown in Fig. 2 (each point shown is the average of three or more samples; standard deviations ≅ 0.02). It is interesting to note that while sugar delays hydration for several days, once these

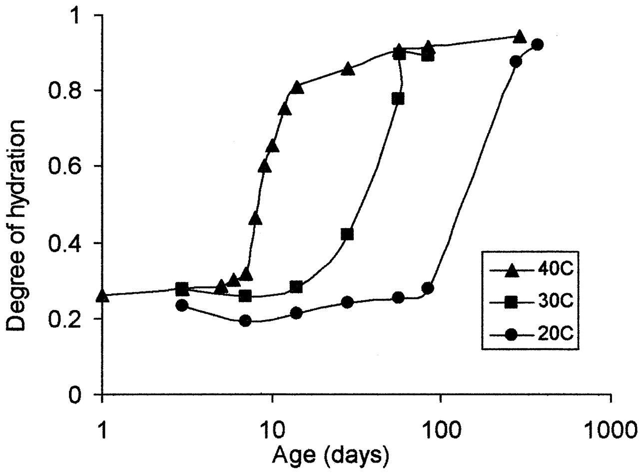

Fig. 1. Effect of curing temperature on the degree of hydration of cement pastes containing 1% sugar.

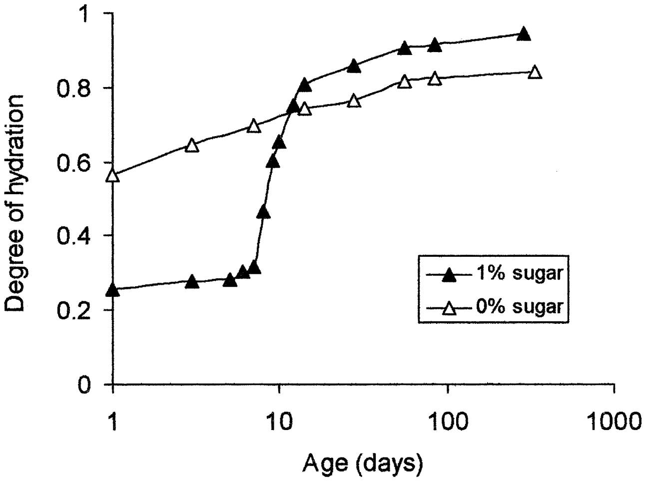

Fig. 2. Effect of 1% sugar on the degree of hydration of cement pastes cured at 40 °C.

