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Alkali activation of reactive silicas in cements: *in situ* ^{29}Si MAS NMR studies of the kinetics of silicate polymerization

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In the highly alkaline environment of the cement paste of a concrete, a source of silica can potentially react in two ways. In the pozzolanic reaction, it can combine with free lime to generate additional calcium silicate hydrate binding phase. Alternatively, reaction with alkali to form a gel can occur; this gel may swell and degrade the concrete. ^{29}Si magic angle spinning (MAS) and cross-polarization (CP) MAS nuclear magnetic resonance (NMR) studies have been performed to determine the silicate connectivity in some model cement systems; ^{29}Si enrichment was utilized to enable a series of spectra to be acquired *in situ* from a single sample.

The hydrate from pozzolanic reaction of lime with silica was similar to the hydrate formed around silica in blended pozzolanic cements, with a relatively high crystallinity and long silicate chains. In the absence of lime, silica reacted with an alkaline solution to produce a gel having a high degree of cross linking, and a range of silicate mobilities. Tricalcium silicate hydration was found to be accelerated significantly by high levels of alkali (KOH) in solution; the hydrate formed had shorter silicate chains and was more crystalline than that produced by reaction in pure water. Hydration in alkali solution of a model blended cement, comprising a mixture of tricalcium silicate and silica, gave rise to two products, a long chain calcium silicate hydrate (C–S–H) and an alkali silicate of low rigidity. The alkali silicate phase gradually polymerized; at later ages it underwent a phase change, although no crystalline phase appeared to be formed. Silicate exchange took place between the C–S–H and the alkali silicate phase at a slow rate.

1. Introduction

Basic oxides, including alkalis, can affect significantly the hydration reactions of cementitious materials. Calcium hydroxide or alkalis, either added as activators or generated by the hydration of ordinary Portland cement (OPC), can activate pozzolanic material to form C–S–H (Cement chemist's notation: C = CaO, S = SiO_2, H = H_2O, N = Na_2O (e.g. C_3S = Ca_3SiO_5, C–S–H = Calcium silicate hydrate of variable stoichiometry.).) Alkalis, however, can also be deleterious. Reactive silica, or silicate containing materials, in the aggregate of a concrete can react with alkali in the cement pore fluid to form potentially expansive amorphous alkali silica gels. In this paper we use ^{29}Si magic angle spinning (MAS) and cross-polarization (CP) MAS nuclear magnetic resonance (NMR) to study the evolution of silicate polymerization in the pozzolanic and alkali silica reactions. The use of ^{29}Si enrichment enables the acquisition of multiple spectra from a single sample as the reactions proceed [1].

The hydration of tricalcium silicate has previously been studied by ^{29}Si MAS NMR [2, 3] which provides a sensitive probe of silicate polymerization [4]. Clearly separated peaks are resolved for the isolated (Q^0) silicate groups in the anhydrous silicate, and for chain end (Q^1) and middle chain (Q^2) groups in the hydrate; more highly polymerized (Q^3 or Q^4) species are not observed. (In the Q^n notation, used to describe silicate polymerization, Q signifies an SiO_4 tetrahedron, and n signifies the number of oxygens bridging to adjacent tetrahedra.) Similar results are obtained by TMS derivatization of the silicates [5]. The degree of polymerization at a given extent of reaction is also

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found to increase with increasing temperature [1,6]. C–S–H pastes can, however, also be synthesized by the direct pozzolanic reaction of calcium hydroxide with a reactive silica. We are not aware of any studies of the connectivity of silicate species contained in these systems; we report here a ^{29}Si MAS NMR study of this simple pozzolanic reaction of lime with silica.

The reaction of silica with a soluble alkali is very different; the products are alkali silicate solutions and gels. The speciation of alkali silicate solutions has been studied in detail by ^{29}Si solution NMR; work prior to 1986 is reviewed in reference [4]. A kinetic study of the distribution of species during the dissolution of silica has been carried out using ^{29}Si MAS NMR [7]. It was found that dissolution does not simply depend upon hydroxide ion concentration, but is fastest in KOH, and slowest in LiOH or CsOH. A range of silicate connectivities was observed, with the degree of polymerization increasing as dissolution proceeds, as might be expected upon the basis of speciation of solutions observed at equilibrium. Higher cation to silicate ratios than are common in cements were utilized, and the motional properties of the hydrates were not investigated. In this paper we study the reaction of 5 M KOH with silica using ^{29}Si enriched SiO_2 to enable series of MAS and CPMAS NMR spectra to be acquired rapidly as the sample reacts [1]; this avoids problems associated with poor signal-to-noise ratios or with dissolution of soluble silicate components if quenching procedures are used.

It has also been shown that alkalis can be incorporated into pure C–S–H gels [8,9], but the effect that this has upon silicate polymerization has not been studied. In this paper we report ^{29}Si MAS NMR studies of the silicate polymerization of a sample of C_3S hydrated with a concentrated solution of KOH. The kinetics of the reaction will be reported at a later date, along with other data concerning alkali hydration of calcium silicate cements.

These reactions are of considerable importance, because they are related to the alkali silica reaction (ASR), which occurs in concretes. The pore solution in the cement paste component of a concrete can contain high levels of alkali (e.g. 0.7 M MOH, M = Na, K), which has been released from the cement, but not incorporated into the products of hydration. Some aggregates contain sources of reactive silica which can react with this alkali to form an alkali silica gel; some of these gels can imbibe water, swell with considerable force, and cause failure of the concrete. There is not good agreement as to the calcium or alkali content of these expansive gels. In synthetic alkali silica gels precipitated from alkali silica solutions with the pessimum alkali to silica ratio, experimentally observed to be the region of maximum swelling, Q^3 and Q^4 species were found [10,11]. In contrast to the original silica gels, the Q^3 species had a significant downfield shift. However, these gels contain no calcium, and the presence of calcium in expansive alkali silica gels has been noted by a number of authors [12–14].

