Hydration of Tricalcium Silicate followed by Solid-state ^{29}Si N.M.R. Spectroscopy

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Solid-state ^{29}Si n.m.r. spectroscopy has been used to follow the kinetics of the hydration of tricalcium silicate and to provide details concerning the reaction course.

Orthosilicates will react with water to give silicate polymers.[1] A number of practical difficulties are involved when trying to investigate these hydration reactions since the silicate product is often precipitated from solution as an amorphous material making *X*-ray diffraction techniques of limited value. On the other hand solid-state n.m.r. is of potential use because the chemical shifts are characteristic of the various silicate connectivities, that is on the nature of X in Si–O–X.[2,3] We can thus ascertain the short-range order in amorphous material based on silicate anions. Previous work has shown that the reaction between water and tricalcium silicate can be studied by ^{29}Si n.m.r. spectroscopy.[4] In this communication we describe studies of the first 24 hours of this reaction and compare the results with those of more conventional techniques, calorimetry and thermogravimetric analysis.

Tricalcium silicate can be considered as a basic orthosilicate $CaO{\cdot}Ca_2SiO_4$ to emphasise the presence of discrete SiO_4^{4-} and O^{2-} anions in the crystal structure.[5] In general terms the hydration reaction leads to the formation of a calcium-silicate-hydrate which is insoluble and of calcium hydroxide which has limited solubility. The reaction is of practical interest as it is the major reaction involved in the setting of ordinary Portland cement.[6]

Representative spectra corresponding to various times into the hydration reaction are shown in Figure 1. The spectrum of anhydrous tricalcium silicate has a number of resonances all with chemical shifts typical of a monosilicate. This is consistent with *X*-ray diffraction studies which show a number of isolated silicate anion environments.[5] The connectivity in a silicate material can be denoted by the symbol Q_n where $n = 0$—4, Q_0 for example corresponds to a monosilicate anion, Q_1 to a chain end unit, and Q_2 to a chain middle unit.[7] A qualitative description of the hydration reaction as shown by the ^{29}Si n.m.r. results reveals a number of features. First, there is an induction period of 6 hours during which no reaction appears to occur, as evidenced by the absence of Q_1 resonances or changes in the appearance of the Q_0 resonances. Secondly, as the reaction proceeds a silicate dimer is formed as shown by the appearance of a Q_1 resonance but no Q_2 resonance. Thirdly, only small differential changes occur in the intensities of the Q_0 peaks indicating the structure of unreacted tricalcium silicate is unchanged. Fourthly, the Q_1 resonance of the hydration product has a greater linewidth than the individual resonances of the anhydrous tricalcium silicate. We must be careful when interpreting this difference in linewidth in terms of structural heterogeneity since the range of chemical shifts for the Q_0 resonances in anhydrous tricalcium silicate exceeds the linewidth of the Q_1 resonance, although each Q_0 resonance itself is narrow.

Under non-saturating conditions we can use the relative intensities of the Q_0 and Q_1 resonances in the ^{29}Si n.m.r. spectra to determine the extent of reaction with respect to the silicate species. This is equivalent to the degree of hydration of the tricalcium silicate. For the same samples we have used thermogravimetric analysis to determine the weight of calcium hydroxide produced in the reaction. A plot of the degree of hydration against the weight % of calcium hydroxide produced is shown in Figure 2. The correlation is extremely good indicating the formation of a calcium-silicate-hydrate of definite composition. This is a necessary condition in order to use calcium hydroxide data as a measure of the reaction course.[8]

We have also found that the induction period and the appearance of a Q_1 resonance observed in the n.m.r. spectra correlate closely with results from calorimetric studies. Thus after an initial exotherm involving the wetting of the surface of the tricalcium silicate grains the heat evolution decreases and remains at a low level for a few hours during which we observe no changes in the ^{29}Si n.m.r. spectra. Then, as the second exotherm begins so the Q_1 resonance starts to appear in the