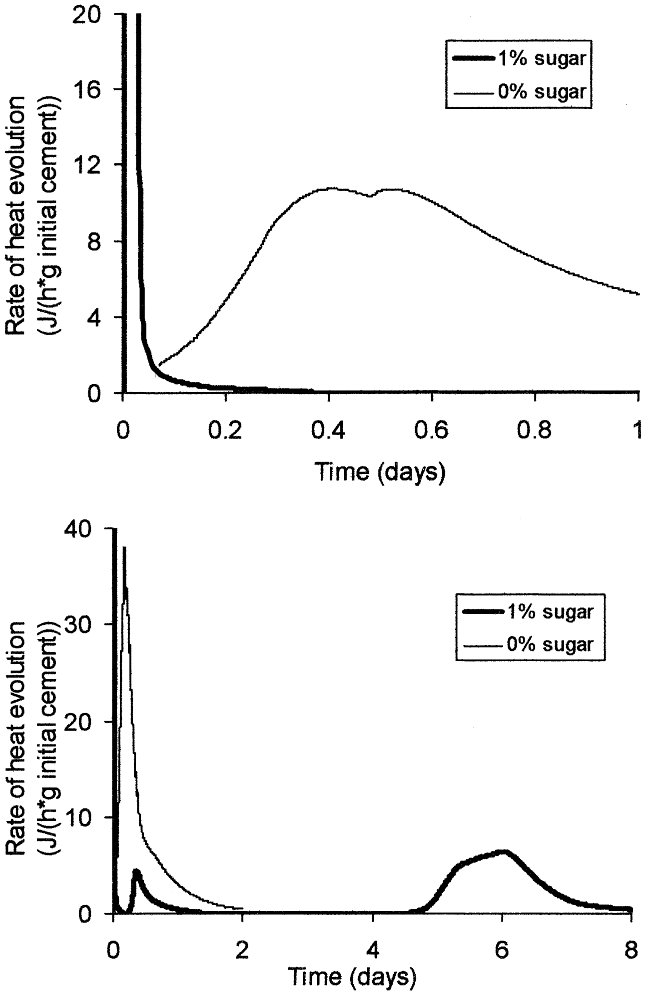

Fig. 3. Effect of 1% sugar on the rate of heat evolution of Cement B pastes: (a) 20 °C, (b) 40 °C.

samples react, they soon surpass the control. The exact age at which sugar-containing samples start reacting quickly at 40 °C varies between 7 and 10 days.

Isothermal calorimetry results at 20 and 40 °C are shown in Fig. 3 (Cement B). During hydration at 20 °C (Fig. 3a), the addition of sugar results in no peaks in the rate of heat evolution during the first 10 days aside from the initial dissolution of ions. Although the samples were tested for 10 days, results are only plotted to 1 day for clarity. Therefore, sugar retards hydration of all phases at 20 °C.

Isothermal calorimetry at 40 °C (Fig. 3b) shows two peaks with a very wide separation between them for the sugar-containing paste. The first peak occurs at the same time as that of the control paste, although the control paste peak is much higher. It is possible that one of these peaks corresponds to the hydration of calcium silicates and the other to calcium aluminates. Perhaps hydration of one of these phases is not significantly retarded by the addition of sugar at 40 °C. Alternatively, calcium-silicate and/or calcium-aluminate phases are partially hydrating during the first peak and the process is interrupted and continued later. As discussed later, X-ray diffraction was used for further examination of these questions.

It should again be noted that Cement B was used for the calorimetry studies in Fig. 3a and b, while that used for all other studies is Cement A. When Cement A is used, the wide separation between the peaks is also observed for sugar-containing pastes, but the heights and times of the peaks are slightly different (Fig. 4). The first peak is earlier and shorter for Cement B, while the second peak is earlier and taller for the Cement A. This difference is likely due to compositional differences (Table 1).

It is useful to compare the calorimetry data from Fig. 3 to the degree of hydration data in Fig. 2. The rate of heat evolution for the control paste (40 °C) tails off at 2 days; the degree of hydration at this point is approximately 0.6. The rate of heat evolution for the sugar-containing paste tails off between 6 and 8 days; the degree of hydration for samples of this age is also approximately 0.6. Furthermore, the areas under the curves in Fig. 3b are identical, 10.8 J day/(h·g initial cement). Therefore, one can say that the results from calorimetry and loss-on-ignition experiments concur.

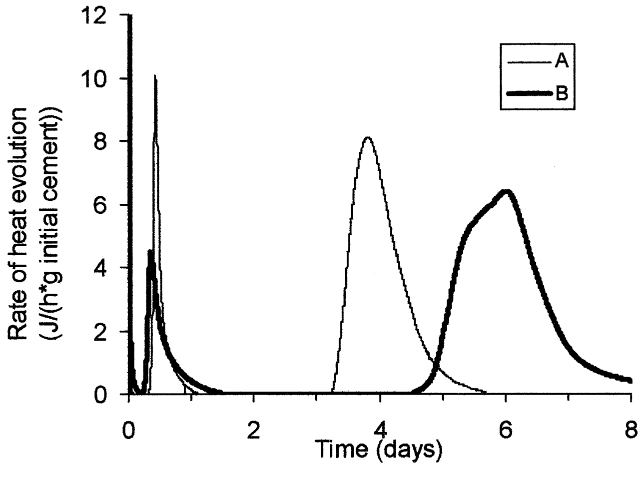

Fig. 4. Effect of 1% sugar on the rate of heat evolution of cement pastes at 40 °C (Cements A and B).