Recently, Cong and Kirkpatrick [15] studied some synthetic alkali silica reaction product gels by ^{29}Si MAS NMR. In the presence of calcium hydroxide, products similar to C–S–H gel were observed, with Q^1 and Q^2 silicate species (an additional peak at approximately − 82.5 p.p.m. may result from C–S–H generated from pozzolanic reaction of C_3S and silica [16–19]). In these gels, more highly polymerized species were also present, but again having chemical shifts consistent with a C–S–H formulation. In the absence of calcium hydroxide, rather different products were formed, which contained hydrated Q^3 and Q^4 species; the samples were quenched by washing with acetone, so less highly polymerized alkali silicate species may have been lost.

Reaction of silica in cement pastes also takes place in blended cements where calcium hydroxide, generated *in situ* by the hydration of C_3S, reacts with silica, or a silica source, such as a coal combustion fly ash, to form additional C–S–H binding phase; such blended cements are widely used. ^{29}Si MAS NMR has been applied to simplified pozzolanic systems which contain calcium silicates blended with up to 30% of an active silica [20–22]. Hydration of the calcium silicates was accelerated initially and, in addition, longer chains were found in the hydrates formed in the presence of silica than in those hydrates formed by the hydration of the calcium silicates alone. No cross linked silicate species were observed in any of these systems. At higher levels of pozzolan addition, significant quantities of cross-linked species were also formed [23] in both simplified and realistic blended cements.

^{29}Si MAS NMR studies of the pure C_3S/SiO_2 system, with the use of selective ^{29}Si labelling, have shown that both the C_3S and silica initially contribute mainly dimers to the C–S–H gel; at later stages of hydration, silicate from the silica takes part in the formation of a C–S–H which has a longer chain length and a more ordered structure than the rest of the C–S–H [17–18]. Low levels of alkalis have little effect upon the silicate polymerization observed in pozzolanic hydrates [23], but the effects of higher levels have not been studied. In this paper we report *in situ* ^{29}Si MAS and CPMAS NMR studies (with and without CP) of the silicate polymerization of a system containing C_3S and SiO_2, and hydrated with concentrated alkali. In MAS NMR, the observed species are excited directly; the MAS technique increases the resolution of the spectra by averaging anisotropies in the chemical shift and other broadening interactions. In CPMAS NMR, the magnetization is initially placed upon hydrogen nuclei, and then transferred to the nuclei of interest. For transfer to occur, there must be hydrogen nuclei close to the species of interest; CP spectra are not observed from species free of hydrogen atoms, such as anhydrous C_3S. Q^4 species generally cross-polarize relatively poorly, since they cannot by definition have directly bound silanol groups. The CP process takes place by through space interactions that enable transfer of magnetization between the proton nuclei, and the nuclei of interest; motion can reduce the efficiency of transfer of polarization by averaging these interactions.

2. Experimental procedure

NMR spectra were acquired at 39.76 MHz with MAS at approximately 2 kHz, in a standard Bruker CPMAS probe, using a Bruker MSL200 spectrometer equipped with a 4.7 T Oxford Instruments wide bore magnet. The probe was shimmed by observation of the ^{13}C signal from adamantane. The magic angle was set by observation of the ^{79}Br free induction decay (FID) from KBr. ^{1}H decoupling was performed at ~60 kHz; the Hartman–Hahn match for CP was set by maximization of the signal from kaolinite, or from the enriched samples when appropriate. Chemical shifts were referenced to tetramethylsilane (TMS) at 0 p.p.m., with the use of the kaolinite as a secondary standard (– 91.2 p.p.m.). The MAS spectra were acquired with a $\pi/6$ pulse and a recycle delay of 20 s; a few experiments with longer recycle delays indicated that some saturation of the silica resonance occurred. CPMAS spectra were acquired with a recycle delay of 10 s and a contact time of 4 ms. The number of FIDs averaged to generate each spectrum was determined by the time available; at early ages the spectra changed rapidly, limiting the number of FIDs that could be averaged before it was necessary to acquire a new spectrum.

The ^{29}Si enriched SiO_2 used in this study was obtained from the Oak Ridge National Laboratory, USA. ^{29}Si enriched C_3S was prepared from this material as described previously [18]. Four series of experiments were performed. In each case, the solids were mixed and placed in a small kel-f rotor insert. 5 M KOH solution or deionized (DI) water was then added and mixed for 5 min. The insert was sealed with quick-setting epoxy resin, and placed in a 7 mm external diameter zirconia MAS NMR rotor. ^{29}Si MAS and CPMAS NMR spectra were acquired continuously for the first few days of hydration; at later ages the samples were only subjected to MAS intermittently to acquire spectra; otherwise they were stored in sealed containers with water present.

The following samples were studied; unless otherwise stated, hydration was performed at room temperature.

- *Simple pozzolanic reaction*: ^{29}Si enriched silica was mixed with CaO (BDH, Analar) to give an overall Ca/Si atomic ratio of 3.0, and hydrated at 40 °C with deionized water at a solution/solids ratio of 0.7 (by weight).
- *Alkali silica reaction*: ^{29}Si enriched silica was hydrated with 5 M KOH solution at a solution/solids ratio of 0.7.
- *Alkali hydration of C_3S*: ^{29}Si enriched C_3S was hydrated with 5 M KOH solution at a solution/solids ratio of 0.5.
- *Alkali activated simplified blended cement hydration*: C_3S containing ^{29}Si at natural abundance (5.5%) was mixed with ^{29}Si enriched silica to give an overall Ca/Si atomic ratio of 1.0; the mixture was hydrated with 5 M KOH at a solution/solids ratio of 0.5.

