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Estimation of C-S-H content in a blended cement paste using water adsorption

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Abstract

A new technique for measuring the quantity of calcium silicate hydrate (C-S-H) in hydrated, blended cement pastes containing class F fly ash, ground granulated blast furnace slag, or silica fume is based on water adsorption. The rate of C-S-H formation was determined to be logarithmic in all pastes. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Calcium silicate hydrate (C-S-H); Characterization; Hydration products; Microstructure

1. Introduction

The research reported here is part of a larger study to establish quantitative relationships between the microstructure and drying shrinkage of cement paste. The strategy was to vary the composition of cement paste through the addition of mineral admixtures, which alters the microstructure, then correlate this with drying shrinkage. A major problem, however, has been to measure the quantity of calcium silicate hydrate (C-S-H) in a paste containing glassy reactive additives.

The quantity of C-S-H can be determined easily in Portland cement paste using standard indirect techniques, such as loss on ignition or quantitative X-ray analysis of unreacted cement and calcium hydroxide. C-S-H is very difficult to measure directly due to both a lack of crystallinity and an indefinite composition. The pozzolanic reaction between calcium hydroxide and mineral admixture (typically a glassy or partly glassy phase, which cannot be quantified by X-ray diffraction) produces C-S-H, which confounds indirect techniques because it generates C-S-H and consumes unknown amounts of calcium. In addition, the calcium/silicon (C/S) ratio of the C-S-H may be lower than it is in neat paste in the presence of mineral admixtures. Given these difficulties, a new method had to be developed using a simple yet physically meaningful approach. This paper describes how to measure C-S-H directly and reports some results on how admixtures influence formation of C-S-

Hydration Time (days)	1	3	7	14	28	60	90	120
OPC	x	x	x	x	x	x	x	x
BFS								
25%	x	x	x	x	x	x	x	x
50%	x	x	x	x	x	x	x	x
75%	x	x	x	x	x	x	x	x
100%			x	x	x	x	x	x
FA								
7.5%	x	x	x	x	x	x	x	x
15%	x	x	x	x	x	x	x	x
30%	x	x	x	x	x	x	x	x
SF								
10%	x	x	x	x	x		x	x
20%	x	x	x	x	x	x		x

Fig. 1. The independent variables in the experimental matrix were composition and hydration time. Compositions were chosen based upon experimental limitations. OPC = ordinary Portland cement, BFS = ground granulated blast furnace slag, FA = fly ash, and SF = silica fume.

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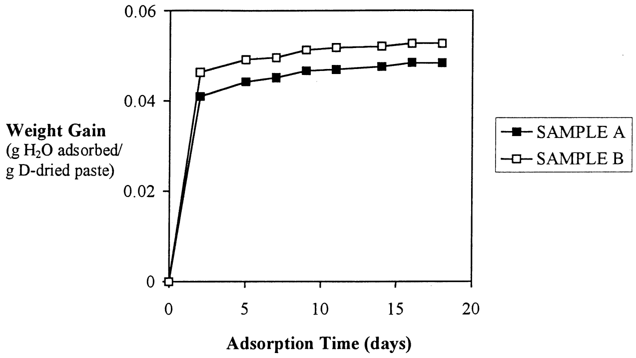


Fig. 2. Weight gain during rehydration at 20% RH for two samples of Portland cement paste that were hydrated at 100% RH for 21 days, D-dried for at least 2 weeks, and dried at 105°C for 48 h. Final values were 0.0484 and 0.0528 g H_2O/g D-dried paste for samples A and B, respectively.

H. The experimental matrix used in the overall study is shown in Fig. 1.

2. Strategy

C-S-H gel has a surface area per unit volume (or unit mass) at least an order of magnitude greater than any other component in hardened Portland cement paste. Since mass and volume are nearly equivalent, parts of these will discuss both. Specific volume is unusual, but it is important when analyzing microstructure. If a unit volume of dried C-S-H adsorbs a specific amount of water when equilibrated at a specific relative humidity (RH) and all dried C-S-H is equally accessible to water, then the quantity of C-S-H in a blended paste can be deduced. To do this, the amount of adsorbed water per unit volume of C-S-H must be determined. To test this hypothesis, water adsorption experiments were performed on pure tricalcium silicate pastes of known C-S-H contents.