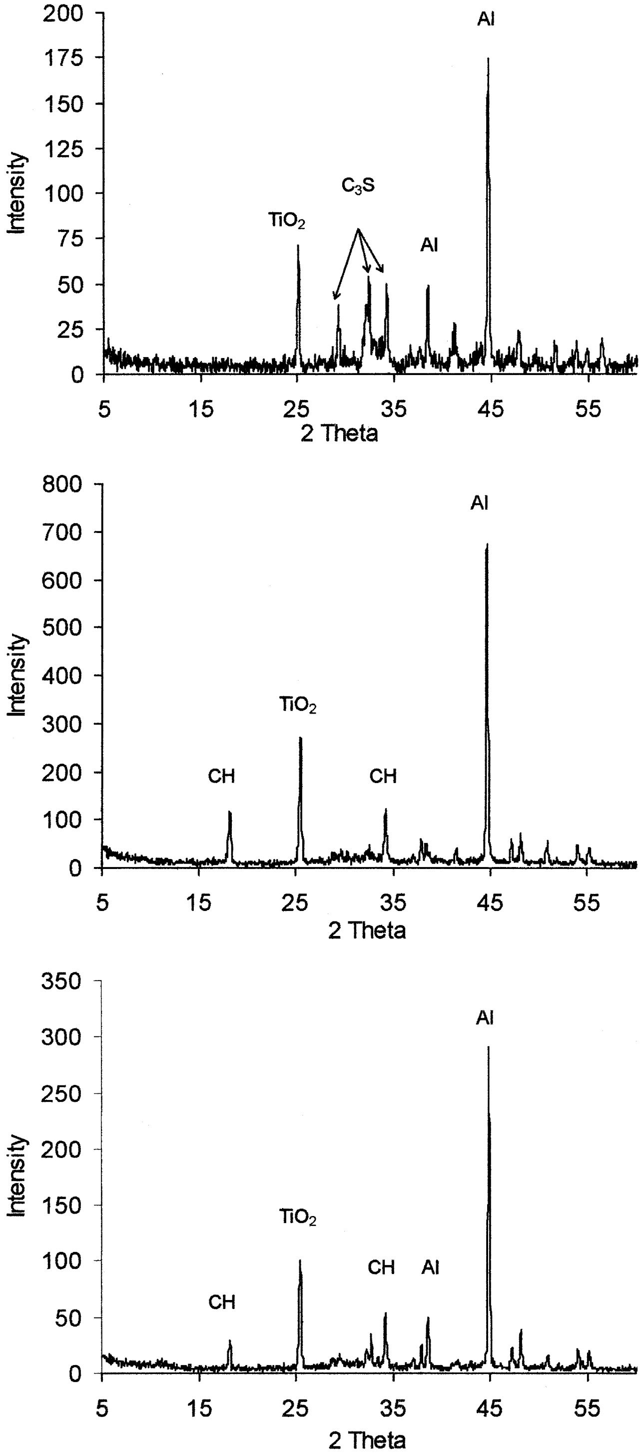

Fig. 5. X-ray diffraction data for cement pastes cured at 40 °C; unlabeled, small peaks correspond to C_3S, C_2S, and TiO_2 (internal standard): (a) 1% sugar, 3-day-old sample; (b) 1% sugar, 12-day-old sample; (c) no sugar, 7-day-old sample.

3.2. X-ray diffraction

X-ray diffraction analysis was performed in order to see if one phase was not retarded by sugar at 40 °C. The results for a 3-day-old sugar-containing sample cured at 40 °C are shown in Fig. 5a. The largest peaks correspond to the anatase internal standard, aluminum sample holder, and unhydrated C_3S. Results for a 12-day-old sample are shown in Fig. 5b. Large CH peaks are apparent, along with the anatase and aluminum. For comparison purposes, Fig. 5c shows an X-ray diffractogram for a 7-day-old paste without sugar, cured at 40 °C, with the same degree of hydration as the sample in Fig. 5b.