3. Results

3.1. Simple pozzolanic reaction

Calcium oxide was reacted with silica at 40 °C; selected ^{29}Si MAS NMR spectra showing the time

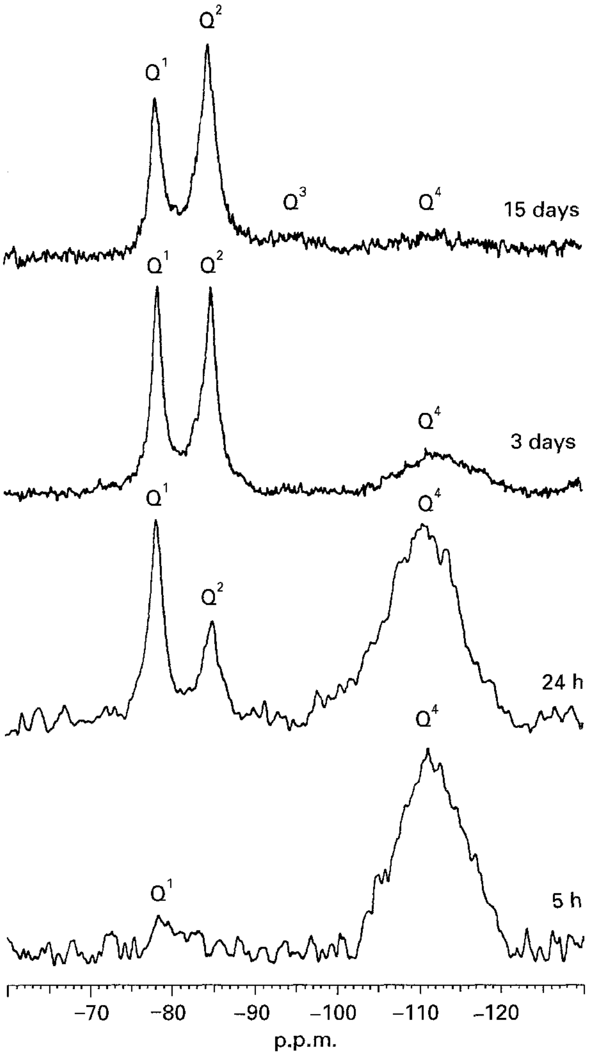

Figure 1 Selected ^{29}Si MAS NMR spectra showing the reaction of calcium oxide with water and silica. 5 Hz of exponential line-broadening was applied to these spectra, except at early ages, when 20 Hz was applied. The Q^n notation is described in the text. Hydration times are indicated on the figures.

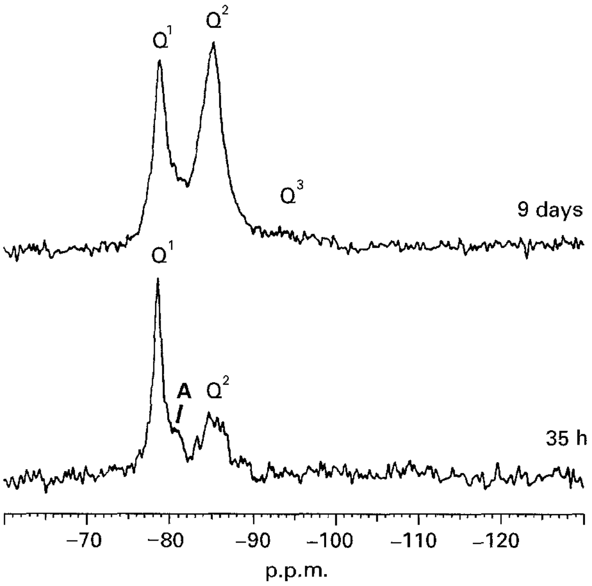

Figure 2 Selected ^{29}Si CPMAS NMR spectra showing the reaction of calcium oxide with water and silica. 5 Hz of exponential line-broadening was applied to these spectra. The nature of the peak **A** is described in the text.

evolution of this reaction are shown in Fig. 1. At early ages, when little hydrate had formed, it was necessary to apply extra line-broadening to the spectra to improve signal-to-noise ratios. The broad peak centred at approximately -112 p.p.m. results from Q^4 sites in the amorphous silica. As hydration proceeds, additional peaks due to hydrate appear at approximately -79 and -85 p.p.m.; these may be assigned to Q^1 and Q^2 species, respectively, in a C–S–H type hydration product, by analogy with spectra acquired from samples of hydrated C_3S. The ratio of areas of the two C–S–H peaks in the early spectra is approximately 2 : 1, indicating an average chain length in the hydrate of approximately 3. Beyond 24 h of hydration, the chains start to increase in length. By 6 days of hydration, a broad Q^3 peak centred around -95 p.p.m. appears; this increases in intensity up to 15 days hydration. At this time, the temperature of the oven in which the sample was stored was raised inadvertently to 105 °C; the experiment was terminated. Both the Q^1 and Q^2 peaks have a half height line width of ~ 40 Hz; the Q^1 peak is reasonably symmetrical, while the Q^2 peak has a shoulder of low intensity to low field. The Q^4 peak has a line width of ~ 450 Hz, and the Q^3 line width appears similar, although the low intensity of this peak makes the line width difficult to measure accurately. Indeed, the peak could comprise of a number of narrower overlapping peaks.

^{29}Si CPMAS NMR spectra were also acquired; selected spectra are shown in Fig. 2. At early ages, the Q^1 and Q^2 peaks are observed. In addition, there is a small shoulder, **A**, to high field of the Q^1 peak, at a shift of about -80.5 p.p.m. At later ages, the Q^3 species can also be observed.

