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A study of the pozzolanic reaction by solid-state ^{29}Si nuclear magnetic resonance using selective isotopic enrichment

A. R. BROUGH*, C. M. DOBSON, I. G. RICHARDSON‡†, G. W. GROVES‡
Inorganic Chemistry Laboratory, and ‡Department of Materials, University of Oxford, Oxford, UK

The hydration of a mixture of tricalcium silicate and silica has been studied by ^{29}Si solid-state nuclear magnetic resonance, using selective enrichment of the reactants with ^{29}Si in order to follow and compare the behaviour of the silicon nuclei originating from either source. This approach shows for the first time that the silicon atoms from the two components are not equilibrated throughout the hydration products but are preferentially located in distinct species. In particular, from the distinctive spectra observed when the silica only is enriched, it is concluded that the part of the calcium silicate hydrate gel formed which incorporates silicon from this source has a longer chain length and a slightly better-ordered structure than the remainder. The spectra obtained with selective enrichment are interpreted in terms of a model based on a dreierkette chain structure for C–S–H.

1. Introduction

In the pozzolanic reaction, lime reacts with a silica-containing material in the presence of water to generate a hydrated gel. The reaction is named after the reaction of lime with pozzolana, a volcanic ash, which was used by the Romans to make an early hydraulic cement. Reactions of this type are also of considerable current engineering interest. The most frequent application of the pozzolanic reaction is in blended cements, where the calcium hydroxide is generated by the hydration of the calcium silicate components. Solid-state ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) is a useful tool for studying the pozzolanic reaction. The peak originating from amorphous silica is well separated from other peaks arising from hydration products and anhydrous calcium silicates. The hydration of C_3S or Portland cement with microsilica additions has been investigated using ^{29}Si NMR by various authors [1–5]. Among the main conclusions to emerge are that the presence of silica increases the rate of hydration of C_3S and that the calcium silicate hydrate (C–S–H) gel formed is of lower Ca/Si ratio, and more highly polymerized, than that formed when C_3S alone is hydrated.

The use of ^{29}Si enrichment in the present study allows spectra with good signal-to-noise ratios to be collected in a relatively short time and this allows reactions to be followed in real time even at early stages. More importantly, however, selective enrichment of the C_3S or silica with ^{29}Si overcomes a limitation of previous work, which was that the origin of the silicon giving rise to the observed spectra could not be distinguished. In the present work, because of the low natural abundance of ^{29}Si, the contribution of silicon originating from the unenriched reagent to the observed spectra can be neglected, and the silicon originating from the enriched component can be followed throughout the hydration reaction. It is thus possible to determine, for example, whether silicon atoms from the silica and from the C_3S, occupy different positions in the C–S–H gel that forms.

2. Experimental procedure

C_3S was prepared by firing pelletized Analar grade calcium hydroxide mixed with silica at 1385 °C for approximately 5 h. The pellet so formed was ground, re-pelletized and refired under the same conditions and this was repeated until powder X-ray diffraction showed no lines for CaO. Four firings were generally sufficient. To prepare normal C_3S, colloidal silica was used. In the preparation of ^{29}Si-enriched C_3S, the source of silica was a silicon dioxide powder containing silicon enriched to 95% with ^{29}Si, obtained from the Oak Ridge National Laboratory, USA. This powder was used directly as the silica labelled with ^{29}Si in the pozzolanic reaction. C_3S and silica were mixed in proportions to give an overall Ca/Si ratio of 1.0 and deionized water was added to the mixture in a kel-f insert, using a water/solids ratio of 0.7. The insert was sealed with epoxy resin and a series of ^{29}Si NMR spectra of the same sample was then obtained so that the progress of the reaction could be studied in real time. NMR spectra were obtained with MAS at

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* *Present address*: Centre for Advanced Cement Based Materials, University of Illinois at Urbana Champaign, Urbana, IL, USA.
† *Present address*: Materials Unit, Department of Civil Engineering, University of Leeds. Leeds, UK.

1–2 kHz and ^1H decoupling was performed with an r.f. field of 60 kHz. Chemical shifts were referenced to TMS by use of kaolinite as a secondary reference (− 91.2 p.p.m.). The cross-polarization (CP) Hartman–Hahn match was set by maximization of the CP signal from kaolinite or the ^{29}Si-enriched samples. Single-pulse MAS spectra were acquired with a recycle delay of 20 s, and the use of short ($\pi/6$) pulses. CPMAS spectra were acquired with a contact time of 4 ms and a recycle delay of 10 s. T_1 values were measured by least squares fitting a series of 11 or more inversion recovery experiments, with relaxation delays of 200 s, and inversion recovery delays of up to 100 s; where possible, excitation was performed by CP in order to permit the use of shorter relaxation delays, and to enable more rapid acquisition of data. CP relaxation parameters, T_{HSi} and $T_{1\rho}$, were calculated by least squares fitting a series of 20 or more CP experiments with a range of contact times. For all series of relaxation measurements, the individual experiments were performed in a random order. Owing to the nature of the samples, problems were experienced with obtaining suitable spinning speeds in some cases and many of the spectra contain spinning sidebands as a result. Intermittent problems were experienced with the shim power supply which lead to slightly increased line widths in some of the spectra, and is particularly noticeable for the Q_0 species. (In the Q_n notation, Q refers to a silicate tetrahedron and n refers to the number of oxygens that are bridging to adjacent tetrahedra.)

