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^{29}Si MAS NMR study of the hydration of tricalcium silicate in the presence of finely divided silica

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^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy has been used to investigate the effect of finely divided silica on the hydration of tricalcium silicate (C_3S). In order to reduce the time needed to obtain quantitative results, low levels of paramagnetic iron oxide were added to materials to increase the nuclear relaxation rate. The reactions of the C_3S and the finely divided silica could then be monitored separately and without chemical modification. The results were correlated with data from microcalorimetry, thermogravimetric analysis and electron microscopy. Under the conditions used here the presence of the silica accelerates greatly the hydration process, and results in a markedly increased degree of polymerization in the resulting gel, without significantly affecting the induction period of the reaction. The significance of these results for understanding the hydration process of C_3S in the presence of silica is outlined.

1. Introduction

Tricalcium silicate (C_3S) is the main reactive component of Portland cement. It contains monomeric silicate units [1], which polymerize during hydration to form an amorphous calcium silicate hydrate (CSH) gel [2], along with crystalline calcium hydroxide. The polymerization reaction has been followed using a variety of analytical techniques including trimethylsilylation [3], paper chromatography [4] and the molybdate reaction [4]. These methods are, however, limited to a study of species in solution and thus involve chemical manipulation of the hydrated cement prior to analysis. ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) has recently been shown to be a powerful technique for the study of the reactions in the powdered solid matrix of hydrating calcium silicates [5–7]. The chemical shifts of the resonances of the ^{29}Si nuclei in silicates are dependent on the degree of condensation of the silicate tetrahedra; increasing diamagnetic shielding of the ^{29}Si nucleus with increasing condensation leads to higher field chemical shifts. Resonances can therefore be assigned to ^{29}Si nuclei in units of particular condensation [8] namely Q_0, Q_1, Q_2 and Q_4). In addition, provided there are no saturation effects, the NMR signal intensity is proportional to the number of nuclei present, so the extent of the reaction can be easily determined.

In order to increase the strength of cement systems, methods for reducing the overall porosity and optimizing the pore size distribution have been explored. One approach has been to use "densified systems containing homogeneously arranged ultra fine particles" or DSP materials [9]. These systems contain ordinary Portland cement, finely divided silica and a superplasticizer. The superplasticizer acts as a dispersing agent facilitating the dense packing of the cement and silica. Finely divided silica consists of between 85 and 96% amorphous silica with a surface area of about 20 $m^2 g^{-1}$. The particle size lies between 0.01 and 0.3 μm with about 70% less than 0.1 μm, which is two orders of magnitude smaller than that of the cement grains. The silica does not act simply as a physical filler; chemical analysis shows that it reacts with ions in the alkaline pore solution and may interact with the CSH gel material produced during the hydration of the calcium silicate phases [10, 11]. Studies using electron microscopy and calorimetry show that the silica accelerates the early hydration of the cement phase, and demonstrate that increasing quantities will reduce the length of the induction period of C_3S (11, 12).

In this paper, ^{29}Si MAS NMR has been used in conjunction with other techniques to study the reaction of pure C_3S with finely divided silica under carefully controlled conditions. The investigation provides further information about the nature of the hydration

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reaction and the interaction with the finely divided silica present in the system.

2. Experimental procedure

Tricalcium silicate was prepared from colloidal silica and $CaCO_3$ using standard techniques [13]. Samples containing varying amounts of iron were prepared by grinding C_3S with an appropriate quantity of Fe_2O_3 to give an homogeneous mix. This was then formed into pellets and fired at 1500° C for 6 h. The resulting powders were characterized using XRD to confirm retention of the triclinic C_3S crystal structure, and atomic absorption spectroscopy to determine the quantity of iron present.

The finely divided silica was provided by Aalborg Portland. It was found to have a surface area of $19\,m^2\,g^{-1}$ as measured from an adsorption isotherm of nitrogen (at 77 K) obtained volumetrically using a commercial instrument (Carlo Erba, Sorptomatic) [14]. The silica containing up to 0.4% of iron was mixed with samples of the doped C_3S in the ratio of 1 to 4 by weight, respectively. A water-to-solid ratio of 0.5 was used for the hydration reaction and the samples were placed in sealed tubes in a water bath at 25° C. Sample tubes were removed after various times between 2 h and 28 days and the reaction quenched by the addition of propan-2-ol, followed by drying in a vacuum desiccator.

