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An In-Situ Raman Spectroscopy Study of the Hydration of Tricalcium Silicate

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Raman spectroscopy has been used to study the hydration kinetics of tricalcium silicate (C_3S). The progress of the reaction was followed by two different methods: the first one is based on measurement of the intensity of characteristic C_3S Raman bands compared with that of an internal standard Raman peak (TiO_2); the second one consists in measuring the relative intensity of Raman peaks associated with C_3S and calcium hydroxide. These two concordant data sets show that a change in the hydration mechanism occurs at about 13 hours, and enable the kinetic parameters associated with the two hydration processes to be derived. ADVANCED CEMENT BASED MATERIALS 1995, 2, 15–20

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In his pioneering work, Bensted showed that Raman spectroscopy is of great value to quantitatively investigate the hydration behavior of calcium silicates in situ, in particular, tricalcium silicate (C_3S; in the following, C ≡ CaO, S ≡ SiO_2, H ≡ H_2O) [1,2]. The experimental set-up is particularly convenient: no particular preparation of the sample is needed, and the hydration rate can be determined using a single sample over the whole aging period studied. In Bensted's work, the degree of C_3S hydration was calculated from the decrease in intensity of the principal C_3S Raman peak (no internal standard was used) [2]. A ±10% experimental accuracy was obtained for approximately 10 minute scanning times over the spectrum range of this peak [1]. In this article, we show that using an up-to-date Raman spectrometer equipped with adequate software allows us to determine the C_3S degree of hydration with an improved accuracy for scanning times an order of magnitude lower and a scanned spectrum range an order of magnitude wider. With such improved accuracy, interesting phenomena may be evidenced.

Experimental Procedure

C_3S was prepared by successive heatings of a mixture of finely divided silica (Aerosil 200 from Degussa) and calcium carbonate (from Prolabo) until no other X-ray detectable phases were present. The final heating was at 1600°C for 4 hours. Powder X-ray diffraction showed C_3S to exhibit the triclinic crystal structure (T_1) as expected [3]. As prepared, C_3S was then ground to a Blaine area equal to 4100 cm^2/g. A water:cement ratio of 0.40 by weight was used for the hydration reaction study.

To prevent contamination from atmospheric carbon dioxide (leading to the formation of $CaCO_3$), the resulting slurry was cast and stored in about 10-g amounts in airtight quartz test tubes, which were also used for the measurements as sample holders. Although cement is normally hydrated in air, normal concrete usage means that the quantities of materials handled ensure a much lower surface:volume ratio than actually exists with small laboratory samples. Any laboratory comparison between cements is thus more reliable when the hydrating pastes are protected from the air. Several samples were prepared to evaluate the reproducibility of the results. After casting, the tubes were placed in a cure bath set at 20°C, from which they were removed just before analysis.

Unpolarized macro-Raman spectra were recorded on a multichannel Raman spectrophotometer from Dilor over the range of 100 to 1200 cm^{-1}. Exciting light was chosen as the green line (514.5 nm) of an ionized argon laser. Standard conditions for spectra recording were typically 20 accumulations of 2 seconds each, for an incident laser power of 400 mW. To ensure that there was no thermal effect under the laser beam leading to an increase in the rate of hydration, we have recorded,

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at a given aging time, some Raman spectra under different laser power (from 20 to 600 mW) on the same sample. Results give the same advancement of the reaction, showing that the amount of heat transferred to the sample is negligible and has no effect on reaction kinetics. In the intervals between measurements, the tubes were replaced in the bath at 20°C.

In one series of experiments, Raman peak intensities were calibrated using TiO_2 (from Prolabo; grain size below 10 μm) as an internal standard mixed with C_3S at a dose rate of 0.1 weight percent. At such a rate, TiO_2 addition cannot affect C_3S hydration [4]. In another set of experiments, calibration was done from mixing curves, as discussed below, using calcium hydroxide (CH) from Aldrich.