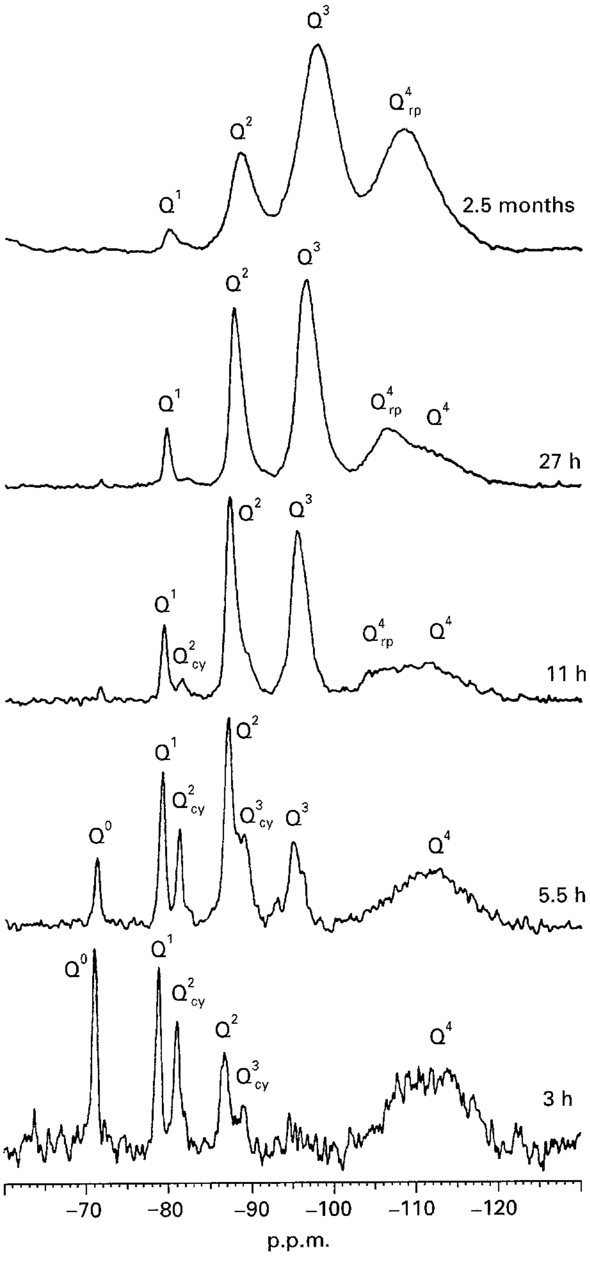

Figure 3 Selected ^{29}Si MAS NMR spectra showing the reaction of 5 M KOH solution with silica. 10 Hz of exponential linebroadening was applied to these spectra. The notation Q^2_{cy} and Q^3_{cy} denotes Q^2 and Q^3 species contained in cyclic trimers; Q^4_{rp} denotes Q^4 species contained in the reaction products.

3.2. Alkali silica reaction

Silica was reacted with 5 M KOH; selected ^{29}Si MAS NMR spectra are shown in Fig. 3. The broad peak Q^4 at -112 p.p.m. results from the amorphous silica reagent. Selected CPMAS spectra are shown in Fig. 4. Resonances from the initial products of reaction appear only in the ^{29}Si MAS NMR spectra, and not in the CP spectra; since this is a hydrous system, with abundant protons, the absence of the resonances in the CP spectra suggests that the dipolar interactions required for CP are averaged by the motion of the protons. This is fast on the timescale of the CP contact time (4 ms). The silicate species may either be in a motional gel, or alternatively, in solution. Peaks are observed at chemical shifts of -71, -78.5, -81, -87, and -88.5 p.p.m. By consideration of the

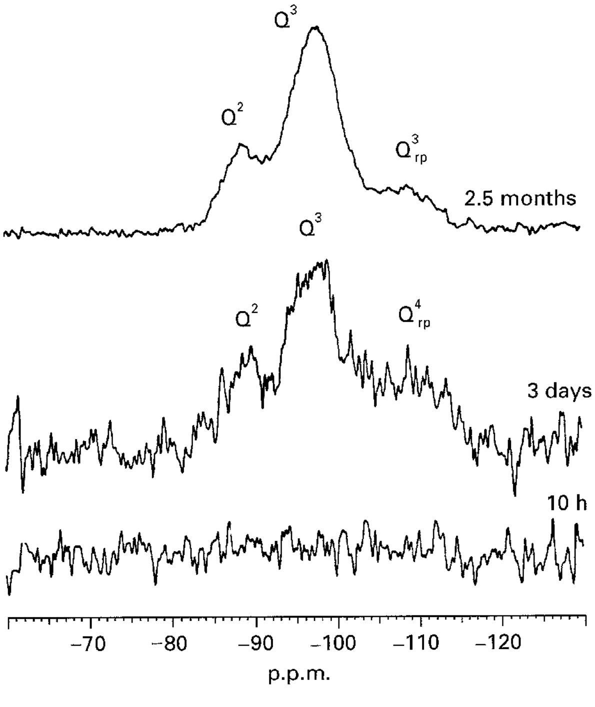

Figure 4 Selected ^{29}Si CPMAS NMR spectra showing the reaction of 5 M KOH solution with silica. 10 Hz of exponential linebroadening was applied to these spectra. Q^4_{rp} denotes Q^4 species contained in the reaction products.

chemical shifts expected for silicate solutions, (see Engelhardt and Michel [4]), the resonances at chemical shifts of − 71, − 78.5, and − 87 p.p.m. can be assigned to Q^0, Q^1, and Q^2 species respectively, with the Q^1 and Q^2 species contained in linear chains. The resonances at − 81 and − 88.5 p.p.m. can be assigned to cyclic Q^2_{cy} and Q^3_{cy} species respectively, both contained in three membered rings. As the reaction proceeds, the proportion of more highly polymerized species within the hydrate increases, and additional peaks appear. The peak at − 94 p.p.m. can be assigned to Q^3 species not contained in three membered rings. The peak at − 108 p.p.m. can be assigned to Q^4_{rp} species within the hydrated reaction products. The linewidths of the resonances increase with time up to 2.5 months. At later ages the peaks assigned to the more highly polymerized species appear also in the CP spectra. No further significant changes were detected in the MAS and CPMAS spectra of this system on continued hydration from 7 months to 2.5 years.

3.3. Alkali hydration of C_3S

C_3S was hydrated with 5 M KOH solution; selected ^{29}Si MAS NMR spectra are shown in Fig. 5. The sharp peaks in the range − 68 to − 75 p.p.m. arise from isolated Q^0 silicate tetrahedra in the C_3S. As hydration proceeds, a major peak is formed at − 79 p.p.m., and can be assigned to dimeric (Q^1) silicate species in a C–S–H; minor peaks are also observed at approximately − 81, − 85, and − 88 p.p.m. The peak at − 85 p.p.m. can be assigned to Q^2 species in the C–S–H, but the peaks, **B** and **C**, at − 81 and − 88 p.p.m., respectively cannot be assigned by reference to spectra of C–S–Hs produced in the absence of alkali. Reaction of the C_3S is nearly complete at 15 days hydration. The linewidths of the Q^1 and Q^2 species are approximately 40 Hz, although the peak at − 81 p.p.m. may be somewhat broader.