^{29}Si NMR spectra was recorded using MAS at 39.73 MHz using a Bruker CXP200 solid state NMR spectrometer with an Aspect 2000 data system. Powdered samples were packed into mushroom Andrew-type rotors. Rotation rates were typically 3 kHz. Proton decoupled single pulse spectra were accumulated using recycle delay times for the doped samples (see below) of typically 2 sec. Cross polarization (CP) spectra [8, 15] were aquired using a contact time of 0.75 msec and recycle delay times of 3 sec. Longitudinal relaxation times (T_1) were measured by the standard inversion–recovery pulse sequence (180°–τ–90°) under MAS. ^{29}Si chemical shifts are given relative to trimethylsilane (TMS), with a trimethylsilylester of a double four-ring silicate (Q_8M_8) used as a secondary standard [5–7].

The process of hydration was followed by other more standard techniques. Microcalorimetric data were obtained using a "Calox" calorimeter [16]. Electron microscopy was carried out using a Jeol 2000FX STEM microscope. Transmission electron microscopy specimens were prepared using conventional ion-beam milling [17]. Thermogravimetric analysis (TGA) was performed with a Stanton-Redcroft TG.750 balance as previously described [18].

3. Results

3.1. NMR spectra of anhydrous materials

Fig. 1a shows the NMR spectrum of pure C_3S mixed with a finely divided silica having a low iron content (0.01% by weight). The pulse repetition rate used was 2 sec and over 1000 scans were collected. It is possible to observe the C_3S resonances between −69 and −75 p.p.m. [5–7]; the broad resonance at −113 p.p.m. is attributed to the silica. The signal-to-noise ratio in the spectrum is, however, extremely poor. The spectrum of the sample was greatly improved by increasing the time between pulses to 60 sec (Fig. 1b) showing that at the shorter delay time considerable saturation of the nuclear resonances must be occurring. The observed saturation in the spectrum recorded with the shorter delay between pulses indicates that the starting materials have long T_1 relaxation times; indeed measurements indicate that both anhydrous C_3S and the silica have T_1 values of more than 60 sec. Relaxation times of this order make it impossible to acquire spectra with good signal-to-noise ratios and reliable relative peak intensities in acceptable lengths of time. In glasses similar problems are encountered where trace paramagnetic ions have been used to considerably increase rates and hence reduce the delay required between pulses [19]. Investigation of the effects of trace paramagnetic ions on the relaxation rates of C_3S and silica was