Three types of sample were studied. In the first, both C_3S and silica were enriched with ^{29}Si, while in the second, only the silica was enriched. These first two reactions could be considered to be completely comparable, because the same enriched silica was used in both and the C_3S was prepared in an identical way and was the same crystallographically. The third case, using unenriched silica with enriched C_3S could not be considered as quantitatively comparable since the reactivities of the enriched and unenriched silicas, from different sources, could not be expected to be closely similar. Attention was therefore focused mainly on the first two types of sample.

3. Results

3.1. Hydration of silica and C_3S both isotopically enriched in ^{29}Si

A selection of a sequence of ^{29}Si MAS NMR spectra obtained from a single sample progressively hydrating at room temperature is shown in Fig. 1. At early stages of hydration, up to 3 days, Q_1 species resonating at − 79 p.p.m. are the predominant species produced. The gel at this stage, therefore, contains mainly dimeric silicate species. Q_0 species with chemical shifts in the range − 68 to − 75 p.p.m. arise from the different sites in the crystalline C_3S and the broad Q_4 peak at around − 110 p.p.m. arises from the amorphous silica. Spectra obtained with cross-polarization (CPMAS) are shown in Fig. 2. These reveal only silicate species close to protons, i.e. hydrated material. Compared to the single-pulse spectra of Fig. 1, the CP spectra show a slight preferential excitation of the Q_1 species, relative to Q_2. A small peak evident in the CP spectra at a chemical shift of approximately − 75 p.p.m. can be assigned to minimal quantities of $Q_0^{(H)}$ species which are obscured in the single-pulse spectra by the Q_0 resonances of the C_3S. The occurrence of $Q_0^{(H)}$ species in the early stages of hydration of C_3S has previously been reported [6]. As reaction proceeds, the ratio of Q_2 to Q_1 species is found to increase slowly so that, at 19 days hydration, an average chain length of approximately 3 is implied. Finally, as the reaction proceeds further, the chain length continues to grow and, in addition, Q_3 species located at a chemical shift of approximately − 95 p.p.m. start to form. The CP spectra also clearly show excitation of Q_3 species. Even after 3 months, a small residue of unreacted C_3S and silica is indicated by the continued presence of Q_0 and Q_4. The average chain length after 3 months is approximately 4.

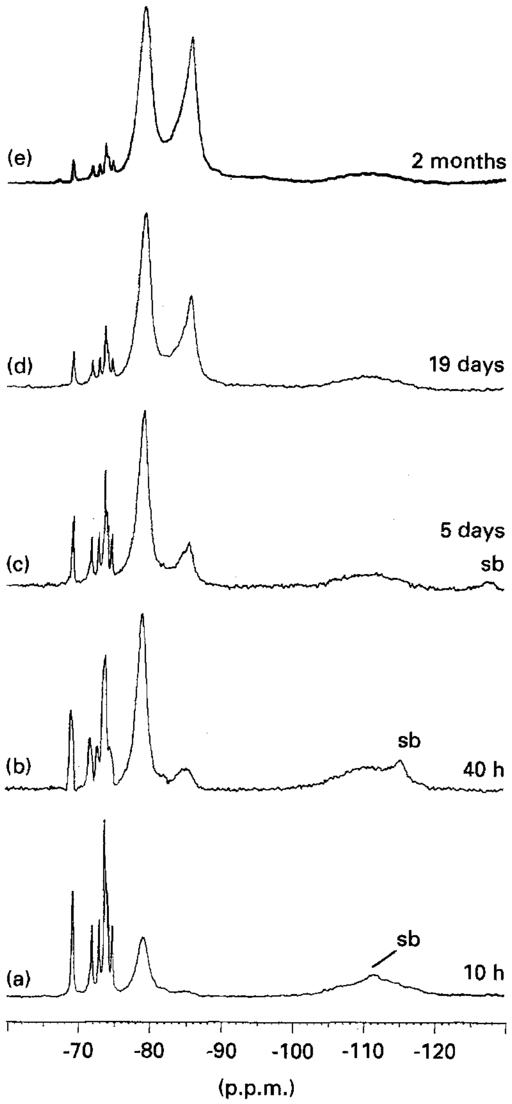

Figure 1 Selected ^{29}Si MAS NMR spectra showing the reaction of water with SiO_2 and C_3S, both enriched in ^{29}Si. 5 Hz exponential broadening was applied to these spectra.

