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The solid state chemistry of metakaolin-blended ordinary Portland cement

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The hydration of ordinary Portland cement (OPC) pastes containing 0 and 20% metakaolin was monitored by differential thermal analysis (DTA) and solid state magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR). The presence of hydrated gehlenite and a relative reduction in calcium hydroxide content of the metakaolin-blended OPC pastes observed by DTA are indicative of the pozzolanic reaction of metakaolin. An increase in the capacity of metakaolin-blended OPC pastes to exclude chloride ions from the pore electrolyte phase, via solid phase binding, has been reported. It is proposed that this increase in chloride binding capacity could be attributed to the participation of calcium aluminate species in the formation of Friedel's salt which would otherwise be engaged in the formation of hydrated gehlenite and other AFm phases. The accelerating effect of replacement additions of metakaolin has been shown by ^{29}Si NMR and was denoted by a comparative increase in the intensity of resonances arising from Q^1 and Q^2 species compared with that of Q^0 species for metakaolin-blended specimens. The primary reactive centres of the pozzolan have been shown to be the 5-coordinate aluminium and amorphous silica. The spreading of the Q^4 resonance of the amorphous silica of metakaolin through the Q^3 and into the Q^2 and Q^1 regions of the NMR spectrum during pozzolanic reaction has been observed.

1. Introduction

Metakaolin, $Al_2Si_2O_7$, is a largely amorphous dehydration product of kaolinite, $Al_2(OH)_4Si_2O_5$, which exhibits strong pozzolanic activity [1–9]. In the pozzolanic reaction a finely divided silica-containing material, which exhibits little or no cementitious behaviour, reacts with calcium hydroxide in the presence of water at ambient temperatures to form compounds (calcium silicate hydrate gels) which possess cementitious properties. Thus, when blended with Portland cement clinker and water, metakaolin combines with portlandite, $Ca(OH)_2$, formed by hydration of the minerals alite ($3CaO{\cdot}SiO_2$ containing substituted Mg^{2+}, Al^{3+}, Fe^{3+} and other metal ions) and belite (substituted $2CaO{\cdot}SiO_2$), to yield cementitious products. The replacement of cement clinker by pozzolanic materials is advantageous in reducing the total energy cost and carbon dioxide emission [7]. Modified cements incorporating metakaolin have several characteristics that make them potentially attractive for the production of high performance concretes and cement-based composites but they have yet to be used extensively except in the manufacture of glass-fibre reinforced cement components.

Whilst there have been reports of the role of metakaolin in modifying the microstructure and solid phase composition of the hydrated OPC matrix [1–9], there is no information about changes in the nature of solid hydration products formed in metakaolin-cement paste systems under conditions where chloride salts are present as contaminants. Chloride salts are of particular significance with regard to applications of steel-reinforced concrete owing to their tendency, when present at substantial concentrations in concrete pore electrolytes, to promote pitting corrosion of embedded steel [10].

In a study of the pore solution phase chemistry of metakaolin-cement pastes with controlled additions of sodium chloride, the presence of metakaolin was shown to enhance the extent of chloride binding exhibited by the solid hydration products but the mechanism of this effect was not determined [11]. The investigation, by DTA and MAS NMR, reported herein, was undertaken to elucidate the solid phase hydration products formed in metakaolin-cement systems in the presence and absence of sodium chloride.

2. Experimental

2.1. Sample preparation

The chemical compositions of the minerals used in this investigation are presented in Table I. The mineralogical composition of the metakaolin, hereafter referred to as MK501, is listed in Table II. The specific surface area of MK501 was 12 m^2g^{-1}. In order to produce a consistent fineness of powder all materials were sieved to 150 μm. Samples containing 'internal' chloride ions were prepared by dissolution of the required quantity of sodium chloride in the mix water prior to mixing. Distilled water was used for mixing. All cement paste samples were prepared at a total water:solids ratio (by mass) of 0.5 (according to the mix proportions shown in Table III). Blended cement paste samples were produced by partial replacement of the OPC with MK501. The sample mixes were cast into plastic cylinders, 49 mm diameter × 80 mm, compacted by vibration, sealed, rotated about their longitudinal axes for 24 hours to minimise segregation and stored at 22 ± 2°C for periods of 1, 7, 36 and 100 days.