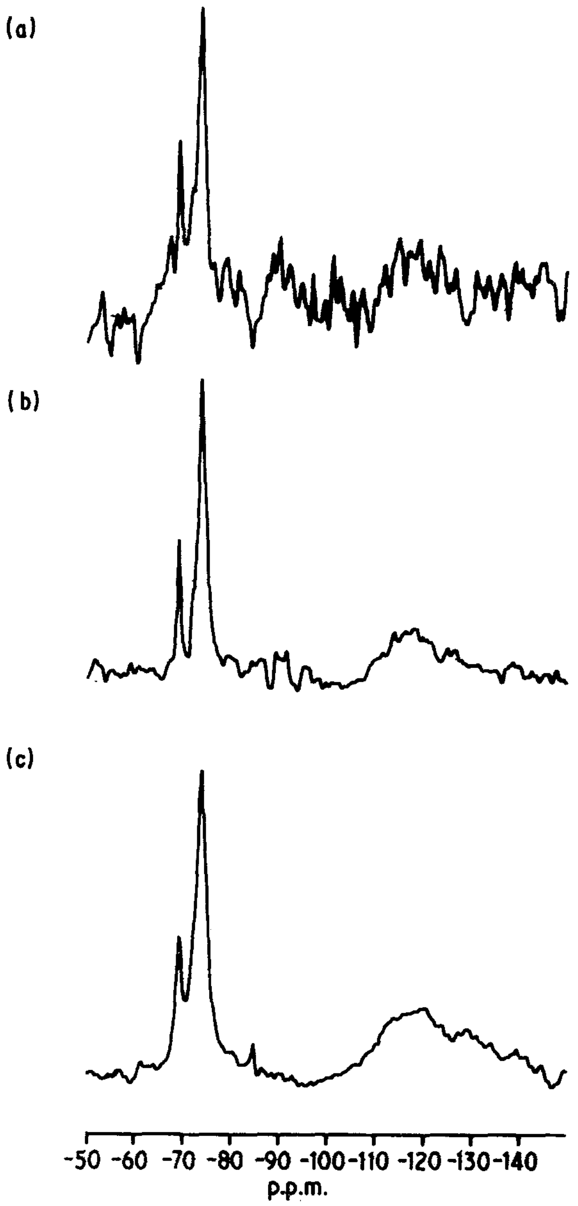

Figure 1 ^{29}Si MAS NMR spectra of (a) C_3S mixed with silica of low iron content (0.02% by weight) recorded using a recycle delay time (D_0) of 2 sec; and (b) the same sample recorded with a D_0 of 60 sec; and (c) doped C_3S mixed with silica containing 0.4% by weight of iron, recorded with a D_0 of 2 sec.

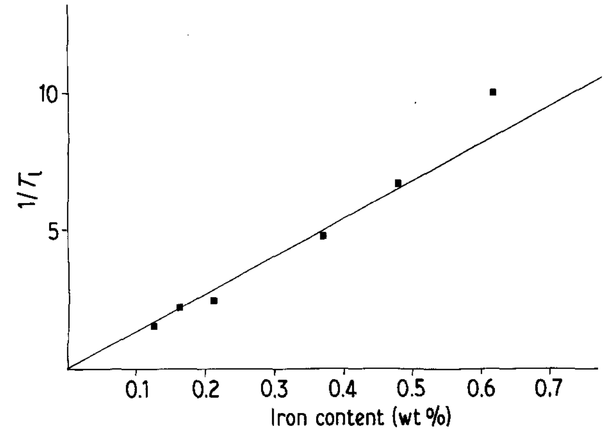

Figure 2 The reciprocal of the longitudinal relaxation time constant ($1/T_1$) plotted against percentage of iron content for a series of doped C_3S samples.

therefore carried out prior to study of the hydration process.

The ^{29}Si MAS NMR spectrum of pure C_3S is consistent with the crystal structure evidence for nine different sites [1] and at least six different lines can be completely resolved [5–7]. The T_1 values were found to show a dramatic decrease with increasing levels of iron (see Fig. 2); there is a reduction of at least two orders of magnitude resulting from levels of iron as low as 0.2% by weight. As the level of iron in the doped sample is increased, however, the linewidths of the resonances increase and resolution in the spectra is progressively lost. Despite this, at a level of 0.3% iron by weight, five resonances in the spectrum can be observed.

Finely divided silica gives rise to broad lines in the NMR spectra even in the absence of paramagnetic ions. The linewidths are comparable with those of glasses [19, 20], and results from the presence of a distribution of Si–O–Si bond angles and Si–O bond lengths. Commercially available finely divide silica contains varying levels of iron and the relaxation behaviour of these was investigated. An iron level content of 0.4% was found to reduce the T_1 value from more than 100 sec to less than 1 sec without significant additional linebroadening.

Fig. 1c shows an accumulation using a pulse repetition rate of 2 sec from a mixture of doped C_3S (0.3% iron by weight) and a fume with a high iron content (0.4% iron by weight). The C_3S and silica resonances can be observed with excellent signal-to-noise ratios without preferential saturation of either component. The relative areas of the C_3S and fume peaks are 52% and 48%, respectively, which are very close to the values expected for this composition (54% to 46%). Thus by doping the system to a suitable level with iron, spectra with accurate peak intensities can be acquired over a much shorter period of time, for example (Fig. 1c) in 40 min (for 1200 scans) instead of in excess of the 20 h that is required for a comparative spectra of an undoped sample.