A similar hydration to the above was carried out, but at a temperature of 40 °C. Fig. 3 shows that reaction and, particularly, polymerization occurs much more rapidly at 40 °C than at room temperature. Thus

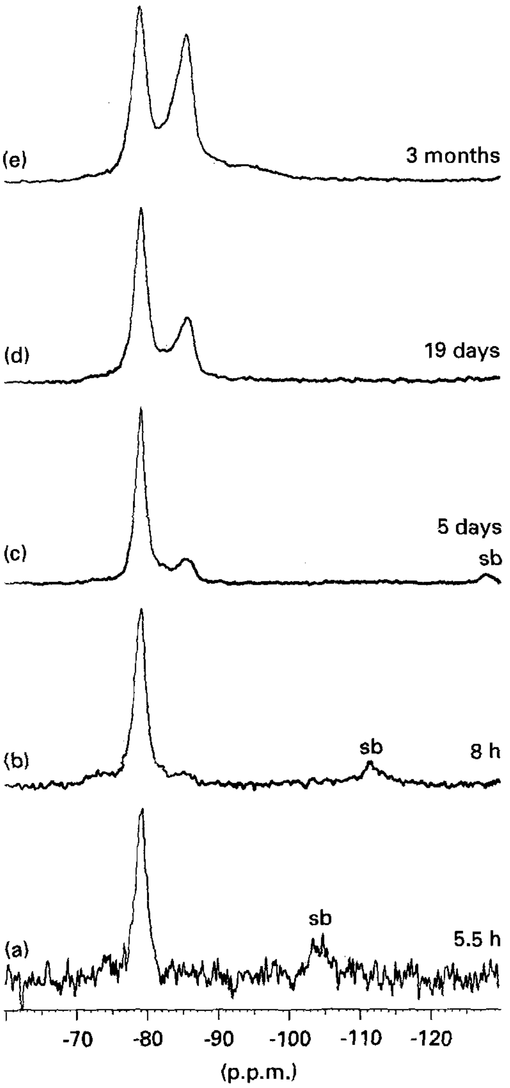

Figure 2 Selected ^{29}Si CPMAS NMR spectra showing the reaction of water with SiO_2 and C_3S, both enriched in ^{29}Si, for the sample of Fig. 1. 5 Hz exponential line broadening was applied to these spectra.

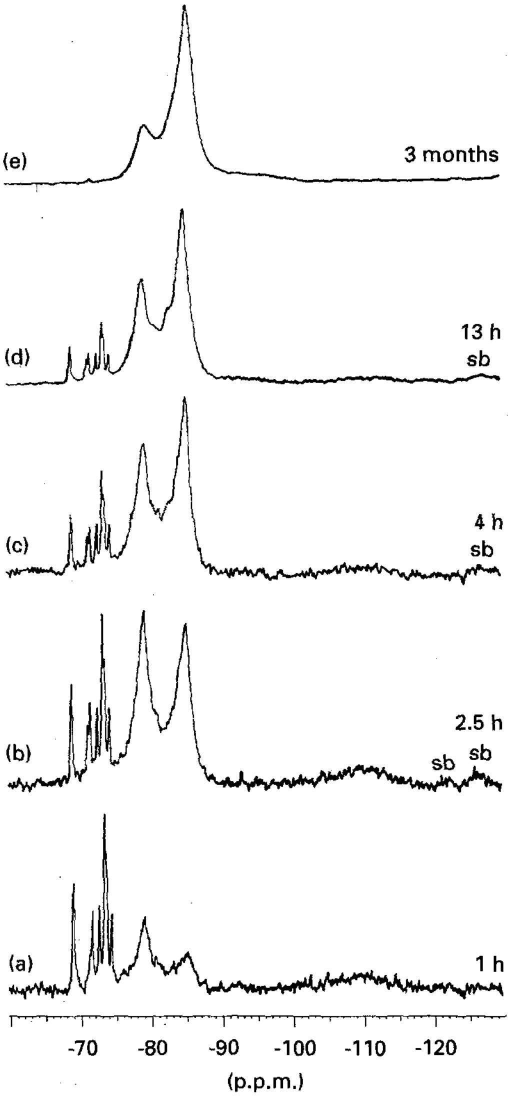

Figure 3 Selected ^{29}Si MAS NMR spectra showing the reaction of water with SiO_2 and C_3S, both enriched in ^{29}Si, at 40 °C. 5 Hz exponential line broadening was applied to these spectra.

a chain length of 4 is reached after 2.5 h instead of 3 months, and after 3 months the average chain length is approximately 8, neglecting the small Q_3 intensity. At this time, the Q_0 and Q_4 signals have disappeared, implying that the reaction has gone to completion and therefore that the Ca/Si ratio of the C–S–H gel is 1.0.