In Raman spectrometry, the incident beam only penetrates in the outermost layer of the sample, at a depth difficult to evaluate. Therefore, to ensure that there is no surface effect giving different results between the outermost layer and the bulk of the paste, we broke three quartz test tubes after 0.5, 1, and 10 days and recorded Raman spectra on the surface in contact with the sample holder and in the bulk of the sample. Results were found to be identical, showing that expected surface effects such as interaction with the quartz tube, preferred orientation of CH at the glass surface, or cement grains packing modification, do not significantly affect the obtained results. The results presented in this work can therefore be regarded as giving information about what happens in the bulk paste.

Results

During the hydration of the C_3S phase, monomeric silicate units polymerize to form a nearly amorphous calcium hydrosilicate (C-S-H) gel, along with crystalline CH. The calcium hydrosilicate gel has a variable composition [5] characterized by its calcium:silicon ratio, labeled x, and its water content, labeled y. The idealized overall reaction of hydration can be written as follows:

$$C_3S + (3 - x + y)\,H \rightarrow C_xSH_y + (3 - x)\,CH \quad (1)$$

where y depends on the water:cement ratio and on the hydrometry conditions. x was generally believed to vary with both time and space. Depending on the analysis method used, the mean value of x in mature pastes was found to be in the range of 1.4 to 2.0 [5]. Provided that the composition of C-S-H is taken as $C_{1.7}SH_{4.0}$ for well-hydrated pastes in the nearly saturated condition, the calculated volume change following hydration was found to agree with the experiment [6]. A minimum water:cement ratio of 0.42 was then required for complete hydration [6]. A recent elaborate analysis of Portland cement pastes cured in nearly saturated conditions, using transmission electron microscopy [7], has confirmed C:S local variations (at a submicrometer scale) and the space-averaged value of about 1.7 (1.75 ± 0.10), but on the other hand has shown no C:S systematic variation with time.

Setting $x = 1.7$ and $y = 4.0$, eq 1 becomes:

$$C_3S + 5.3\,H \rightarrow C_{1.7}SH_{4.0} + 1.3\,CH. \quad (2)$$

Such a reaction stoichiometry, at any rate of hydration, was used by Bentz et al. [8] in a recent computer modeling of the interfacial zone in concrete, which was verified by comparing the model with real concretes. Since the water:cement ratio used in this work is 0.40 and the samples are kept in sealed containers (i.e., under nearly saturated conditions), we also have assumed the hydration equation to be given by eq 2 at any time later than the induction period.

Raman Spectra of Pure C_3S, Synthetic C-S-H, and CH

The Raman spectrum of the pure triclinic C_3S sample possesses three different groups of peaks located at low, mid, and high frequency, respectively (Figure 1). The high frequency region extends from 809 to 936 cm^{-1} and exhibits two strong, two medium, and four weak bands. The line of highest intensity is at 840 cm^{-1}, which is characteristic of C_3S. The lines at 809 and 880 cm^{-1} appear as satellites. Four other satellites of smaller intensity can be distinguished at higher frequencies. These high frequency modes (>800 cm^{-1}) are usually assigned to Si – O stretching motions within tetrahedral SiO_4 groups [9–11]. The mid frequency region extends from 518 to 542 cm^{-1}. This group of vibrational modes has been assigned to

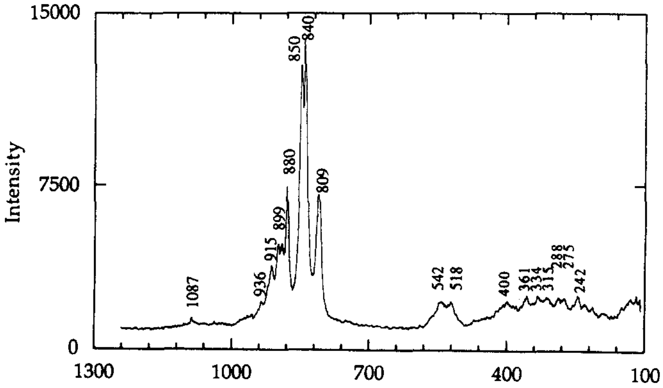

FIGURE 1. Room temperature Raman spectrum of unhydrated C_3S.