A protocol had to be developed to measure the weight difference between samples dried to an equilibrium point and that of the resaturated paste at a particular RH. Samples were D-dried for at least 14 days, weighed, and then oven-dried at 105°C for 48 h. The RH at which the samples were resaturated was chosen with the following reasoning.

Table 1
Procedure for sample preparation and measurement of C-S-H content

(A) Crush cement paste sample.
(B) Sieve crushed particles using nos. 30 and 50 sieves to obtain particles with an approximate size range of 600–300 μm.
(C) Immerse 2 g of crushed particles in 50 ml of isopropanol for 4 days.
(D) Remove particles from alcohol, pat dry, transfer to a glass vial, and D-dry for a minimum of 2 weeks.
(E) Weigh sample.
(F) Oven-dry at 105°C for 48 h.
(G) Weigh sample.
(H) Allow 2 minutes to cool, then insert into 20% RH chamber.
(I) Weigh sample periodically until it ceases to gain weight.
(J) Use the value of adsorbed water per gram of D-dried paste to determine the C-S-H content, i.e. divide the adsorbed water per gram of paste by the calibration value 260-mg H_2O/cm^3 $C_{3.4}S_2H_3$ as in Eq. (1).

Table 2
Water adsorption at 20% RH for 10 C_3S pastes of w/c ratio 0.5 and different degrees of hydration

Hydration time (days)	mg H_2O adsorbed/g D-dried paste	g $C_{3.4}S_2H_3$/g D-dried paste	mg H_2O adsorbed/g $C_{3.4}S_2H_3$
1	22.6	0.23	98.0
1	26.6	0.23	116
4	28.5	0.33	89.1
4	34.7	0.33	108
7	39.8	0.38	105
7	33.3	0.38	87.6
14	47.1	0.44	117
14	42.0	0.44	95.5
28	42.5	0.47	90.5
60	54.4	0.56	97.1
		average	100
		standard deviation	10.7

The relationship between the amount of adsorbed water and the RH is a nonlinear function below about 11% RH. This is because less than the equivalent of a full monolayer is present. Therefore, adsorbed water would not be proportional to the amount of C-S-H.

Multilayer adsorption starts before the monolayer is complete, but enough water is adsorbed by 11% RH to form a monolayer if it were evenly distributed [1]. Multilayers continue to adsorb water between 11% and about 50% RH. For this range, a linear relationship exists between the amount of water adsorbed and the partial pressure. Above about 50% RH, water begins to condense in the pores and a nonlinear relationship is observed.

A value within the multilayer adsorption region seemed promising. A value within 11–50% RH region needed to be chosen. A relatively high value in this region would reduce error because larger weight gains could be measured, but at the same time, a relatively low value was desirable to avoid condensation. A RH of 20% was chosen because it should maximize the amount of water that could be adsorbed by the C-S-H without excessive condensation occurring within the gel pores [2].

Table 3
Calcium hydroxide content for hydrated C_3S pastes

Hydration time (days)	g CH/g D-dried paste
1	0.0535
4	0.1359
7	0.1770
14	0.2058
28	0.2470
60	0.2923[a]

[a] This value was rather high, but it was confirmed with a second test. Some free lime may have been present in the C_3S.