3.2. Hydration of silica enriched in ^{29}Si and C_3S containing ^{29}Si in natural abundance

Fig. 4 shows single-pulse ^{29}Si MAS NMR spectra and Fig. 5 the CPMAS spectra obtained during the hydration at room temperature of the sample in which only the silica was enriched in ^{29}Si. In excess of 97% of the ^{29}Si nuclei found in the system will originate from the silica; the approximately 3% of the ^{29}Si nuclei that originates from the C_3S can essentially be neglected. At early stages of hydration the major new resonances observed again originate from Q_1 species, showing that initially silicon from the silica takes part mainly in dimer formation. Note that in Fig. 4, Q_0 resonances are not seen because the C_3S is not isotopically enriched. The CPMAS spectra (Fig. 5) show no $Q_0^{(H)}$ peak at any stage of hydration, confirming that this peak is associated exclusively with the reaction of the C_3S. The Q_1 resonances are quite sharp, with a half height line width of approximately 40 Hz. After 26 h hydration, Fig. 4, there is a high field shoulder to the Q_1 resonance with a shift of approximately -82 p.p.m. and also a relatively broad Q_2 peak at -85 p.p.m. After 4 days hydration the shoulder is less prominent and the Q_2 resonance has sharpened somewhat. After 5 days, the Q_2 resonance has sharpened to a line width similar to that of Q_1'. The baseline is raised between the Q_1 and Q_2 peaks, however, indicating the presence of other less well-defined resonances in the region from -80 to -84 p.p.m. In the CPMAS spectra, the Q_2 resonances are excited to a slightly lesser extent and appear broadened relative to those in the single-pulse spectra.

As hydration proceeds further, some interesting results are observed. At 8 days, a clear shoulder begins to appear downfield of the Q_2 resonance. Between 9 days and 18 days a considerable increase in the intensity of Q_2 relative to Q_1 occurs. This intensity of the Q_2 resonance now significantly exceeds that of the

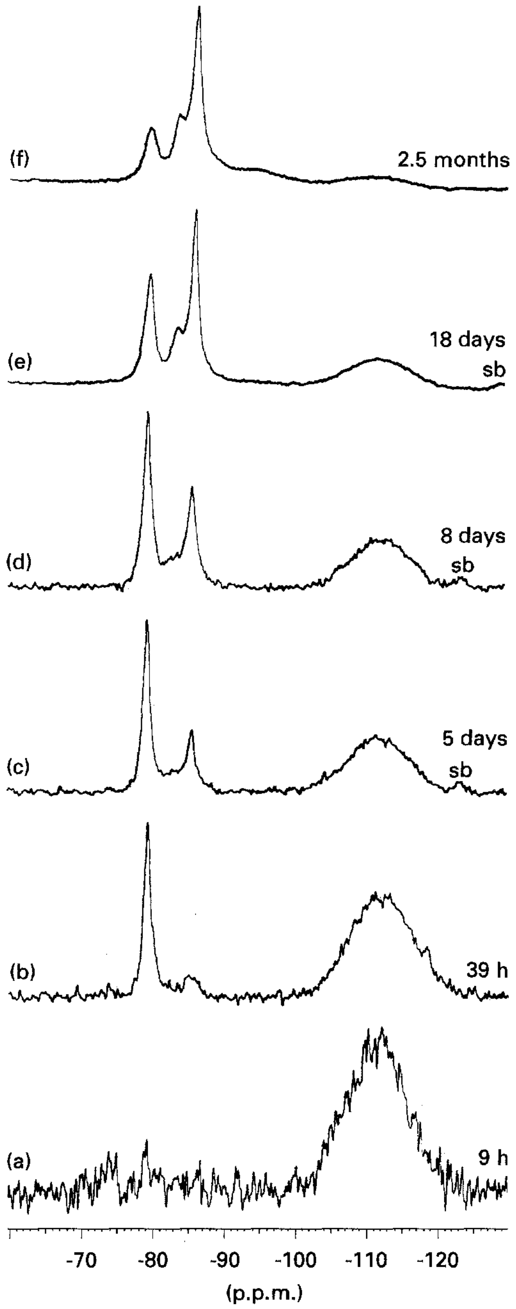

Figure 4 Selected ^{29}Si MAS NMR spectra showing the reaction of water with SiO_2 enriched in ^{29}Si and C_3S containing ^{29}Si at natural abundance. 5 Hz exponential line broadening was applied to these spectra.