O – Si – O bending modes [10]. Finally, the low frequency region extends at frequencies lower than 400 cm^{-1}. No information is available on the attribution of these low frequency modes. The four main lines at 809, 840, 850, and 880 cm^{-1} were used to identify the C_3S phase during the hydration reaction of this compound, as argued below.

The Raman spectrum of CH shows three bands, among them two well-defined peaks located at 253 and 356 cm^{-1}, and a broad band located at about 680 cm^{-1} (Figure 2), in agreement with previously published data [12]. The low intensity peak at 1084 cm^{-1} is assigned to $CaCO_3$ impurities. The highest intensity line is at 356 cm^{-1}, which is characteristic of CH. This feature will be used to follow the appearance of CH during the hydration reaction of C_3S.

The Raman spectrum of synthetic C-S-H prepared in this work from a lime-saturated solution and ethyl tetraorthosilicate (Figure 3) shows two broad bands that are not well separated, probably related to the poor crystallinity of C-S-H. The peak at 662 cm^{-1} is probably due to the symmetric stretching motion of the Si-O-Si bridges [9]. As shown using Raman microprobe [9], C-S-H in a cement paste exhibits a characteristic band slightly shifted to lower frequencies (approximately 640 cm^{-1}). The discrepancy can be attributed to different Ca:Si ratios and degrees of polymerization of the SiO_4^{4-} units.

We also noted that the Raman spectrum of TiO_2 mainly exhibits one intense peak located at 144 cm^{-1}.

In-Situ Study of C_3S Hydration

Three samples of hydrated C_3S have been studied separately over a period of time ranging from 0 to 50 days. Fifty Raman spectra were collected during that period. For example, Figure 4 shows the Raman spectra of hydrated C_3S at 0, 1, and 43 days. The increasing intensity of CH and C-S-H Raman bands at the expense of C_3S peaks as time increases (compared with the constant intensity of the TiO_2 Raman band) is very clear.

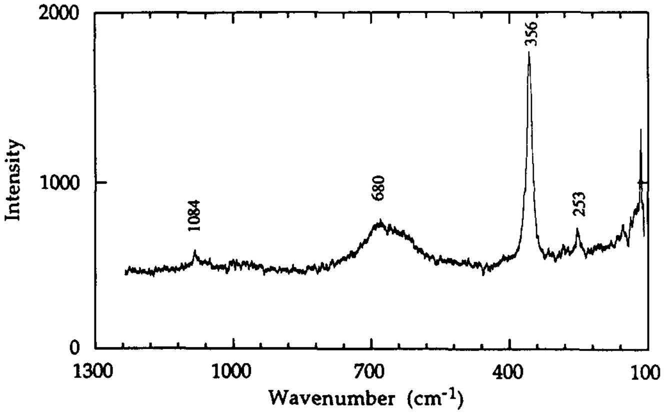

FIGURE 2. Room temperature Raman spectrum of synthetic CH.

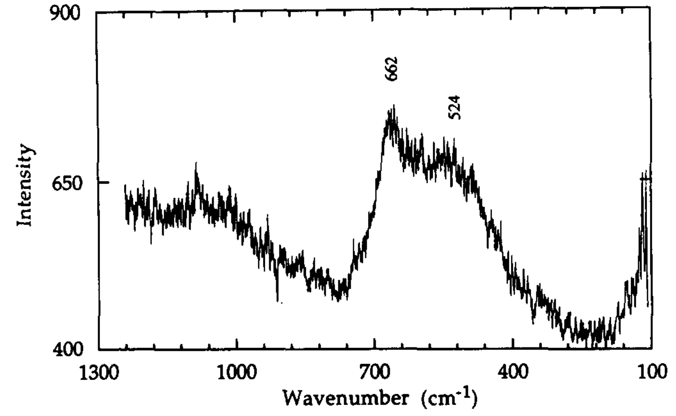

FIGURE 3. Room temperature Raman spectrum of C-S-H.