The striking difference between Fig. 5a and b is that there is absolutely no evidence of CH in the 3-day-old sample. The presence of CH after 12 days but not after 3 days points to calcium-silicate hydration being retarded by the addition of sugar. The data, unfortunately, cannot definitively show whether or not calcium-aluminate hydration is retarded because of insufficient instrument sensitivity. Any changes in the amounts of unhydrated and hydrated aluminates cannot be detected in either sample. Furthermore, if a small portion of the calcium-silicate phases hydrated (the first peak in Fig. 3b), it is possible that it would be undetectable. Therefore, X-ray diffraction results are inconclusive about the retardation of aluminate hydration.

3.3. Surface area and porosity

The effects of sugar on the surface area of cement pastes cured at 40 °C are shown in Fig. 6 (each point shown is the average of three or more samples; standard deviations ≅ 3.5). The youngest control samples tested were 1 day old with degrees of hydration of approximately 0.55. As many of the sugar-containing samples have degrees of hydration of 0.3, these cannot be compared to controls. In the degree of hydration region of 0.55–0.80, it is clear that sugar significantly increases the surface area. At degrees of hydration greater than 0.80, the surface areas are similar for the two types of samples. This could be due to space limitations. Once the available space is consumed, the formation of further products cannot increase the surface area [16]. The large scatter in older sugar samples is most likely caused by variations in the drying process. This is consistent with similar studies showing that the higher the surface area, the higher the scatter [16].

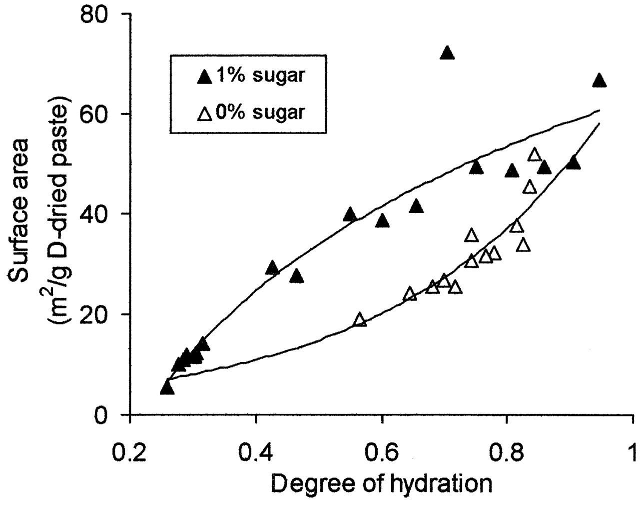

Fig. 6. Effect of 1% sugar on surface area development of cement pastes cured at 40 °C.

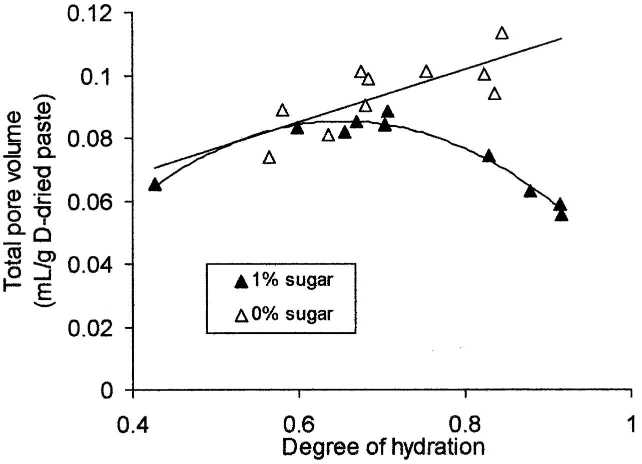

Fig. 7. Effect of 1% sugar on the total pore volume available to nitrogen of cement pastes cured at 40 °C (1–40 nm pore radius range).