Dehydration of the specimens by solvent exchange was carried out to stop the hydration process prior to analysis. This was the favoured method of pore solution removal as it is an inexpensive and effective process which is reported to have minimal effect on the solid phase [12, 13]. Samples were de-moulded and broken into portions of approximately 5 mm diameter which were immersed in ten times their own volume of propan-2-ol and subjected to ultrasound. After ten minutes the supernatant liquor was decanted away and replaced with fresh propan-2-ol. The process was repeated five times. Sample portions were then dried in a pumped vacuum desiccator after remaining in their final solvent washings overnight. Dried samples were stored in a desiccator containing a self-indicating silica gel and 'Carbosorb,' a self-indicating carbon dioxide absorbent. The dried samples were prepared for analysis by DTA and MAS NMR by grinding and sieving to 150 μm.

2.2. Differential thermal analysis (DTA)

DTA data were obtained from a Stanton Redcroft 673-4 Differential Thermal Analyser using a calcined alumina reference. Samples were heated at a rate of 20°C min^{-1} to a maximum temperature of 950°C. A glossary of the symbols used to depict the presence of the different solid phases in the DTA curves shown in Figs 1–4 is

TABLE I The chemical analyses of OPC and MK501 (weight %)

Compound	OPC	MK501
CaO	65.3	0.4
SiO_2	20.6	54.2
Al_2O_3	5.3	40.8
Fe_2O_3	2.6	0.6
SO_3	3.0	0.3
MgO	1.2	0.2
K_2O	0.8	2.1
Na_2O	0.1	0.1
Cl	0.02	—
P_2O_5	—	0.1
TiO_2	—	0.04
Mn_2O_3	—	0.04
L.O.I.	0.8	1.0

TABLE II Mineralogical composition of MK501

Constituent	Proportion
Mica	Trace
Quartz	Trace
Feldspar	3.0 wt%
Amorphous	Remainder

TABLE III Mix proportions of OPC paste samples for solid state analysis

% MK501	% Chloride	W:S ratio	Age (days)
0	0, 1.0	0.5	1, 7, 36, 100
20	0, 1.0	0.5	1, 7, 36, 100