At the very early stage of the reaction (i.e., during the induction period, $t < \sim 4$ hours), the hydrated phases (CH and C-S-H) are difficult to identify unambiguously, because their proportions are much less than that of C_3S. At longer times ($t > \sim 4$ hours), the intensity of the Raman bands characteristic of C_3S decreases significantly as those of C-S-H and CH increase. As deduced from the data presented above, overlapping between the Raman bands of CH, C-S-H, and C_3S in the range of 500 to 700 cm^{-1} is expected, therefore, only the CH band at 356 cm^{-1}, the TiO_2 Raman peak at 144 cm^{-1}, and the high frequency modes of C_3S located above 800 cm^{-1} can be assigned without ambiguity. Only these features have thus been used to follow the progress of C_3S hydration.

To quantify the reaction coordinates, two different methods have been used. The first and more reliable method consists in following the decrease in intensity of the C_3S peaks compared with the constant one of TiO_2 used as an internal standard. Using the Dilor soft-

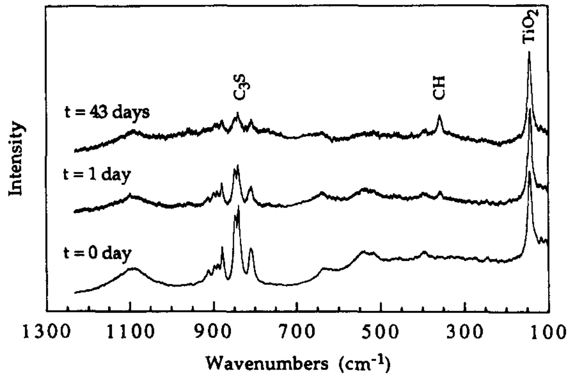

FIGURE 4. Room temperature Raman spectrum of hydrated C_3S at 0, 1, and 43 days.

ware (EASY), the integrated area of any region of the Raman spectrum can be calculated. The degree of hydration, $\alpha(t)$, is then derived, setting

$$\alpha(t) = 1 - \frac{I(t)}{I(0)}$$

where $I(t)$ and $I(0)$ are the integrated area ratio at any time and $t = 0$, respectively, with:

$$I = \frac{C_3S \text{ (integrated area)}}{TiO_2 \text{ (integrated area)}}.$$

The second method consists first in determining a mixing curve connecting the relative intensities of the CH and C_3S Raman bands of interest. Different mixed samples were prepared with various known molar proportions of C_3S and CH and then Raman spectra were recorded. The integrated area of a characteristic Raman region of the two phases (between 937.5 and 784.7 cm^{-1} for C_3S and between 372.4 and 345.8 cm^{-1} for CH) was obtained using the Dilor software (EASY). The plot of the molar ratio of the two phases (mol% of CH:mol% of C_3S) as a function of the integrated area ratio allows us to establish the following empirical relationship for the mixing curve:

$$\frac{\text{mol\% of CH}}{\text{mol\% of } C_3S} = a + b\left(\frac{\text{CH [integrated area]}}{C_3S \text{ [integrated area]}}\right) \qquad (3)$$

where the empirical coefficients, a and b, were found to be equal to -0.033 ± 0.002 and 19.2 ± 0.8, respectively. This relationship was then used to determine the molar ratio of the two phases in any Raman spectrum of hydrated C_3S using the same procedure as that used for the mixed samples.

To apply the second method, the stoichiometry of the hydration reaction must be known. Assuming that, later than the induction period, the C:S ratio is constant with time and equal to 1.7, one can express the progress of the hydration reaction introducing the C_3S degree of hydration $\alpha(t)$ as:

$$\begin{aligned} C_3S + 5.3\ H \rightarrow 1.3\ \alpha(t)\ CH + \alpha(t)\ C_{1.7}SH_{4.0} \\ + [1 - \alpha(t)]\ C_3S + 5.3[1 - \alpha(t)]\ H. \end{aligned} \qquad (4)$$