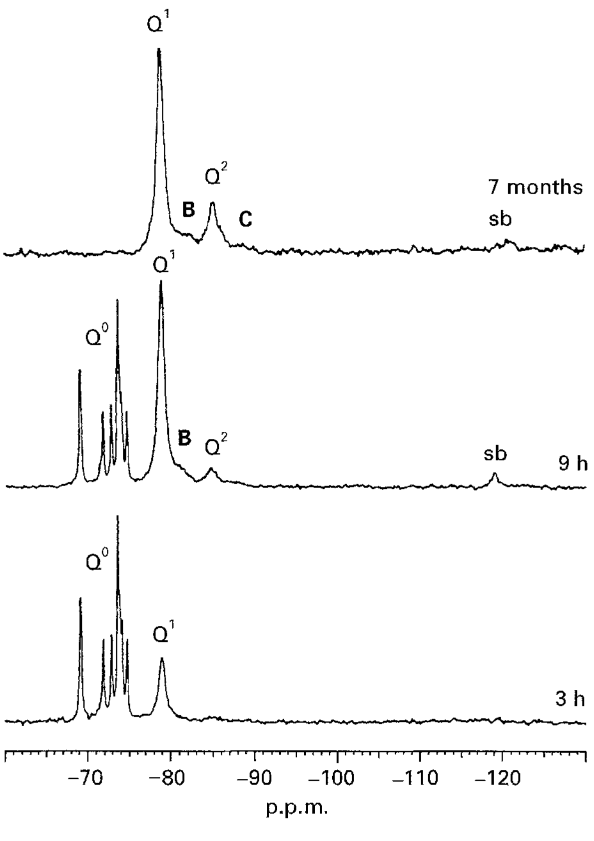

Figure 5 Selected ^{29}Si MAS NMR spectra showing the reaction of 5 M KOH solution with tricalcium silicate. 5 Hz of exponential linebroadening was applied to these spectra. The nature of the peaks **B** and **C** is discussed in the text. Spinning sidebands are indicated by **sb**; they are an artifact of the MAS technique.

Selected ^{29}Si CPMAS NMR spectra are shown in Fig. 6. The intensities of the peaks **B** and **C** are strongly preferentially excited, relative to the intensities of the Q^1 and Q^2 peaks. The line widths of the Q^1 and Q^2 peaks (~ 80 Hz) are also increased relative to those in the MAS spectra.

3.4. Alkali activated simplified blended cement hydration

In this experiment, C_3S containing ^{29}Si at natural abundance (5%) and SiO_2 enriched in ^{29}Si to 100% were hydrated with 5 M KOH. ^{29}Si MAS and CPMAS NMR spectra are shown in Figs 7 and 8, respectively. Over 97% of the ^{29}Si nuclei in this system are initially contained in the SiO_2, and thus signal from silicate species originating in the C_3S is not expected to contribute significantly to the ^{29}Si spectra. At early ages, the amorphous silica can be seen clearly as the broad Q^4 peak at − 112 p.p.m., while the major C_3S resonances are observable as the two small peaks **D** just visible at approximately − 69 and − 73 p.p.m.

As hydration proceeds, peaks are observed at chemical shifts of − 70, − 79 and, after 12 h, − 85 p.p.m.; these peaks may be assigned to Q^0 species in solution or in a motional gel, and Q^1 and Q^2 species in a C–S–H type hydrate, respectively. After 22.5 h of hydration, a wider range of silicate species is observed, with resonances appearing which have similar chemical shifts to those formed in the reaction of alkali with

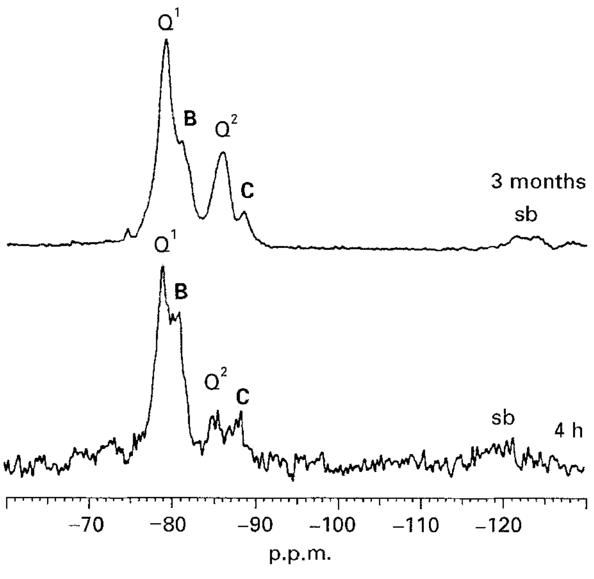

Figure 6 Selected ^{29}Si CPMAS NMR spectra showing the reaction of 5 M KOH solution with tricalcium silicate. 5 Hz of exponential linebroadening was applied to these spectra. Notation as Fig. 5.