3.2. NMR studies of the hydration of C_3S in the presence of finely divided silica

Fig. 3 shows the NMR spectra of samples of C_3S

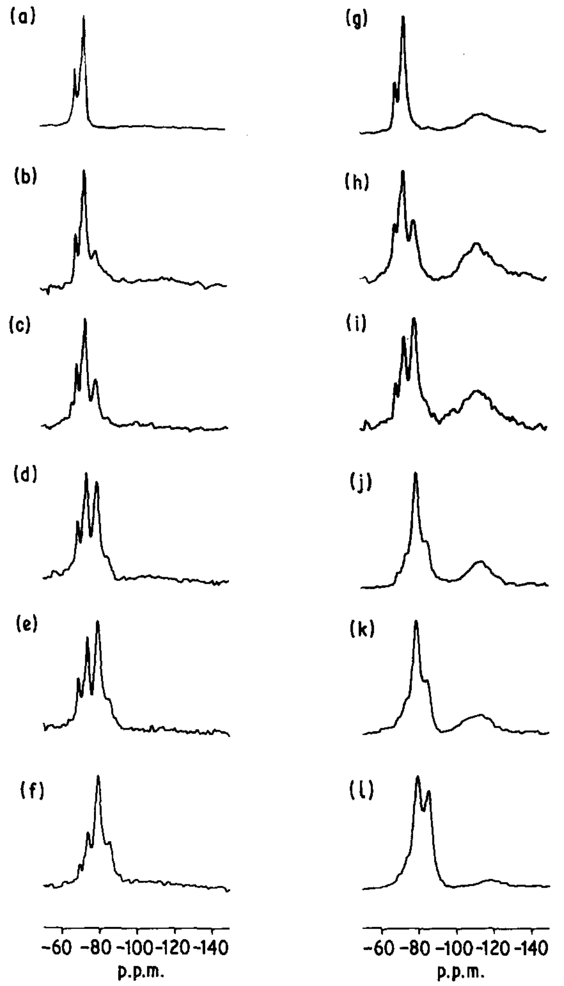

Figure 3 ^{29}Si MAS NMR spectra of the progressive hydration of doped C_3S in the absence of finely divided silica after (a) zero time; (b) 12 h; (c) 24 h; (d) 4 days; (e) 8 days and (f) 24 days. The corresponding spectra for the hydration of C_3S in the presence of finely divided silica are shown after (g) zero time; (h) 12 h; (i) 24 h; (j) 4 days; (k) 8 days and (l) 28 days. All the spectra are shown scaled relative to the most intense peak. This accounts for the apparent change of intensity of the Q_4 peak between spectra (g) and (h), as the spectra are scaled relative to the peak at -73.9 p.p.m., which decreases in intensity over this time period relative to the Q_4 peak.

hydrated in the presence and absence of finely divided silica; in these and all subsequent spectra C_3S contains 0.3% iron by weight. The hydrated species even in the absence of iron have short T_1 values, less than 1 sec; there is therefore no saturation of these resonances in the spectra under any conditions used here. The hydration reaction was followed in detail by recording spectra of samples hydrated for different lengths of time and then analysing the spectra by means of a lineshape simulation program (Fig. 4). Iterative calculations were carried out varying the relative intensities of the different components to determine the best fit to the experimental spectra. The anhydrous C_3S spectrum was simulated by a set of five resonances between -69.1 and -74.8 p.p.m. The results are represented graphically in Figs 5a and b, which shows the relative proportion of the different chemical species as they vary during the course of the reaction.

The results for the hydration of C_3S in the absence of silica are fully in accord with previous data obtained for undoped C_3S [6, 7]. This experiment shows that the presence of small amounts of iron does