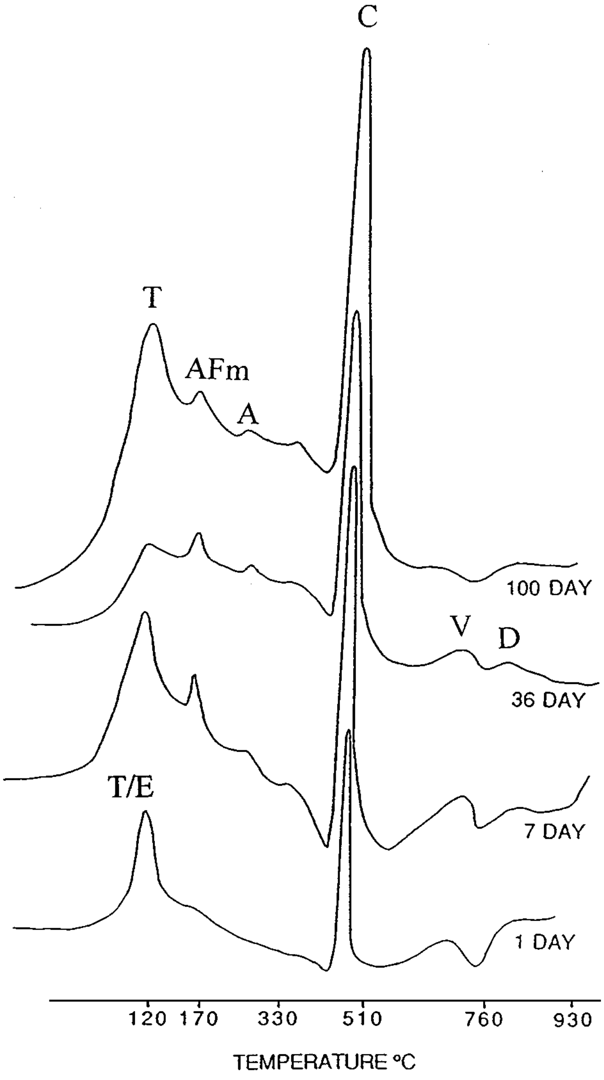

Figure 1 DTA traces of the hydration products of ordinary Portland cement.

TABLE IV DTA glossary [1–3, 14, 15]

Symbol	Cement constituent	Temperature (°C)
T	Calcium silicate hydrate gel	115–125
E	Ettringite, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4.32H_2O$	130–140
AFm	Al_2O_3-Fe_2O_3-mono phases	185–200
G	Hydrated gehlenite, $2CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}8H_2O$	180–210
A	Tetracalcium aluminate hydrate, $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$	253–266
F	Friedel's salt, $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$	130 and 310–335
X	'Exothermic trough'	—
C	Calcium hydroxide, $Ca(OH)_2$	515–550
V	Calcium carbonate, $CaCO_3$	750–800
D	Devitrification of the glassy phase	800–950

listed in Table IV. The reported temperature ranges over which the characteristic thermal transitions for each mineral occur are also tabulated [1–3, 14, 15]. The Friedel's salt transition at 130°C in OPC is obscured by that of calcium silicate hydrate gel. Transition temperatures vary with technique, instrument configuration and heating rate but the relative peak positions generally remain unchanged.

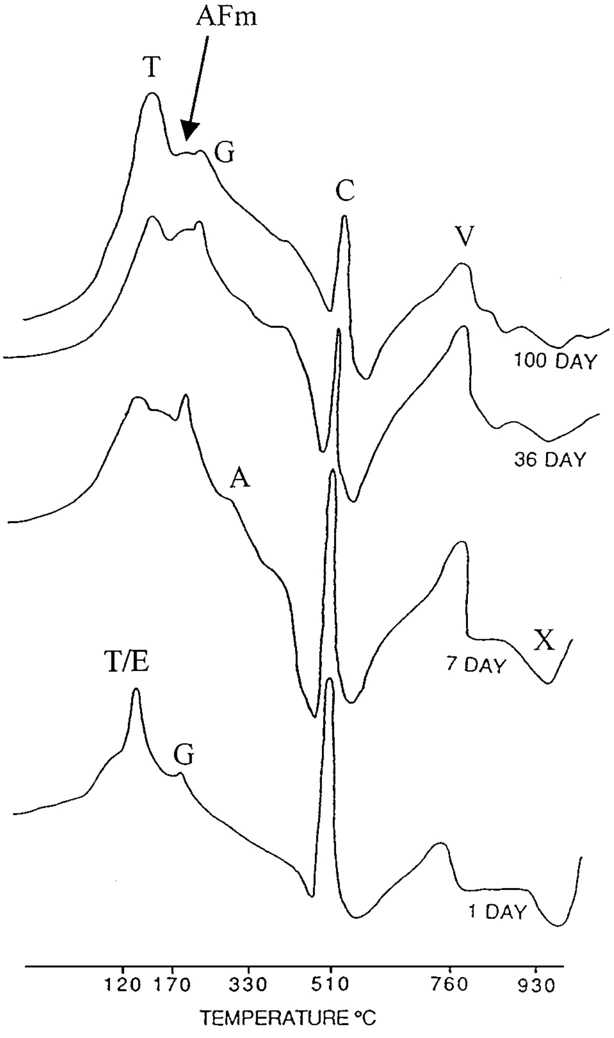

Figure 2 DTA traces of the hydration products of a blend of 80% ordinary Portland cement and 20% metakaolin.