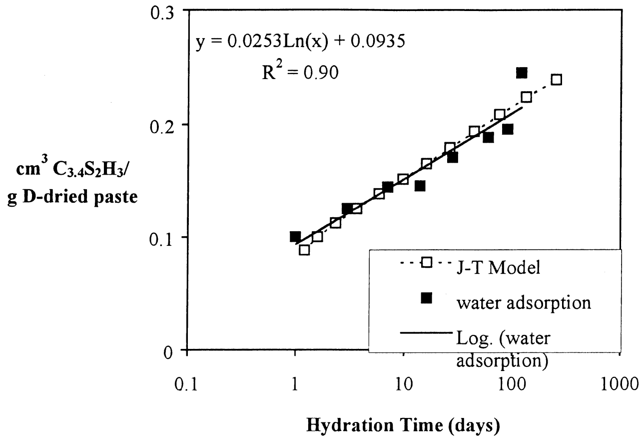
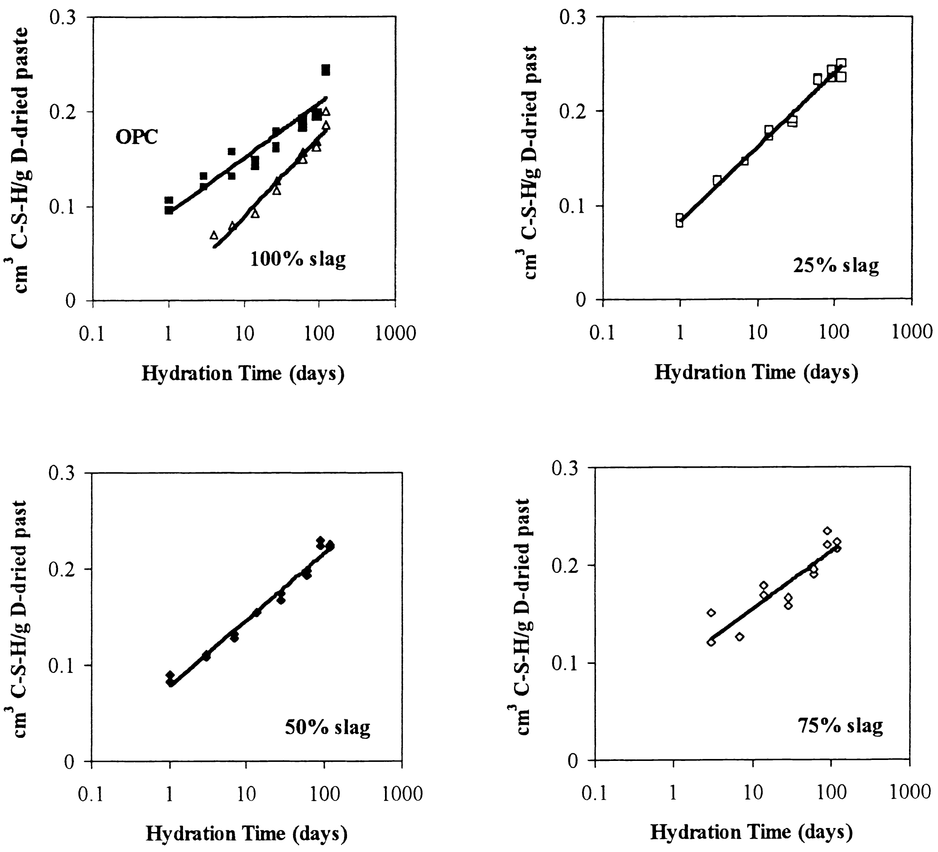


Fig. 3. A comparison between the volume of $C_{3.4}S_2H_3$ (excluding gel pores) in D-dried Portland cement paste measured using water adsorption and calculated using the J–T hydration model. Each datum in the water adsorption set is an average of two points. The equation for the logarithmic fit to the water adsorption data is provided.

3. Sample preparation and measurement

The RH was monitored using a hygrometer (Dickson, model THDX). A polycarbonate glove box was used as the chamber and a four-place digital balance was kept inside the box.

Since no salt solution is known to equilibrate at a RH of 20%, one was formulated using data from Young [3]. Saturated LiCl solution generates a partial vapor pressure of 11% RH at room temperature. Equilibrium at 20% RH was achieved by diluting a saturated LiCl solution; water was added to a large amount of saturated LiCl solution over time until the chamber equilibrated at 20% RH. A relatively large amount of solution was used (0.5 l) so that as the dried samples adsorbed water, the change in the concentration of the solution remained insignificant. Nitrogen gas was bubbled through the solution every other day for about 10 min to facilitate the transfer of water from the solution to the



OPC: y = 0.0253*Ln(t) + 0.0935; R^2 = 0.88
25 wt%: y = 0.0341*Ln(t) + 0.0844; R^2 = 0.99
50 wt%: y = 0.0300*Ln(t) + 0.0784; R^2 = 0.98
75 wt%: y = 0.0254*Ln(t) + 0.0973; R^2 = 0.82
100 wt%: y = 0.0368*Ln(t) + 0.0047; R^2 = 0.96

Fig. 4. Volume of C-S-H per gram D-dried paste vs. hydration time for blended slag pastes. R^2 values and equations for curve fits are given. The average sample-to-sample standard deviations were OPC = 5.2%, 25-wt.% slag = 2.3%, 50-wt.% slag = 2.1%, 75-wt.% slag = 5.3%, and 100-wt.% slag = 2.7%.