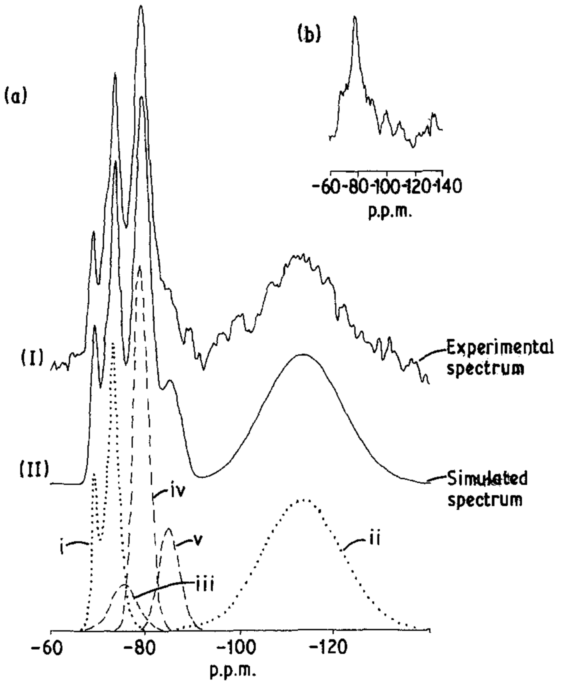

Figure 4 (a) Experimental ^{29}Si MAS NMR spectrum of doped C_3S and finely divided silica hydrated for 24 h (I). The simulated spectrum (II) is shown offset. The deconvoluted Gaussian components of (II) correspond to the anhydrous starting material, (i) and (ii) (C_3S (Q_0) and the silica (Q_4), respectively); and the developing hydrated material, (iii), (iv) and (v) (hydrated monomer (Q_0^H) and polymerized silicate units (Q_1 and Q_2), respectively). (b) ^{29}Si CP MAS NMR spectrum of the same sample showing the hydrated silicate species. i.e. Q_0^H, Q_1 and Q_2. In the CP spectrum the relative intensities of the peaks need not correspond directly to the relative intensities of the species [13]. Note that no silica (Q_4 species) is detected.

TABLE I TGA results in the absence and presence of silica

Silica	Time (days)	$Ca(OH)_2$ (%)	Degree of hydration of C_3S (%)	C/S ratio
Absent	0	0	0	–
	1	16.4	40	1.7
	4	23.8	55.5	1.7
	8	26.0	59	1.6
	14	29.5	71	1.7
	28	30.8	76	1.8
Present	0	0	0	–
	1	18	21	1.8
	2	16.7	22	1.8
	4	14.5	20	1.7
	7	14.2	17	1.6
	8	13.0	84	1.6
	14	12.8	82	1.5
	28	10.2	83	1.5

not result in significant changes in the time course or nature of the hydration reaction. Dimeric silicate species are the initial hydration product. These then react to form higher polymers with the C_3S being steadily consumed. This can be seen in the spectra of Fig. 3 as the build up of Q_1 and Q_2 species at the expense of the anhydrous C_3S. After 28 days, just over 75% hydration has occurred and the reaction has slowed considerably.

In the presence of silica, marked differences in hydration behaviour are revealed from the NMR spectra. First, the intensity of the Q_0 (anhydrous C_3S) peak is reduced to less than 20% of its original value after the first 24 h hydration, in the absence of silica this figure is 60%. In accord with this the hydration products, revealed by the Q_1 and Q_2 peaks in the spectra are formed much more rapidly than during hydration in the absence of silica. Second, the intensity of the Q_4 (silica) peak decreases steadily during hydration, showing that the silica is undergoing reaction. The rate of this reaction is, however, much slower than that of C_3S. Third, whilst the Q_2 peak increases markedly throughout the reaction, the Q_1 peak having increased steadily, begins to decrease in intensity after about 8 days. It can be calculated that the average chain length of the silicate in the hydrated gel increases, from 2.3 (after 24 h) to 3.6 (after 28 days). In the absence of silica the average chain length only reaches a value of 2.6 even at the end of the time course (see Table I). Fourthly, the Q_0 region of the system shows a broad peak over which the anhydrous C_3S peaks are superimposed. Cross polarization (CP) MAS NMR experiments show that this arises from hydrated monomeric silicate units [13]; this experiment only detects resonances from species close to protons (see Fig. 4b). The spectrum of the Q_0 region shows a broad peak of low intensity. This peak was previously obscured by the anhydrous C_3S resonances in the single pulse experiments. Simulations of this peak show that the amount of hydrated Q_0 material appears to remain constant at about the 5% level throughout the time course of the reaction. Previous work in the absence of finely divided silica has shown the presence of hydrated Q_0 species at a level below 2% during the induction period [13].