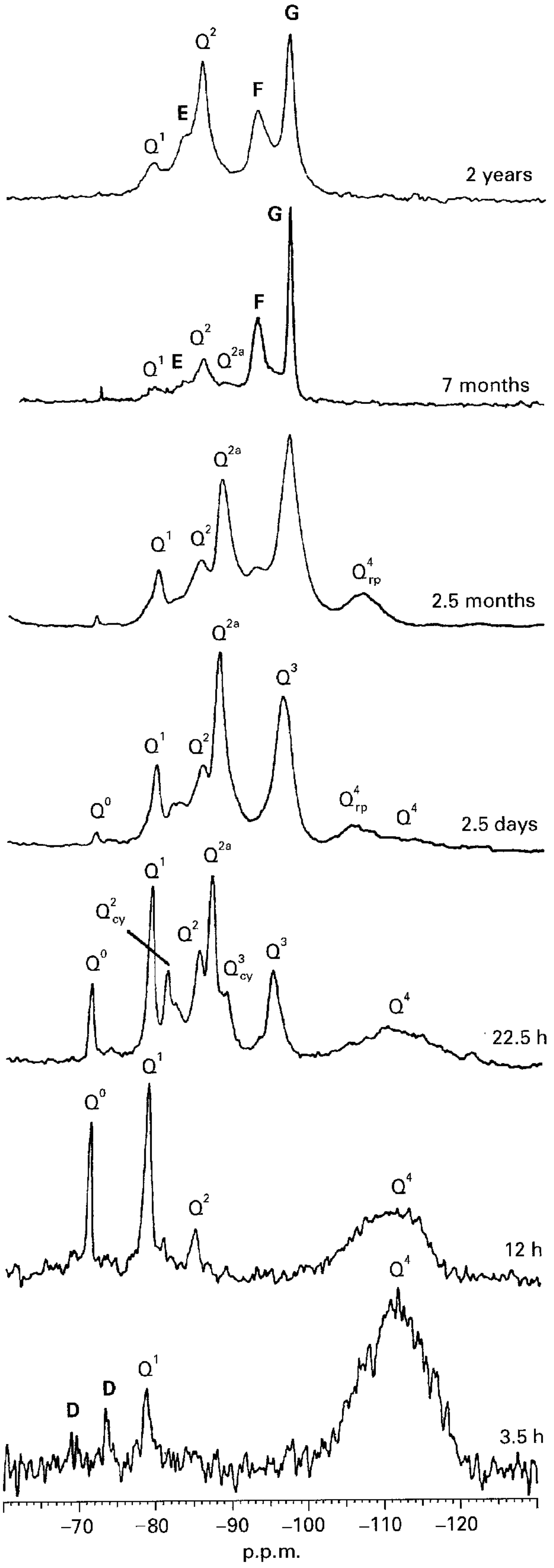

Figure 7 Selected ^{29}Si MAS NMR spectra showing the reaction of 5 M KOH solution with a blend of tri-calcium silicate and silica. 10 Hz of exponential linebroadening was applied to these spectra. Notation as Fig. 3. The nature of the peaks **D**, **E**, **F**, **G** and Q^{2a} is discussed in the text.

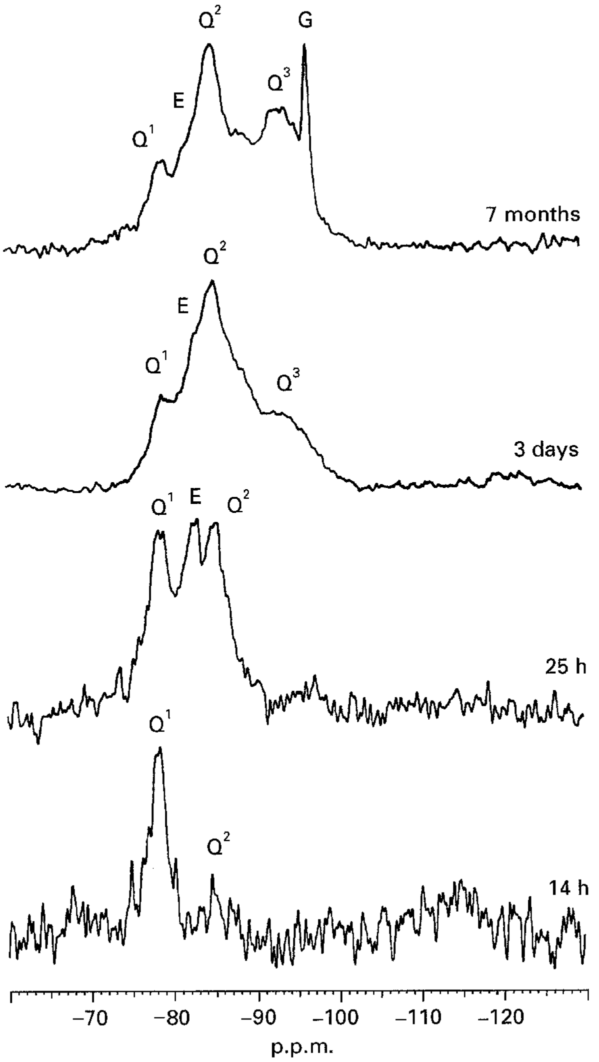

Figure 8 Selected ^{29}Si CPMAS NMR spectra showing the reaction of 5 M KOH solution with a blend of tricalcium silicate and silica. 10 Hz of exponential linebroadening was applied to these spectra. The nature of the peaks **E** and **G** is discussed in the text.

silica discussed above. The resonances at − 81, − 87, and − 88.5 p.p.m. are assigned respectively as Q^2_{cy}, Q^2, and Q^3_{cy} species; the Q^2 resonance is labelled Q^{2a} to distinguish it from the distinct Q^2 resonance due to C–S–H. The CP spectra only show excitement of the peaks at − 79 and − 85 p.p.m.

After three days of hydration, the various peaks start to broaden and overlap; additionally a broad Q^3 resonance is excited in the CP spectra. At the latest ages studied, the ^{29}Si MAS spectra change significantly, with loss of the broad peaks at − 88, − 96, and − 105 p.p.m., assigned to Q^2, Q^3, and Q^4 species in a hydrated alkali silicate. Relatively sharp peaks **F** and **G** appear at − 93 and − 97 p.p.m., but are inefficiently excited in the CP spectrum. Peaks Q^1, **E**, and Q^2, at − 79, − 82.5, and − 85 p.p.m., respectively, remain in the MAS spectra and are also excited in the CP spectra. The peak **E** is also prominent at earlier ages in the CP spectra, while barely detectable in the MAS spectra.

X-ray diffraction (XRD) spectra acquired after the experiment was terminated at 2 years of hydration time showed no peaks due to crystalline phases; some diffuse peaks, probably due to C–S–H, were observed.

From 7 months to 2 years, the ^{29}Si MAS NMR peak positions remain constant, but there are large changes in their relative intensity. The Q^2 resonance increases slightly relative to Q^1, while the peaks **F** and

G have considerably reduced intensities relative to the other peaks.