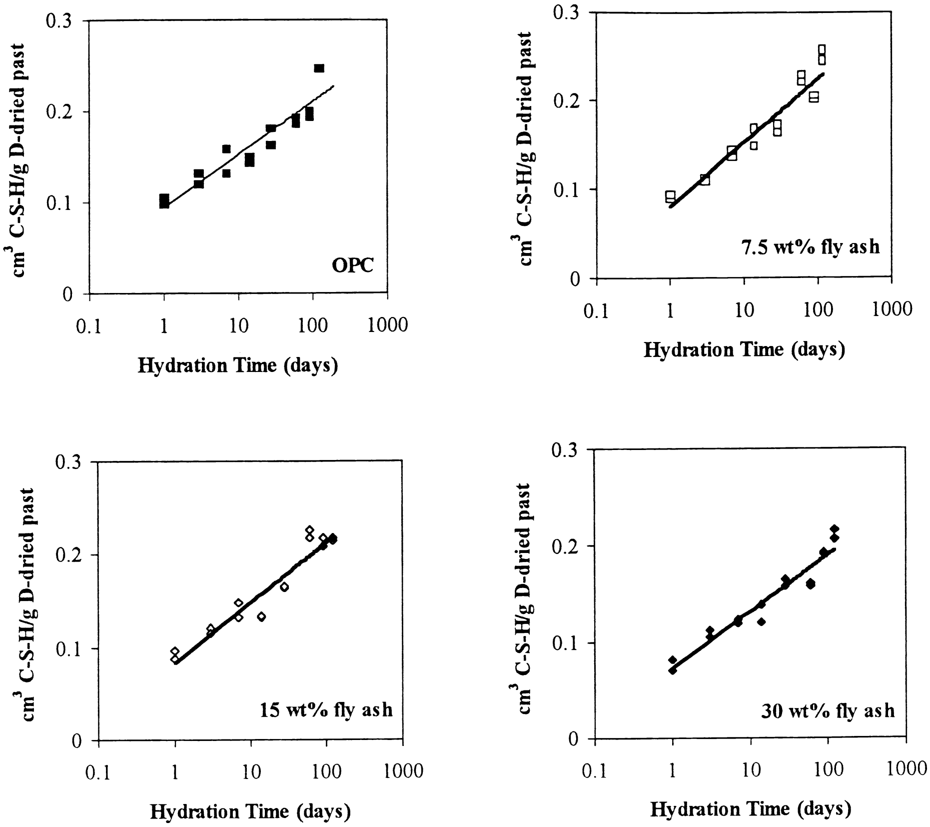
vapor phase and to keep the solution in equilibrium with the rest of the chamber. Both a continuous flow of nitrogen and continuous stirring of the air with a fan were found to be unnecessary. The RH never varied more than ± 1%.

An example of a weight gain curve is given in Fig. 2. Samples approached equilibrium very quickly during the first couple of days but then required between 14 and 16 days to fully equilibrate. Upon reaching full equilibrium, the total amount of water adsorbed for each sample was recorded. Two trials were performed for each sample and averaged. Error due to measurement of weight (± 0.0001 g) was below 3%.

3.1. Calibration of water adsorption using samples in which C-S-H content was measured by an independent technique

To calibrate the technique, the C-S-H contents for 10 C_3S pastes having different degrees of hydration were calculated. This was accomplished by determining the amount of calcium hydroxide in each sample using thermogravimetric analysis. Given that these samples were D-dried then oven-dried, the stoichiometry of the C-S-H was assumed to be $C_{3.4}S_2H_3$ [2]. The nonevaporable water not associated with calcium hydroxide was assumed to be associated with $C_{3.4}S_2H_3$. This is not the most accurate method of calculating the C-S-H content for these samples, but it was acceptable for our purposes. The amount of water adsorbed per gram of $C_{3.4}S_2H_3$ was calibrated for each of these pastes. The sample preparation procedure is given in Table 1, and the calibration value of 100-mg water adsorbed per gram of $C_{3.4}S_2H_3$ was determined by averaging the data in Table 2. Table 3 provides the calcium hydroxide data for these pastes.