As discussed above, this reaction can only be followed on two phases, CH and C_3S. Therefore, a new parameter may be introduced, $A(t)$, expressing the appearance of CH and the disappearance of C_3S with time:

$$A(t) = \frac{1.3\ \alpha(t)}{[1 - \alpha(t)]} = \frac{\text{molar amount of CH formed}}{\text{remaining molar amount of } C_3S}. \qquad (5)$$

Consequently, the degree of hydration $\alpha(t)$ corresponds to:

$$\alpha(t) = \frac{A}{1.3 + A}. \qquad (6)$$

The evolution of the calculated $\alpha(t)$ versus time (in days) beyond the induction period is reported in Table 1 for both methods, where the data corresponding to the three different samples have been gathered. Within experimental accuracy, it appears that both

TABLE 1. Raman data expressing the variation of the C_3S degree of hydration versus time

t (day)	α^a	α^b	*t* (day)	α^a	α^b	*t* (day)	α^a	α^b
0.174	0.23	0.26	0.778	0.49	0.53	4.849	0.59	0.63
0.198	0.23	0.24	0.785	0.48	0.47	5.722	0.56	0.67
0.201	0.24	0.24	0.814	0.46	0.53	7.823	0.63	0.69
0.260	0.24	0.29	0.920	0.49	0.50	8.708	0.61	0.68
0.264	0.25	0.26	0.924	0.46	0.50	11.815	0.66	0.63
0.344	0.27	0.37	0.972	0.48	0.56	12.701	0.67	0.66
0.347	0.30	0.38	0.976	0.51	0.47	15.701	0.72	0.70
0.382	0.33	0.38	0.983	0.51	0.46	15.705	0.72	0.78
0.406	0.38	0.40	1.056	0.52	0.60	18.944	0.73	0.78
0.413	0.35	0.45	1.077	0.50	0.46	18.958	0.71	0.79
0.444	0.40	0.38	1.819	0.50	0.55	19.833	0.71	0.83
0.465	0.43	0.47	1.958	0.49	0.60	21.861	0.73	0.77
0.490	0.41	0.47	1.965	0.49	0.58	22.750	0.74	0.78
0.500	0.44	0.50	2.077	0.49	0.57	28.722	0.77	0.80
0.503	0.44	0.45	2.695	0.52	0.55	43.021	0.76	0.79
0.764	0.44	0.58	2.951	0.49	0.58	43.882	0.77	0.77
0.767	0.46	0.58	4.837	0.52	0.52			

α^a, determined by internal standard method.
α^b, determined by mixing curve method.

methods give the same degree of hydration. However, the standard error on the $\alpha(t)$ parameter determined by the internal standard method is close to 10% for registered data between 4 and 10 hours, 5% for data collected between 10 hours and 1 day, and less than 2% after 1 day, while it is about twice these values following the mixing curve method. Hence, the former method can be considered more reliable.

The data set corresponding to the internal standard method has been fitted with the classical kinetic relation of Avrami:

$$\alpha(t) = 1 - \exp(-Kt^n) \qquad (7)$$

where K and n, respectively, correspond to the constant and the exponent of the reaction. The values of K and n can be calculated using a least-squares regression of the logarithm form of eq 7 [13]:

$$\ln\left\{\ln\left[\frac{1}{1-\alpha}\right]\right\} = \ln K + n \ln t. \qquad (8)$$

The plot corresponding to eq 8 is shown in Figure 5. From Figure 5, it can be seen that a change in hydration kinetics occurs at 0.5 ± 0.1 days (13 ± 2 hours). Before this limit, n is equal to 0.85 ± 0.008, and after this limit it is four times lower (n = 0.20 ± 0.01). There is no significant difference between the values of K. K is equal to 1.0 ± 0.1 before 13 hours, and to 0.7 ± 0.1 after. The change in the behavior of the hydration reaction at 13 hours corresponds to a hydration ratio $\alpha(t)$ of 0.43 ± 0.03, which corresponds to a fraction of C_3S consumed of 43 mol%.