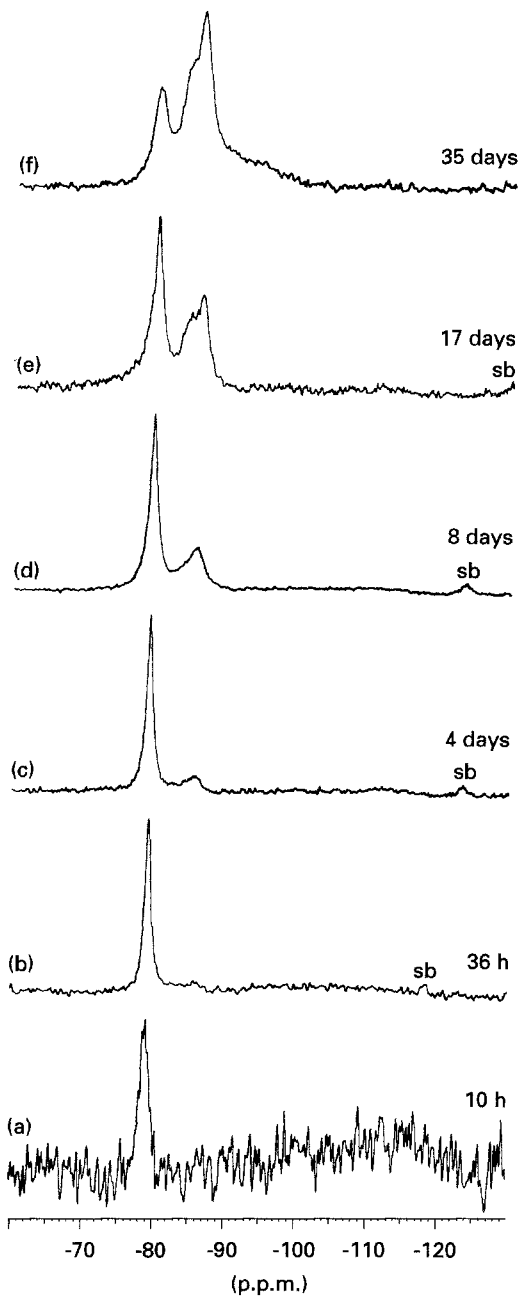

Figure 5 Selected ^{29}Si CPMAS NMR spectra showing the reaction of water with SiO_2 enriched in ^{29}Si, and C_3S containing ^{29}Si in natural abundance. 5 Hz exponential line broadening was applied to these spectra.

Q_1, a result not found in the sample where both C_3S and silica were enriched, even after 3 months hydration at room temperature. The line width of the Q_2 resonance is reduced to 40 Hz and this enables the observation of a separate $Q_2^{(L)}$ peak at -83.5 p.p.m., using the notation in Brough *et al.* [7]. The CP spectrum, Fig. 5, also shows this peak clearly; both it and the Q_1 species appear to be preferentially excited relative to the ordinary Q_2 peak. In the CP spectra the peaks at -83.5 and -85.5 p.p.m. are not resolved distinctly because of significantly larger line widths than those observed in the single-pulse spectra. At 18 days, there is still no evidence of the formation of Q_3 species. As hydration proceeds, a further increase of Q_2 relative to Q_1 occurs, but the ratio of the intensities of the $Q_2^{(L)}$ and Q_2 peaks at -83.5 and -85.5 p.p.m. respectively, remains approximately constant. Additionally, significant quantities of Q_3 species begin to form, which are seen in both single-pulse and CP spectra.

3.3. Hydration of C_3S enriched in ^{29}Si with silica containing ^{29}Si in natural abundance

Because the silica used was not from the same source as the ^{29}Si-enriched silica, this experiment was not completely comparable with those described in Sections 3.1 and 3.2. From observations of its wetting characteristics the silica used appeared to have a higher surface area than the enriched silica. A major result is that again initial hydration gave rise to predominantly Q_1 species. $Q_0^{(H)}$ species were observed in CPMAS spectra, at a shift of approximately -75 p.p.m. After further hydration, the Q_2 peak increased and was higher than Q_1 after 47 days, but much less so than in the case of C_3S reacting with enriched silica, Fig. 4. In no spectrum was a peak or shoulder seen in the region of -83 p.p.m. A minor amount of Q_3 species is formed at later times. A small peak at approximately -82 p.p.m. can be followed back through the series of spectra to the low-intensity shoulder upon the Q_1 species present at an early stage of hydration. A selection of spectra for this specimen is shown in Fig. 6.

3.4. Relaxation properties of the hydrates

Approximate T_1 values for the systems studied are recorded in Table I. The values recorded for most of the species are of the order of 20 s, and hence, in the single-pulse spectra presented in this paper, these resonances will only be saturated to a limited degree. In contrast, the relaxation times for the Q_4 species are considerably longer, and these resonances are likely to be partially saturated under the conditions used to record MAS spectra and to measure T_1 values. In addition, the shape of the inversion recovery curve indicates that species with a range of T_1 values contribute to the Q_4 resonance. The values reported are from spectra acquired at later stages of hydration, when sufficient time was available to record full data for the Q_4 resonance, which has low intensity; limited experiments performed during the early stages of hydration suggest that changes in the ranges of T_1 values may occur for this resonance, during hydration. A single T_1 value was assumed in order to generate the value reported by least squares fitting.