4. Discussion

The use of ^{29}Si enrichment has enabled excellent NMR spectra to be obtained for all of the reaction systems studied in this work. The use of this material, however, in small quantities, and in a sealed rotor insert, makes it impossible to check other properties of the samples, except at the conclusion of the experiment. Despite long T_1 values of the Q^4 resonances, good signal-to-noise ratios were obtained, although partial saturation of the Q^4 species limits the quantitative interpretation of the results.

4.1. Simple pozzolanic reaction

The reaction of CaO with amorphous SiO_2 at 40 °C (Figs 1 and 2) proceeds very differently from the hydration of C_3S [1] (which has the same overall Ca/Si ratio as the pozzolanic system studied here). At all ages, the pozzolanic hydrate has longer chains. In addition, the peaks have narrower line widths in the pozzolanic hydrate (40 Hz) than those in samples of pure C_3S hydrated at a similar temperature (typically 80 Hz – see for example [1]). The asymmetry of the Q^2 peak seen in this pozzolanic sample is not seen in hydrated samples of C_3S. Similar narrow line widths and asymmetry, or even resolution of a distinct peak at -82.5 p.p.m., is found for C–S–H produced in the proximity of reacting silica in the hydration of C_3S in the presence of high levels of admixed silica [18, 19].

Q^3 species are also observed in the pozzolanic hydrate; such highly polymerized species have never been observed in samples of hydrated calcium silicates, but are instead characteristic of hydrate produced in blended cements having relatively low Ca/Si ratios [23]. The linewidth of the Q^3 resonance is similar to that for the amorphous silica Q^4; it is unclear if the Q^3 species are present in a modified silica phase, or simply are present in highly disordered cross-linked regions of the C–S–H.

Little change occurs in the spectra observed from 6 to 15 days of hydration, but longer-term experiments are required to determine if the distinctly pozzolanic hydrate persists to later times, or if a more ordinary C–S–H forms as the system approaches equilibrium. The pozzolanic C–S–H presumably is generated by formation of C–S–H in a relatively calcium deficient environment close to the silica grains. The presence of peaks from all the phases in the CP spectra indicates a relatively rigid hydrate. Peak **A** experiences considerable preferential excitement; its origin is unclear, but it may arise from similar material to that giving rise to peaks **B** and **C** in the alkaline hydration of C_3S (see below).

4.2. Alkali silica reaction

Silica dissolution in the absence of calcium ions (Figs 3 and 4) gives products very different from those formed in the presence of calcium. A process of gradual polymerization occurs [7], starting from monomeric silicate species, and proceeding through a range of more highly polymerized species. The lower cation-to-silica ratio of the system studied in this paper, relative to that in reference 7, results in products that are more highly polymerized. As hydration proceeds, and further silica reacts, the line widths in the spectra also increase, and some of the peak positions shift upfield. The Q^3 peak, for example, gradually broadens and shifts from -94 to -97 p.p.m., which is consistent with a change from Q^3 species which are cross-linking chains of Q^2 and Q^1 species, to Q^3 species which are present within a highly cross linked hydrate. Similarly, Q^4 species in the fully cross-linked amorphous silica reagent resonate at -112 p.p.m.; Q^4_{rp} species in the early reaction product resonate at approximately -104 p.p.m. but move upfield to about -108 p.p.m. as the reaction products become more highly cross-linked.

Initially protons within the gel undergo significant motion on the timescale of the CP contact time (4 ms), as shown by the lack of signal in the CP spectra; once significant quantities of silica react, and Q^4 species are formed in the hydrate, the products become more rigid, as indicated by the appearance of signal in the CP spectra. Only the more highly polymerized species are seen in the CP spectra. A multiphase system may form, in which a highly cross-linked alkali silicate phase is distributed within a solution phase containing less polymerized species; alternatively, there may be a single phase, in which Q^1 and some Q^2 species, due to their lack of three-dimensional cross-linking, are able to undergo motion and thus do not appear in the CP spectra.

4.3. Alkali hydration of C_3S

The alkaline hydration of C_3S (Figs 5 and 6) differs significantly from hydration in DI water (the hydration in DI water of a similar sample of C_3S is discussed in [1]). The reaction of the C_3S is accelerated significantly, with almost complete hydration in 15 days in 5 M KOH, in contrast to hydration in H_2O, where 20% of the C_3S remains unreacted at the same age. Under alkaline conditions, the hydrate is significantly less polymerized both after a given time, and for a given extent of reaction of the C_3S. At 90% reaction, for example, the average chain length is approximately 2.3 for alkaline hydration, but approximately 3 for hydration in DI water [1]. If a model of C–S–H formation is adopted in which silicate dimers are formed initially, and then linked with monomers to form longer chains, then the formation of mainly dimeric species in alkaline hydration of C_3S may arise simply by acceleration of the hydration reaction to form dimeric (Q^1) silicate species, without an acceleration of the linking reaction that creates longer chains (containing also Q^2 species). As a result, the supply of monomer runs out while the chains are still relatively short, and further polymerization cannot occur without rearrangement of the existing silicate species in the C–S–H.

We are not aware of previous reports of peaks similar to **B** and **C** at − 81 and − 88 p.p.m. respectively, contained in pastes formed by hydration of C_3S; a peak at − 81 p.p.m. has, however, been observed in samples of synthetic jennite [24]. The peak widths in these alkali hydrated materials are exceptionally narrow for C–S–H gels, and closer inspection of ^{29}Si MAS NMR spectra of samples hydrated in water [1] reveals the possibility of a minor peak similar to **B**, which had not been identified previously due to severe overlap with the intense and relatively broad Q^1 peak at − 79 p.p.m. The considerable preferential excitement in the CP spectra of the peaks at − 81 and − 88 p.p.m. is not observed in samples hydrated with water; this suggests that **B** and **C** may, in the present case, arise from protonated groups. This is consistent with the increased shielding [4] of the chemical shifts by 2–3 p.p.m. upfield of the normal positions for Q^1 and Q^2 species in C–S–H. An assignment to Q^2 and Q^3 groups in cyclic trimers in solution, consistent with the chemical shift values, can be eliminated because such species would not be excited in CP spectra.