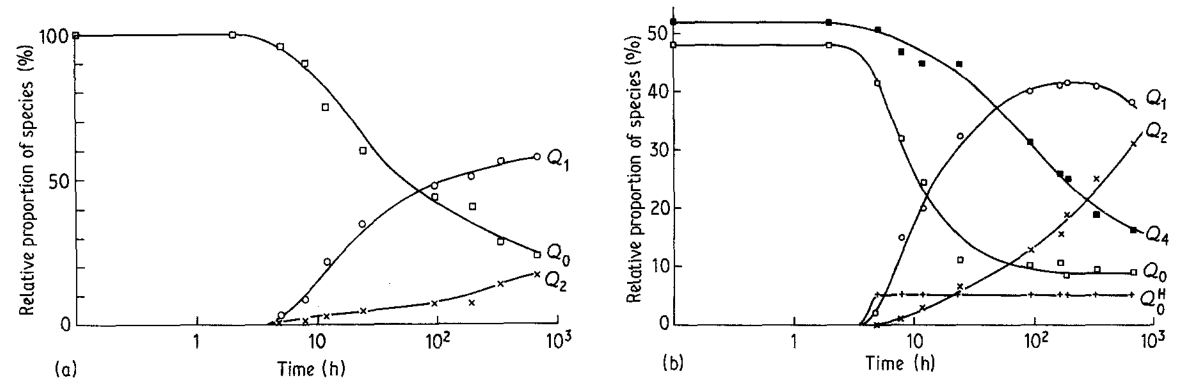

Figure 5 Relative proportions of silicate species present during the progressive hydration of (a) doped C_3S, and (b) doped C_3S and finely divided silica. N.B. Curves show proportions of respective silicon species as designated and described in text.

3.3. Investigation of the hydration by other techniques

3.3.1. *Microcalorimetry*

Results of microcalorimetric studies show that the induction period is 190 ± 10 min in the presence of finely divided silica and 190 ± 20 min in its absence; the induction period is not therefore significantly affected by the presence of this level of silica. This is in agreement with the NMR spectra; which show no change during this period, even in the presence of finely divided silica. The overall heat output for the first 24 h hydration in the presence of silica was $208\,J\,g^{-1}$, compared with $152\,J\,g^{-1}$ in its absence. There is, therefore, considerably higher heat output in the presence of silica, which might be expected from the much greater extent of reaction in the first day evident in the NMR spectra. The increased heat output is, however, less than that anticipated from the increased extent of reaction which would be $232\,J\,g^{-1}$.

3.3.2. *Thermogravimetric analysis*

The TGA data enable the quantity of $Ca(OH)_2$ in the hydration product to be determined, and measurements were made, as described previously [18], on samples prepared for the NMR experiments. In the absence of finely divided silica the quantity of $Ca(OH)_2$ formed increases regularly as the reaction proceeds. In the presence of silica, however, the $Ca(OH)_2$ level reaches a maximum, well below that finally reached in the absence of silica and begins to fall within the first 2 days (see Table I). These data are consistent with the reaction of silica with the $Ca(OH)_2$ generated by the hydration of C_3S in accordance with previous conclusions [11, 12, 21]. On the assumption that the silica reacts only with the $Ca(OH)_2$, and using the direct measurement of the degree of reaction of the silica determined by NMR, the calcium-to-silicon (C/S) ratio of the CSH gel can be calculated for the system [7]. The average C/S ratio of the CSH gel in the absence of silica remains constant at 1.7 ± 0.1 (see Table I), but in its presence the overall C/S ratio falls throughout the time course (see Table I); after 28 days it is approximately 1.5. This value is in good agreement with the data of Wu and Young [11].

3.3.3. *Electron microscopy*

Scanning electron microscopy of the fracture surfaces was carried out for the samples hydrated both in the presence and absence of finely divided silica. They show very similar features, see Figs 6a and b. In both cases large lamellar $Ca(OH)_2$ crystals can be seen running between the fibrillar masses of the CSH gel. As is common in mature C_3S pastes [22], fracture has taken place between the inner and outer hydration products revealing areas of fairly featureless gel. Transmission electron microscopy of the ion-beam thinned specimens provides a more accurate indication of the location of the silica particles. Fig. 6d shows a sample of C_3S hydrated for 28 days in the presence of silica. The silica particles can be seen in the outer regions of the CSH gel. No particles are detectable in the inner product. The reaction of the silica particles is evident from the boundary between the silica and the outer CSH gel becoming less distinct. Indeed some of the smaller particles have completely disappeared.