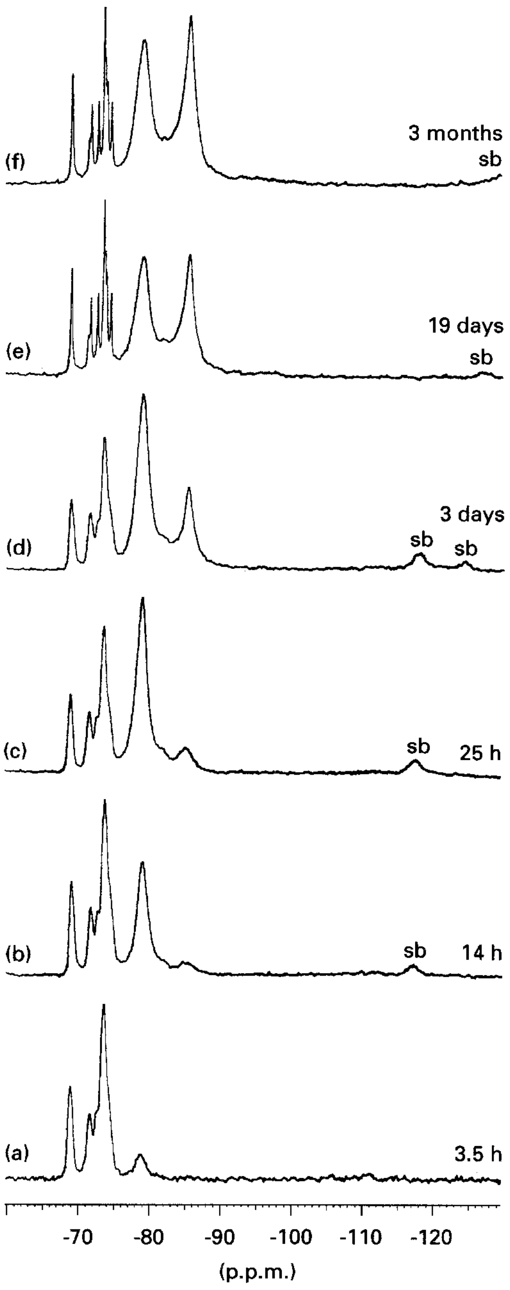

Figure 6 Selected ^{29}Si MAS NMR spectra showing the reaction of water with SiO_2 containing ^{29}Si in natural abundance and C_3S enriched in ^{29}Si. 5 Hz exponential line broadening was applied to these spectra.

TABLE I T_1 values, for Q_n species in the hydrates formed by hydration of the three mixtures of C_3S and silica, selectively labelled in ^{29}Si, as indicated under the "Enrichment" column label. The relaxation time for the peak at -83.5 p.p.m. observed in the spectra of the system with ^{29}Si enrichment of silica only was approximately 22.5 s, close to the values of 21 and 25 s for Q_1 and Q_2, respectively

Enrichment		T_1 for the Q_n species (s)					Hydration time (months)
C_3S	SiO_2	Q_0	Q_1	Q_2	Q_3	Q_4	
95	95	12	9	17	–[a]	> 100	3
5	95	–[a]	21	25	16	> 100	9
95	5	15	14	25	–[a]	–[a]	2

[a] Species not present, or present with too low an intensity for reliable measurement of T_1.

The CP relaxation parameters were also recorded as shown in Table II. There are two distinct ranges of $T_{1\rho}$ values; the Q_1 species cross polarize with a proton spin bath having a $T_{1\rho}$ of approximately 10 ms, while the Q_2 and Q_3 species cross polarize with a proton spin bath having longer $T_{1\rho}$. In all cases the data for each resonance, was fitted to a single pair of relaxation constants, T_{HSi} and $T_{1\rho}$, though there was some evidence for small fractions of the species having longer $T_{1\rho}$ values.

4. Discussion

The most striking feature of the results is that there are significant differences between the hydration product spectra recording silicon from silica alone and the spectra recording silicon from both C_3S and silica or from C_3S alone. This demonstrates for the first time that, in the pozzolanic reaction, silicon atoms from C_3S and silicon atoms from silica are not identically located in the hydration product. The spectra are most similar at the earliest stages of hydration, exhibiting mainly Q_1 species and indicating that silicon from both sources initially takes part in the formation of a dimeric gel. However, when the silica alone was enriched, no $Q_0^{(H)}$ was observed, showing that the monomeric hydrated species is associated exclusively with the C_3S. At later stages of hydration the spectra

TABLE II CP relaxation parameters for Q_n species in the hydrates formed by hydration of mixtures of C_3S and silica, selectively labelled in ^{29}Si as indicated under the "Enrichment" column. The times were generated by fitting data from 20 or more experiments, with contact times in the range 10 μs–30 ms. Significant excitation of Q_4 species was not observed in any of the CPMAS spectra.

Enrichment		Relaxation times for Q_n species (ms)						Hydration time (months)
C_3S	SiO_2	Q_1		Q_2		Q_3		
		T_{HSi}[a]	$T_{1\rho}$[b]	T_{HSi}[a]	$T_{1\rho}$[b]	T_{HSi}[a]	$T_{1\rho}$[b]	
95	95	0.45	9	0.8	17	1.3[c]	16[c]	3
5	95	0.45	8	0.6	13	0.6	13	7
95	5	0.45	9	1.0	20	–[d]	–[d]	2

[a] These resonances had very low signal-to-noise ratios; the results are estimates of the values only.
[b] Proton spin-lattice relaxation time in the rotating frame.
[c] ^1H–^{29}Si cross-polarization relaxation time.
[d] Insufficient Q_3 species were formed for measurement of their relaxation properties.

from the different type of specimen diverge. In particular, in spectra from the specimen in which silica alone was enriched, the ratio of Q_2/Q_1 intensities becomes much larger than in other specimens, the peaks are sharper, and a well-resolved subsidiary peak appears at -83.5 p.p.m. downfield of the main Q_2 peak at -85 p.p.m.