The value 100-mg adsorbed water/g $C_{3.4}S_2H_3$ was converted to a volumetric value using a density of 2.6 g/cm^3 for solid $C_{3.4}S_2H_3$ [2]. The density of $C_{3.4}S_2H_3$ sits somewhere between 2.45 and 2.8 g/cm^3 [2]. The density 2.6 g/cm^3 was chosen here because it sits near the middle of the range, providing a conservative estimate, and also it provided the best fit to C-S-H content data generated by the Jennings–Tennis (J–T) model. Multiplying 100-mg adsorbed water/g



OPC: y = 0.0253*Ln(t) + 0.0935; $R^2 = 0.88$
7.5 wt%: y = 0.0313*Ln(t) + 0.0810; $R^2 = 0.92$
15 wt%: y = 0.0281*Ln(t) + 0.0840; $R^2 = 0.91$
30 wt%: y = 0.0254*Ln(t) + 0.0742; $R^2 = 0.93$

Fig. 5. Volume of C-S-H per gram D-dried paste vs. hydration time for blended fly ash pastes. R^2 values and equations for curve fits are given. The average sample-to-sample standard deviations were OPC = 5.2%, 7.5-wt.% fly ash = 3.6%, 15-wt.% fly ash = 3.4%, and 30-wt.% fly ash = 4.5%.

$C_{3.4}S_2H_3$ by 2.6 g/cm^3 produces the value 260-mg adsorbed water/cm^3 $C_{3.4}S_2H_3$, which was used to estimate the volume of solid C-S-H in D-dried cement paste according to:

$$\frac{\text{cm}^3\ C_{3.4}S_2H_3}{\text{g D} - \text{dried paste}} = \frac{\text{g } H_2O}{\text{g D} - \text{dried paste}}\ \frac{260 \text{ mg } H_2O}{\text{cm}^3\ C_{3.4}S_2H_3} \qquad (1)$$

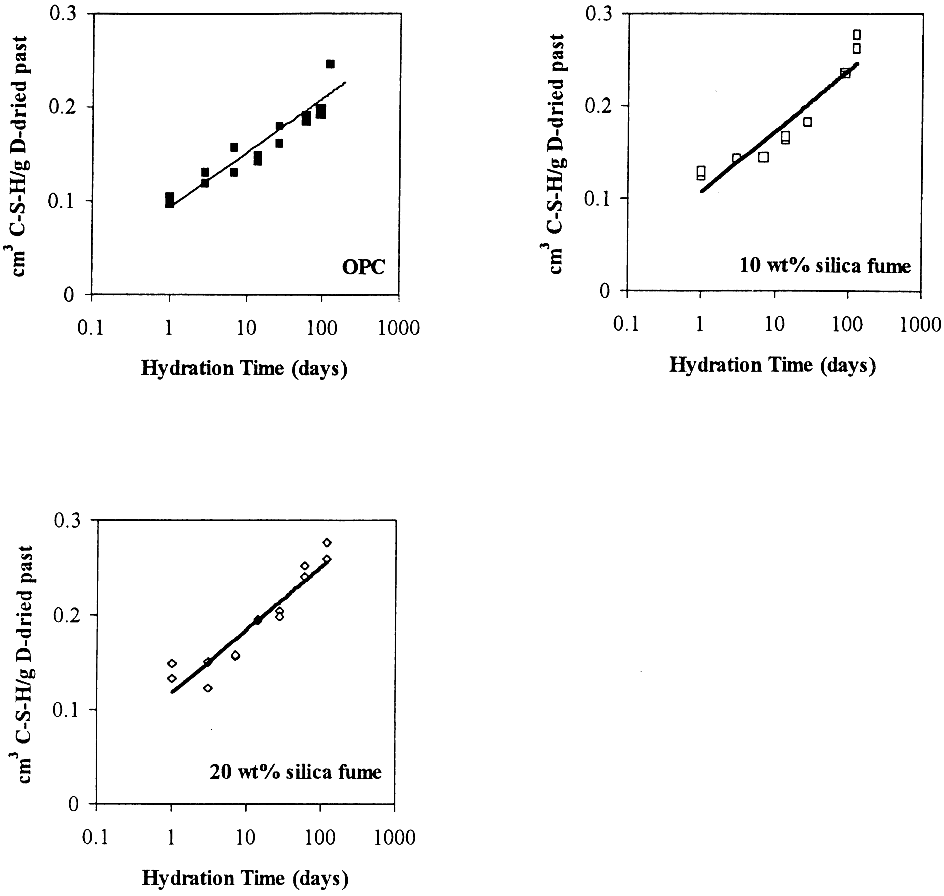
where g H_2O/g D-dried paste = the amount of water adsorbed by a dried cement paste upon readsorption at 20% RH. The C-S-H volume was normalized to g D-dried paste to be consistent with the literature and to compare values with calculations from the J–T model.