Total pore volumes available to nitrogen (1–40 nm) are shown in Fig. 7. While the total porosities are comparable in the degree of hydration region of 0.40–0.70, those of the sugar samples decrease significantly at higher degrees of hydration. This is interesting as the total porosity measured by nitrogen (gel porosity) typically increases with the amount of C-S-H present, and thus with the degree of hydration. Representative pore size distributions are given in Fig. 8. The samples in Fig. 8 with $\alpha = 0.65$ are from the region where sugar produces a higher surface area yet similar total pore volume. The higher volume in the smallest pore radius range (1–2 nm) of the sugar sample accounts for the higher surface area. The pores in this size range have a large surface-to-volume ratio and there is a strong correlation between surface area and the volume of pores in this size range [17]. The samples with $\alpha = 0.83$ in Fig. 8 have similar surface areas and degrees of hydration, but very different total pore volumes. The porosity in the smallest pore radius range (1–2 nm) is similar enough for these samples to have equivalent surface areas.

The drop in total pore volume of the sugar samples with age with no corresponding decrease in surface area is due to a decrease in the volume of mid-sized pores (4–20 nm radius range). Pores of this size have smaller surface-to-volume ratios, thus contributing less to the surface area than the small pores. The decrease in volume of pores from 4 to 20 nm is perhaps due to a coarsening process. Porous systems commonly coarsen with age in

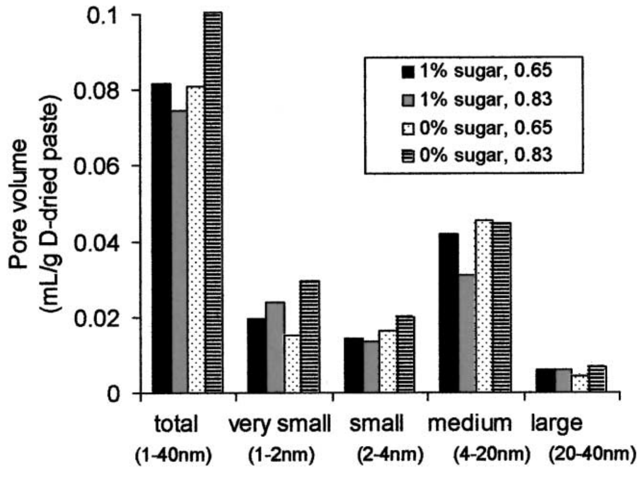

Fig. 8. Effect of 1% sugar on the pore size distribution of cement pastes cured at 40 °C (α = 0.65, 0.83; 1% sugar samples = 10, 14 days old; 0% sugar samples = 3, 56 days old).

order to reduce surface energy. This coarsening does not decrease the surface area, however, since it is only occurring in relatively large pores.

3.4. Proposed mechanism

It is difficult to theorize why sugar increases the surface area of cement pastes because the retardation mechanisms are so poorly understood. Combining the data gained from the hydration and microstructure studies presented in this paper with theories in the literature, the following explanation is proposed.

It is generally assumed that sugar increases the initial dissolution of ions and poisons hydration products or hydrating cement particles, or both. It is possible that these factors increase the number of CH and C-S-H nucleation sites, as will be explained here. Hydration products are not allowed to grow and the hydrating particles cannot react. Yet, there are high concentrations of ions in the pore solution because of the increased initial dissolution of cement grains. These ions nucleate independently (homogeneous nucleation) rather than attaching to the existing poisoned sites (heterogeneous nucleation). These sites are then poisoned in turn, and new ones form. In Fig. 2, there appears to be a retardation period that ends suddenly, as if a barrier is suddenly being overcome and reaction can proceed. This will be called the “retardation barrier.” The retardation barrier may be broken when the number of nucleation sites is greater than the amount of sugar present, and future sites are no longer being poisoned. The unusually rapid progression of hydration from this point onward (Fig. 2) may be caused by the excess of ions in solution finally being able to hydrate on existing sites (heterogeneous nucleation requires less energy and thus is faster than homogeneous nucleation).