In the case where both C_3S and silica are enriched, so that all silicon from whatever source is recorded in the spectra, the $\overline{Q_2:Q_1}$ ratio gives the true average chain length, $\overline{CL}$, of the silicate chains in the C–S–H gel according to the relation,

$$\overline{CL} = 2(1 + Q_2/Q_1) \tag{1}$$

For example, if Q_2 and Q_1 are of roughly equal intensities, as appears after 3 months hydration (Fig. 1) the average chain length is approximately 4. Assuming a polymerization reaction in which dimers are linked by bridging tetrahedra to form pentamers, octamers, etc. [8–10], this could be the result of a mixture containing two pentamers for every dimer or one octamer for every two pentamers and three dimers, for example. However, in the case where one only of C_3S and silica is enriched, the Q_2/Q_1 ratio does not give the average chain length unless the silicons from either source are randomly distributed in a homogeneous hydrate. The relatively high Q_2/Q_1 ratio for the case where the silica alone is enriched shows clearly that silicon from the silica is distributed preferentially in Q_2 sites. However, this could happen in more than one way. The first hypothesis is that after, say, 3 months the silicon from the silica preferentially occupies bridging sites in a homogeneous hydrate with chains of average length 4. According to the polymerization model, Q_2 sites in pentamers, octamers, etc., which are not bridging sites originate from dimers so that the occupancy of these Q_2 sites should be expected to be no different from the occupancy of Q_1 sites which also either exist in dimers or originate from dimers.

If the fraction of bridging Q_2 sites which are occupied by silicon from SiO_2 is p^{-1} and the fraction of non-bridging Q_2 and Q_1 sites which are occupied by silicon from SiO_2 is r^{-1}, it can be shown that the expected ratio Q_2/Q_1 for the case when SiO_2 only is enriched, and the average chain length is β, is given by

$$\frac{Q_2}{Q_1} = \frac{(2+\alpha)(\beta-2)}{6} \tag{2}$$

where $\alpha = r/p$. This can be deduced as follows. Suppose that the distribution of chain lengths is a dimers, b pentamers, ..., $m\,(3n-1)$mers where n is an integer. Then, because the average chain length is β, we have

$$\frac{2a + 5b + \ldots + (3n-1)m}{a + b + \ldots + m} = \beta \tag{3}$$

or

$$\frac{2(a + b + \ldots + m) + 3[b + \ldots + (n-1)m]}{a + b + \ldots + m} = \beta \tag{4}$$

so that

$$\frac{[b + \ldots + (n-1)m]}{a + b + \ldots + m} = \frac{\beta - 2}{3} \tag{5}$$

But the ratio Q_2/Q_1 for silicon from SiO_2 is given by

$$\frac{Q_2}{Q_1} = [b + \ldots + (n-1)m]\left(\frac{1}{p} + \frac{2}{r}\right) \bigg/ \left[\frac{2}{r}(a + b + \ldots + m)\right] \tag{6}$$

Equation 2 follows from Equations 5 and 6. The observed value of Q_2/Q_1 after 2.5 months incorporating both the $Q_2^{(L)}$ and the "normal" Q_2 peak into the measurement of Q_2, is approximately 4. With the average chain length $\beta = 4$, this requires $\alpha \approx 10$ or an order of magnitude difference in the occupancy of bridging sites and other sites by silicon from SiO_2. This seems implausible, especially considering that the Q_1 peak is quite rapidly developed in the early stages of hydration of the mixture with SiO_2 only enriched (Fig. 4). A second hypothesis has therefore been considered, that the hydrate is not homogeneous but that a region of hydrate containing silicon mainly originating from silica exists, and is of substantially greater chain length than the remaining hydrate. This hypothesis has the advantage that the relative sharpness of the peaks in Fig. 4 and the good resolution of the $Q_2^{(L)}$ peak can be explained by the hydrate which originates mainly from silica having a somewhat better ordered structure than the remaining hydrate. It is natural to postulate that the hydrate containing silicon which originates preferentially from silica is located in the neighbourhood of reacting silica particles, and in this connection it is worth noting that microstructure examination by transmission electron microscopy of cement–silica systems has shown that some of the C–S–H gel is in intimate contact with reacting silica particles [4], while other regions of gel, inner product of the C_3S for example, are distant from silica.

The $Q_2^{(L)}$ peak at − 83.5 p.p.m. has been previously reported and discussed [7]. Brough *et al.* [7] tentatively attributed it to bridging tetrahedra in a C–S–H in which the longer silicate chains have a dreierkette structure, developed by joining dimers with the bridging tetrahedra [8–10]. It was argued that the difference between the bond angles for the bridging tetrahedra and the remaining Q_2 tetrahedra could account for the downfield shift of the $Q_2^{(L)}$ peak. If the difference in bond angles for the bridging and the remaining tetrahedra is the same for all chains, this would imply that the relative intensities of the Q_2 and $Q_2^{(L)}$ signals should be in the ratio 2:1, which is a smaller ratio than that observed. However, it has been pointed out [11] that in the crystal structure of 11 nm tobermorite given by Hamid [12], the unit cell contains two chains of slightly different configuration, in only one of which is there a large difference in bond angles for the bridging tetrahedra. If such a situation also occurred for the chains in the very poorly crystalline, or nearly amorphous, C–S–H phase, a ratio of 5:1 for the intensities of the two peaks would be expected which could account for the observed ratio being clearly greater than 2:1. The disorder in the C–S–H structure does, however, suggest that bridging tetrahedra experience a variable environment. According to Taylor [8, 9] and Richardson and Groves [10] models of C–S–H structure there are frequent interruptions in the silicate chains due to many bridging tetrahedra being missing, so that bridging tetrahedra in one layer of the C–S–H structure may experience various environments from the neighbouring layer according as to the presence or absence of bridging tetrahedra nearby in this layer [13]. One or more of these environments may cause a chemical shift opposing the shift due to the bond angle change for the bridging tetrahedra. Lack of knowledge of the details of the structure of C–S–H makes further discussion unprofitable.