3.2. Validation of the water adsorption technique

The C-S-H content of the OPC paste determined via water adsorption was compared to values calculated using the J–T hydration model, which accounts for cement composition, w/c ratio, and degree of hydration [4]. As shown in Fig. 3, the water adsorption technique compared well with the model. The formation of C-S-H appears to have a logarithmic dependence with time beyond 1 day, indicating that it is diffusion controlled for these sample ages. The Avrami equation used in the J–T model approaches a diffusion-controlled rate with time (usually by the first 12–14 h), but this is only an approximation, which apparently is a reasonably good approximation.

4. Rate of C-S-H formation in blended cement pastes

In Eq. (1), the C-S-H content is calculated assuming the surface area of the C-S-H as seen by water is proportional to its volume. In cases where the amount of mineral admixture added to the paste is relatively high, the stoichiometry of the C-S-H may change. In cement pastes with relatively high mineral admixture contents, the C/S ratio could be much lower than 1.7 (approaching 1 in pure slag paste [5]). In



OPC: y = 0.0253*Ln(t) + 0.0935; R^2 = 0.88
10 wt%: y = 0.0285*Ln(t) + 0.1072; R^2 = 0.88
20 wt%: y = 0.0289*Ln(t) + 0.1185; R^2 = 0.89

Fig. 6. Volume of C-S-H per gram D-dried paste vs. hydration time for blended silica fume pastes. R^2 values and equations for curve fits are given. The average sample-to-sample standard deviations were OPC = 5.2%, 10-wt.% silica fume = 1.8%, and 20-wt.% silica fume = 4.7%.

these cases, we must assume that the theoretical density of the solid C-S-H does not vary much from the 2.6 g/cm^3 used to arrive at Eq. (1) and that the specific surface area does not change. We must also assume that the surface area/volume ratio of the solid C-S-H, i.e. the particle size of the C-S-H, does not change considerably. The assumptions must be checked in the future.

Figs. 4, 5, and 6 display the volume of C-S-H per gram of D-dried paste vs. hydration time for the blended cement pastes. The best logarithmic curve fit for each set of data is provided in each figure. The fits were good overall, most having an R^2 value of .90 or above. The average sample-to-sample standard deviation of replicate experiments was 5% or less.

Overall, the presence of admixtures appears to have an effect on the C-S-H formation rate as evidenced by the slopes of the curves (i.e. the coefficients in the equations). The rate of C-S-H formation as a function of time can be obtained for each data set by differentiating the curve with respect to time. For example (see Eqs. (2) and (3)), differentiation of the OPC curve from Fig. 4,

$$y = 0.0253 * \mathrm{Ln}(t) + 0.0935 \tag{2}$$

where y = C-S-H content and t = time, yields

$$\mathrm{d}y/\mathrm{d}t = 0.0253/t \tag{3}$$

The addition of a small amount of admixture increases the slopes over that of OPC paste and further addition decreases the slope, i.e. there appears to be a maximum in the slope at about 25-wt.% slag, 7.5-wt.% fly ash, and 10–20-wt.% silica fume. The cause for this behavior is unknown.

5. Conclusion

A technique is described for estimating the amount of C-S-H in cement paste. This appears to be applicable to blended cement pastes, for which the determination of C-S-H content is otherwise very difficult. This technique is most likely useful for experiments in which a high degree of accuracy is not required for studies that cover a large experimental matrix. Improvements to the technique, such as using a more accurate method to determine the C-S-H content of the C_3S calibration specimens or techniques that are more rapid, are possible. However, the technique provides values that are otherwise unobtainable. Variations in the C-S-H content of cement paste containing mineral admixtures were detected, but these variations were not large. The C-S-H content appeared to be a logarithmic function of time beyond 1 day in all cases. Beyond 1 day, the rate of C-S-H formation in blended cement paste was higher than that for OPC paste when moderate amounts of mineral admixture were added.

Acknowledgments

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