A higher surface area C-S-H forms preferentially in sugar-retarded pastes because it is less limited by space. During normal cement hydration, the cement particles react quickly with water, forming a dense rim of C-S-H. Further hydration takes place when ions diffuse through this rim, nucleate, and grow in the water-filled pore space. The types of C-S-H that form during the different stages of this process have been given many names including inner and outer product [18]; Types I–IV [19]; early, middle, and late products [20]; and phenograin and groundmass [21]. Jennings and Tennis [22,23] have recently proposed that the different types of C-S-H have different densities and different surface areas available to nitrogen. These two types of C-S-H they called HD (high density) and LD (low density). Jennings [22] proposed that the C-S-H forming in the open pore space is predominantly LD (high nitrogen surface area) and C-S-H forming near the hydrating cement particle is HD (low nitrogen surface area). In the sugar-retarded samples, the high initial dissolution and long retardation period provide for the diffusion of many ions far away from the hydrating particle. When the effects of poisoning are overcome, these ions react to immediately form less dense products in the open pore space, resulting in a higher surface area C-S-H.

3.5. Effect of temperature

The influence of curing temperature on the hydration of pastes containing sugar is shown in Fig. 1. Surface area results are shown in Fig. 9. Temperature does not appear to influence the surface area of sugar-containing pastes with equivalent degrees of hydration.

Extending the mechanism proposed in Section 3.4, increasing the temperature decreases the time required to break the retardation barrier (Fig. 1). Verbeck and Helmuth [24] proposed that increasing temperature typically increases the rate of chemical reactions more than the rate of diffusion, resulting in denser C-S-H with higher temperatures. Increasing temperature also causes CH to nucleate

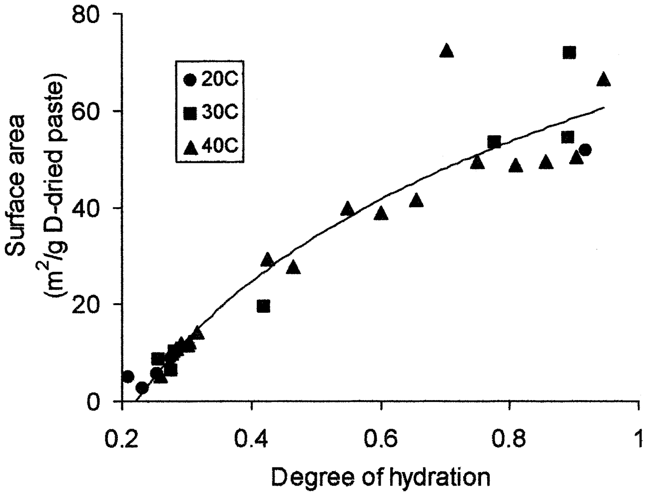

Fig. 9. Effect of curing temperature on the surface area of cement pastes containing 1% sugar.

more quickly, while decreasing the size and increasing the number of CH nuclei [25]. Given the retardation theory discussed above, increasing curing temperature decreases the retardation period because CH nuclei are forming faster. The retardation barrier is overcome more rapidly. After the retardation barrier is broken, the reaction is diffusion controlled, and is thus not influenced as much by temperature. Surface areas are unchanged by temperature because the same total number of nucleation sites is required to overcome the sugar poisoning, and the reaction progress (diffusion controlled) is similar from that point forward.

4. Summary and conclusions

Altering the hydration of cement paste by simultaneously adding 1% sugar and increasing the curing temperature induces the following effects:

1. Sugar retards cement hydration at each temperature examined and the period of retardation is shortened as the curing temperature is increased.
2. Sugar increases the surface area as measured by nitrogen of pastes cured at 40 °C in the degree of hydration range of 0.55–0.80.
3. While curing temperature changes the rate of hydration of sugar-containing pastes, it does not alter the surface area of pastes for a given degree of hydration.

Although this new information fails to clarify whether or not sugar is adsorbing to hydrating phases, hydration products, or both, it does show that sugar has a more profound effect on cement paste than merely stalling the hydration process. The addition of sugar fundamentally changes the microstructure of C-S-H, altering the formation process, surface area, and perhaps the density of this intricate phase.

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