The origin of the weak and very broad Q_3 peak is uncertain, but the fact that the line width of the Q_3 resonance, like that of Q_4, is much greater than that of Q_1 or Q_2 suggests that it is associated with the silica phase rather than with C–S–H.

The T_1 data (Table I) show some variability between the samples, with the lowest values recorded where both starting materials are enriched in ^{29}Si, suggesting that homonuclear ^{29}Si–^{29}Si interactions contribute to the relaxation; this would not, however, be expected to lead to significant line broadening. The $T_{1\rho}$ data (Table II) show the presence of at least two distinct proton spin baths, as has been observed previously for samples of tobermorite [14]. Note that while the Q_3 species have similar relaxation properties to the Q_2 species, they are probably in a different phase, as discussed previously, because they have considerably larger line widths. This contrasts with the case of tobermorite [14], where the Q_2 and Q_3 species are in the same phase, and have similar line widths. The results are, in general, consistent with the presence of considerable heterogeneity in the system.

Owing to the small quantities of enriched material available, it was impossible to carry out TEM microanalysis of the pastes from which the spectra in this paper were obtained. The only certain compositional information is the Ca/Si ratio of 1 which can be assigned to the C–S–H gel in the paste which was fully reacted at 40 °C (Fig. 3). With a chain length of approximately 8 this implies, on current models of C–S–H gels [8–10] an admixture of a small proportion of jennite-like units to mainly tobermorite-like units [8, 9] or alternatively the presence of a small amount of calcium hydroxide in "solid-solution" [10]. It is notable that the spectrum of this paste shows no resolved $Q_2^{(L)}$ peak, although the Q_2 peak is clearly asymmetrical (Fig. 3). It is possible that the spectra from the paste produced with silica only enriched originates from a gel of Ca/Si ratio lower than 1, having a better-ordered purely tobermorite-like structure in which $Q_2^{(L)}$ can be resolved. It is likely that the initial dimeric C–S–H formed by silicon from both C_3S and silica has a Ca/Si ratio in excess of 1.0; for example, according to Taylor's model [8, 9], the minimum possible chain length for a Ca/Si ratio of 1.0 is 5, and the minimum Ca/Si ratio for a dimeric gel is 1.25.

5. Conclusion

The study of the hydration of a mixture of C_3S and silica using ^{29}Si enrichment of one or both of the reactants has shown that silicon originating in the silica has a different location in the C–S–H reaction product from silicon originating in the C_3S. The $Q_0^{(H)}$ resonances are associated exclusively with silicon originating from the C_3S. Although silicon from both sources initially takes part in the formation of a dimeric C–S–H, at later times silicon from silica takes part in the formation of a C–S–H which differs from the rest of the C–S–H in having a longer chain length and a somewhat better ordered structure.

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References

1. C. M. DOBSON, D. G. C. GOBERDHAN, J. D. F. RAMSAY and S. A. RODGER, *J. Mater. Sci.* **23** (1988) 4108.
2. J. HJORTH, J. SKIBSTED and H. J. JAKOBSEN, *Cem. Conc. Res.* **18** (1988) 789.
3. S. S. BEEDLE, G. W. GROVES and S. A. RODGER, *Adv. Cem. Res.* **2** (1989) 3.

4. G. W. GROVES and S. A. RODGER, *ibid.* **2** (1989) 135.
5. H. JUSTNES, I. MELAND, J. O. BJOERGUM and J. KRANE, *ibid.* **3** (1990) 111.
6. S. A. RODGER, G. W. GROVES, N. J. CLAYDEN and C. M. DOBSON, *J. Am. Ceram. Soc.* **71** (1988) 91.
7. A. R. BROUGH, C. M. DOBSON, I. G. RICHARDSON and G. W. GROVES, *ibid.* **77** (1994) 593.
8. H. F. W. TAYLOR, "Cement Chemistry" (Academic Press, London, 1990) pp. 142–52.
9. H. F. W. TAYLOR, *J. Am. Ceram. Soc.* **69** (1986) 464.
10. I. G. RICHARDSON and G. W. GROVES, *Cem. Conc. Res.* **22** (1992) 1001.
11. X. CONG and R. J. KIRKPATRICK, private communication (1994).
12. S. A. HAMID, *Z. Krist.* **154** (1981) 189.
13. A. R. BROUGH, DPhil. thesis, University of Oxford, UK (1993).
14. G. M. M. BELL, J. BENSTED, F. P. GLASSER, E. E. LACHOWSKI, D. R. ROBERTS and M. J. TAYLOR, *Adv. Cem. Res.* **3** (1990) 23.

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