Microanalysis of regions of the CSH gel observed in transmission electron microscopy micrographs reveal that without finely divided silica the inner product CSH has a C/S ratio equal to 1.68 ± 0.07 whilst the inner product CSH with silica present has a C/S ratio equal to 1.6 ± 0.15. However, there are areas of the pastes with silica which appear to consist entirely of CSH gel and give a C/S ratio of 0.92 ± 0.09. These are presumably areas of aggregated silica particles which have reacted completely with the available calcium ions to give a lower than normal C/S ratio CSH. Thus the overall C/S ratio of the gel falls as the reaction proceeds and more of the silica reacts. These results are in full agreement with the TGA and NRM results.

4. Discussion

^{29}Si MAS NMR has enabled the reaction of C_3S and finely divided silica to be followed. Unlike previous methods [23] used to study composite systems the reaction of the different components have been observed directly without dissolution of the species involved. The NMR experiments were found to complement the information from more conventional techniques such as microcalorimetry, thermogravimetric analysis and electron microscopy, and to give additional information about the C_3S silica reaction.

Our previous studies of the reaction between tricalcium silicate and finely divided silica by ^{29}Si NMR have proved difficult because of the very long relaxation time of the ^{29}Si nucleus in both pure C_3S and finely divided silica. This created problems in obtaining quantitative measurements of the different components, and in obtaining sufficient good signal-to-noise ratios in acceptable lengths of time. We have demonstrated that it is possible to reduce significantly the relaxation times of the components of the system by doping with paramagnetic ions so that fully quantitative spectra can be obtained in as little as one-twentieth of the time needed for undoped samples. We have also shown that the addition of the required small amounts of iron does not alter the hydration reaction of the C_3S. This approach is likely to be of considerable value in studying systems of this type.

In accordance with previous studies [10–12, 21, 24], the NMR experiments show that the presence of finely divided silica greatly accelerates the hydration of the C_3S. This acceleration occurs without affecting the length of the induction period, in agreement with the data of Halse *et al.* [12, 24]. Other studies [10, 11] have indicated that when greater amounts of silica are present there is a marked reduction in the length of the induction period. There are, however, significant differences in the details of some aspects of the results from previous studies. First, Wu and Young [11] concluded from a comparison of the degree of hydration as determined by trimethylsilylation and quantitative X-ray diffraction studies that no hydrated monomer is formed in this reaction, despite