Discussion

The two methods used in this work to calculate the C_3S hydration rate from Raman spectroscopy data yield results in good agreement with each other. In particular, this gives evidence that the composition of C-S-H does not change as the reaction proceeds, with C:S = 1.7 being a correct value as found, for example, by Richardson and Groves [7]. Our results are in agreement with previous data such as those of Maggion [14] and Brough et al. [15]. Indeed, using quantitative X-ray diffraction (QXRD), Maggion [14] found for 1 day of hydration and a water:cement ratio of 0.4, a fraction of C_3S consumed of 48%, compared with our value of 46% for the same time and for the same water:cement ratio, whereas using ^{29}Si NMR spectroscopy, Brough et al. [15] found a value of 35%.

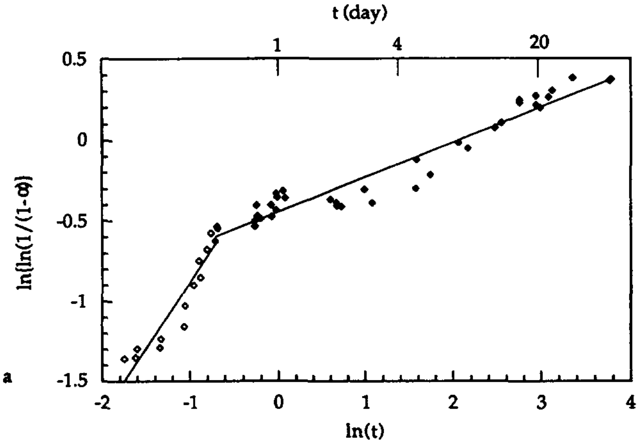

FIGURE 5. ln(ln(1/2 – α)) versus ln(t) plot (internal standard method).

On the other hand, Justnes et al. [16] and Wu and Young [17] both found an approximately 20% degree of hydration of C_3S after only 1 day, for a water:cement ratio of 0.7, using ^{29}Si NMR and chemical analysis (trimethysilylation method), respectively. Likewise, using Raman spectroscopy, Bensted [2] found 22 and 58% degrees of hydration after 1 and 18 days, respectively, while our values were equal to 46 and 70% at the same times. One can note that the water:cement ratio in Bensted's experiments is equal to 1, while our ratio is 0.4. Such a discrepancy between different experiments could be due to differences in C_3S particle-size distribution and/or crystal defect nature, on both of which depends the hydration rate, or could be linked to the different analytical techniques used. Certainly, it cannot be related to the differences in water:cement ratio, since α is expected to increase as this ratio increases [14]. It will require further and comparative studies to clarify this point.

A change in the progress of hydration at 13 hours, as observed in this work, cannot be inferred as easily from thermogravimetry analysis [18], or the QXRD and NMR studies discussed above. The reason for this is that data collection requires a lengthy experimental process, resulting in a small number of data. Such a change, at about the same time (19 hours), could only be inferred (to our knowledge) from the detailed NMR study by Brough et al. [15].

On the basis of heat liberation rate results, several periods of reaction were described [19]: (1) the initial period, (2) the induction period, (3) the acceleratory period, (4) the deceleratory period, and (5) a period of slow, continued reaction. Period 5 is the late stage of the reaction and is assumed to correspond to a volume hydration mechanism via the inward movement of a hydration interface, whereas periods 1 to 4 correspond to a surface hydration mechanism. Significant precipitation of CH begins during the acceleratory period.

Because we observe no significant change in the reaction kinetics between 13 hours and 50 days, we assign the observed change at 13 hours to the onset of the late stage. Periods 1 and 2 occur before 4 hours (no significant CH formation is observed). Hence, periods 3 and 4 occur between 4 and 13 hours.

Conclusion

This new investigation of the hydration reaction of C_3S by Raman spectroscopy has allowed us to establish a precise methodology for determination of the kinetics of hydration of this compound, based on in-situ measurements of a single sample, without stopping the reaction and without any sample preparation. Data collection is straightforward and details concerning the C-S-H composition and the hydration rate evolution may be easily evidenced. All the other methods used seem not to be as powerful in this regard.

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