4.4. Alkali activated simplified blended cement hydration

This system (Figs 7 and 8) is the most complex of the systems studied in this work, with the potential for product formation by alkali dissolution of silica, or by formation of C–S–H either directly from C_3S, or indirectly by pozzolanic reaction of silica with lime generated by hydration of C_3S. In the spectra, two sets of peaks are observed; one set (Q^0, Q^1, Q^2_{cy}, Q^{2a}, Q^3_{cy}, Q^3, Q^4_{rp}, **F** and **G**) can be assigned to alkali silicate hydrates, while the other set (Q^1, **E** and Q^2) can be assigned to a C–S–H like phase. Only the silica was enriched, so silicate species originating from the C_3S will have negligible intensity in these spectra.

The alkali silicate hydrate initially contains Q^0, Q^1, Q^2_{cy}, Q^{2a}, Q^3_{cy}, Q^3 and Q^4_{rp} peaks; it undergoes progressive polymerization. The silicate species in this phase are not in a rigid environment, since none of the resonances is significantly excited in the CP spectra. At a given time of hydration, the apparent degree of polymerization is much lower than for the simple alkali silica reaction studied above, probably because of the higher alkali-to-silica ratio (although the preferential enrichment of silica in this system may result in distortion of relative intensities). At the latest ages studied, peaks from this alkali silica hydrate are reduced in intensity, and formation of a new phase occurs, with appearance of peaks **F** and **G** at − 93 and − 97 p.p.m. respectively, which can probably be assigned to Q^3 species. These peaks are not excited efficiently in the CP spectra, suggesting that the new phase is either highly motional, or that the silicate groups are well separated from protons (i.e. from water molecules). Crystallization of Na_2SiO_3 and $KHSiO_3$ has been observed previously by XRD in similar systems [25], but no crystalline phases were detected by XRD of the sample, which gave rise to peaks **F** and **G**.

The other set of peaks is similar to those formed in the pozzolanic hydration of silica in the absence of alkali to give long chain C–S–H; since the C_3S was not ^{29}Si enriched, the observed silicate species in this C–S–H were originally located in the silica. The preferential enrichment means that it is not possible to determine an average chain length; however, the high proportion of Q^2 species suggests that the silicate chains are fairly long. These peaks are excited efficiently in the CP spectra, which is consistent with their assignment to C–S–H. The minor peak, **E**, at − 82.5 p.p.m. has been observed previously, and has been shown to result from long chain C–S–H formed by pozzolanic reaction of silica [17, 18]. The formation of two distinct hydrates in this system is consistent with the long term equilibrium studies of the C–S–N–H system performed by Kaluosec [8] and by McPhee *et al.* [9], neither of which reported phases which contained high levels of both calcium and alkali.

There was a significant increase in the intensity of the CSH peaks relative to **F** and **G** between the spectra acquired at 7 months and at 2 years; these are changes in areas, not just in maximum intensities. By analogy with hydration of blended cements it is reasonable to assume that much of the C–S–H occurs as inner products immediately surrounding the C_3S, grains, and will thus initially largely contain only silicate species from the C_3S, which are not enriched in ^{29}Si. The intensity changes can be explained by the slow chemical exchange over many months of these unenriched silicate species for silicate species from the amorphous hydrated alkali silicate, which would be expected to contain more enriched ^{29}Si species originating in the ^{29}Si enriched silica. Three other possible mechanisms for the intensity changes can be excluded. Carbonation of the C–S–H would tend to polymerize the C–S–H, and convert Q^1 and Q^2 resonances to Q^3 and Q^4 resonances; crystalline products of carbonation (e.g. calcite) were not observed by XRD. Loss of the phase containing the resonances **F** and **G** from the sealed rotor insert can be discounted. Conversion of the small amounts of Q^{2a} species, and the associated Q^3 species etc., that remain at 7 months to the species **F** and **G** would increase rather than decrease the peaks **F** and **G**.

5. Conclusions

1. *In situ* experiments have enabled excellent MAS NMR spectra to be obtained for the reaction systems studied in this work, although the use of sealed samples limits the use of other techniques to characterize the reactions.

2. The simple pozzolanic reaction of free lime with silica at a Ca/Si atomic ratio of 3.0 produces hydrate significantly different from that formed by hydration of C_3S. The C–S–H is more crystalline, and has much longer chain lengths, at least at the relatively early ages studied. In addition, cross-linking (Q^3) species are observed; such species have not been reported in the hydration of calcium silicates.

3. The hydrates formed in the reaction of alkali hydroxide with amorphous silica differ significantly

from normal C–S–H; a much wider range of species (Q^0–Q^4) are observed, and the degree of polymerization and also of cross-linking progressively increases with time. The absence of signal in CP spectra acquired at early stages of reaction indicates that, at early ages, there is a substantial degree of motion in these alkali silicate hydrates.

4. C_3S hydration is strongly accelerated by alkali. The hydrate formed under alkaline conditions has much shorter chains, and a higher degree of local order, than that produced by hydration of C_3S in DI water. In addition to the Q^1 and Q^2 peaks at -79 and -85 p.p.m. respectively, minor peaks **B** and **C** are observed at -81 and -88 p.p.m., which are strongly excited in CP spectra, perhaps due to attachment of silanol groups. These additional peaks warrant further investigation.

5. The hydration of C_3S and silica in a concentrated alkali solution gives rise initially to two distinct products, an alkali silicate similar to that formed in the reaction of alkali with silica, which undergoes motion at or above the timescale of the CP contact time (4 ms), and a C–S–H like product. The alkali silicate product underwent a phase change to a more ordered gel, containing only two distinct resonances, which was less motional, with one of the resonances undergoing CP. Slow exchange of silicate groups, over periods of months, probably took place between the C–S–H and the alkali silicate phases.

6. A very wide range of products have been observed in this paper, from dimeric silicates through to highly cross linked systems, and from rigid hydrates through to very motional silicates. In realistic OPC systems, the presence of aluminium is likely to add further complexity.

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