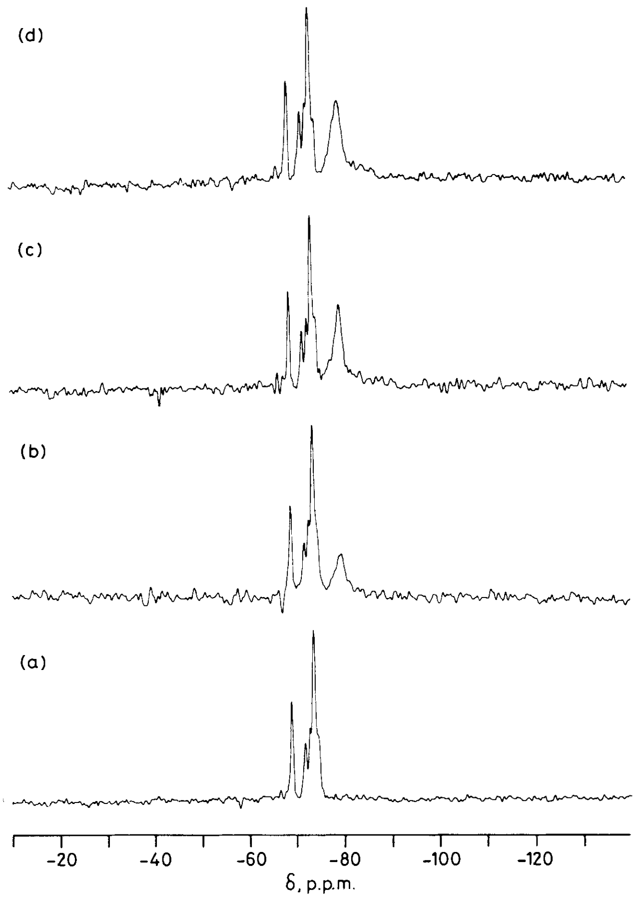

Figure 1. 39.76 MHz ^{29}Si Magic angle spinning n.m.r. spectra of tricalcium silicate hydrated over a 24 hour period run on a Bruker CXP-200 spectrometer. The tricalcium silicate particle size was ≤ 50 μm and the water to silicate ratio was 0.5 : 1. 2000 Transients were accumulated using a 3.5 μs, 60° pulse and recycle delay of 10 s. A Delrin–Andrews type rotor was used with a spinning speed of *ca.* 3.5 kHz. Chemical shifts are given in p.p.m. from tetramethylsilane. The spectra correspond to (a) 6 h, (b) 12 h, (c) 18 h, and (d) 24 h into the hydration reaction.

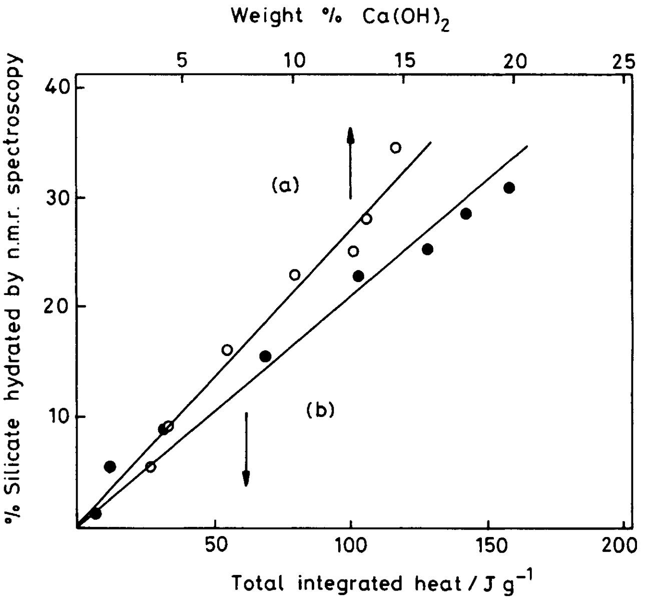

Figure 2. Correlation between the degree of hydration by ^{29}Si n.m.r. spectroscopy and (a),○, the weight % of calcium hydroxide produced and (b),●, the total integrated heat output. The intensities of Q_n resonances have been corrected to allow for the preferential saturation of the Q_0 resonance.

spectra providing evidence for the identification of the early part of the second exotherm as a dimerisation reaction. The high correlation between the total heat output and the degree of hydration observed by n.m.r. spectroscopy, supports this conclusion. Having considered one set of reaction conditions we repeated the reaction at a lower temperature to examine the generality of this observation. We found that the onset of the second exotherm was significantly later but again correlated closely with the appearance of the dimeric silicate resonance Q_1.

Despite the absence of major differential changes in the intensities of the Q_0 resonances we cannot be entirely sure that the calcium-silicate-hydrate does not contain orthosilicate anions. This is particularly relevant since ball-milling the reaction mixture during the hydration reaction has been found to lead to the formation of a hydrated orthosilicate, afwillite.[9] The two resonances of afwillite were found to be at δ −71.3 and −73.3 p.p.m. and hence overlap the chemical shift range seen for tricalcium silicate. We have used a cross-polarisation (CP) experiment[10] from ^{1}H to ^{29}Si to identify which ^{29}Si resonances are dipolar coupled to ^{1}H nuclei and thus come from a hydrated silicate. A CP spectrum of a sample hydrated for 24 hours shows an intense Q_1 resonance but only a very low intensity Q_0 resonance consistent with the silicate present in the hydrated material being predominantly dimeric.

This study has shown solid-state ^{29}Si n.m.r. spectroscopy to be an effective and straightforward method for defining the silicate structure of the amorphous product formed during the initial stages of the hydration of tricalcium silicate. The quantitative interpretation of the degree of hydration and the kinetics of the formation of dimeric silicate units is fully in accord with the results of more conventional techniques.[11] This work provides the basis for further studies of the hydration reactions of calcium silicates including cements.

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