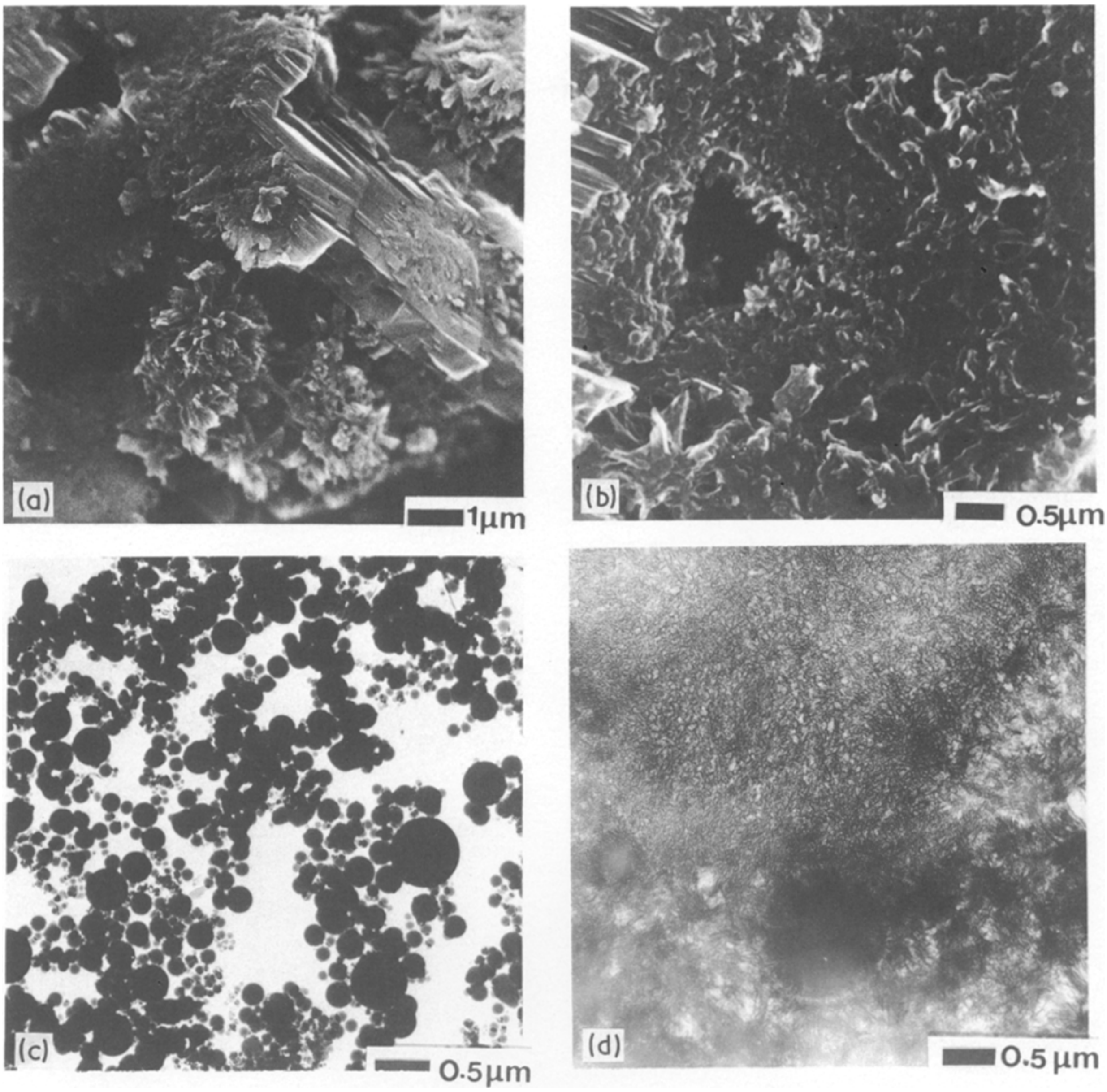

Figure 6 Scanning electron micrographs of the hydration product, after 28 days, of (a) doped C_3S and (b) doped C_3S in the presence of finely divided silica; (c) transmission electron micrograph of finely divided silica and (d) transmission electron micrograph of C_3S hydrated with finely divided silica for 28 days.

the observation of such species in the direct reaction between $Ca(OH)_2$ and silica. From the NMR experiments it is, however, possible to readily distinguish hydrated monomeric and anhydrous species, and show that about 5% of the silicon is present as hydrated monomeric units. Second the trimethylsilylation studies suggested that the distribution of silicate species is roughly independent of the presence of silica provided that appreciable amounts of $Ca(OH)_2$ are present. The present NMR results show that even at early stages of the reaction there is a higher proportion of Q_2 units in samples hydrated in the presence of silica, suggesting a longer average chain length in the gel.

The reasons for the acceleration of the C_3S reaction in the presence of the silica are not clearly defined. This acceleration occurs during the first 24 h of the hydration process; the induction period is, however, unchanged. It would appear that the factors which slow the hydration process after the first 30 to 40% of hydration in the absence of silica do not begin to dominate until 60 to 70% hydration in the presence of silica. The factors may include the build up of CSH around the C_3S grains, and the effective blocking of the access of water to the C_3S surface by the growth of crystalline $Ca(OH)_2$ in the initial space. The finely divided silica may provide another surface for the growth of CSH precipitating from solution, thus producing a reduction of the thickness of CSH around the C_3S grains. The silica may produce a more porous CSH around the grains. The amount of $Ca(OH)_2$ formed is reduced due to reaction with the silica and although there is only a small amount of reaction with the silica during the first 24 h hydration this maybe significant. Further work will be required to determine the dominant effects.

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