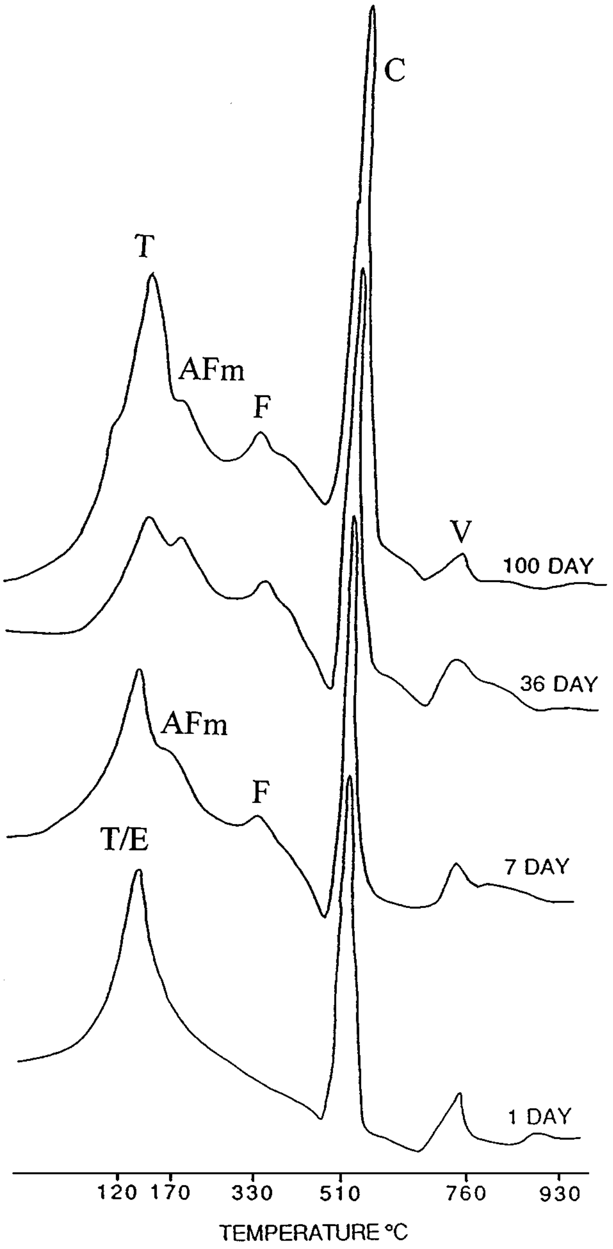

Figure 3 DTA traces of the hydration products of ordinary Portland cement with 1.0% chloride ion addition.

2.3. Magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR)

All NMR spectra were obtained using a Bruker AC 300 multinuclear spectrometer. MAS silicon (^{29}Si) spectra were measured at 59.65 MHz with rotor speeds of 4.0 and 4.2 kHz. Aluminium (^{27}Al) spectra were measured at 78.20 MHz with rotors spinning at 4.8 and 5.5 kHz. ^{29}Si and ^{27}Al chemical shifts were referenced to tetramethylsilane and the aluminium hexaquo-ion $[Al(H_2O)_6]^{3+}$, respectively. The convention of positive δ to low field is used. The ^{29}Si spectra were obtained using a relaxation delay time of 50 s; this was found to be sufficiently long to eliminate saturation effects [16]. Aluminium spectra were obtained using a relaxation delay time of 0.1 seconds.

Rocha *et al.* [17] utilised ^{27}Al NMR in an investigation of the rehydration of metakaolin to kaolinite. Signals corresponding to 6-, 5- and 4-co-ordinated aluminium were observed in the metakaolin spectrum,

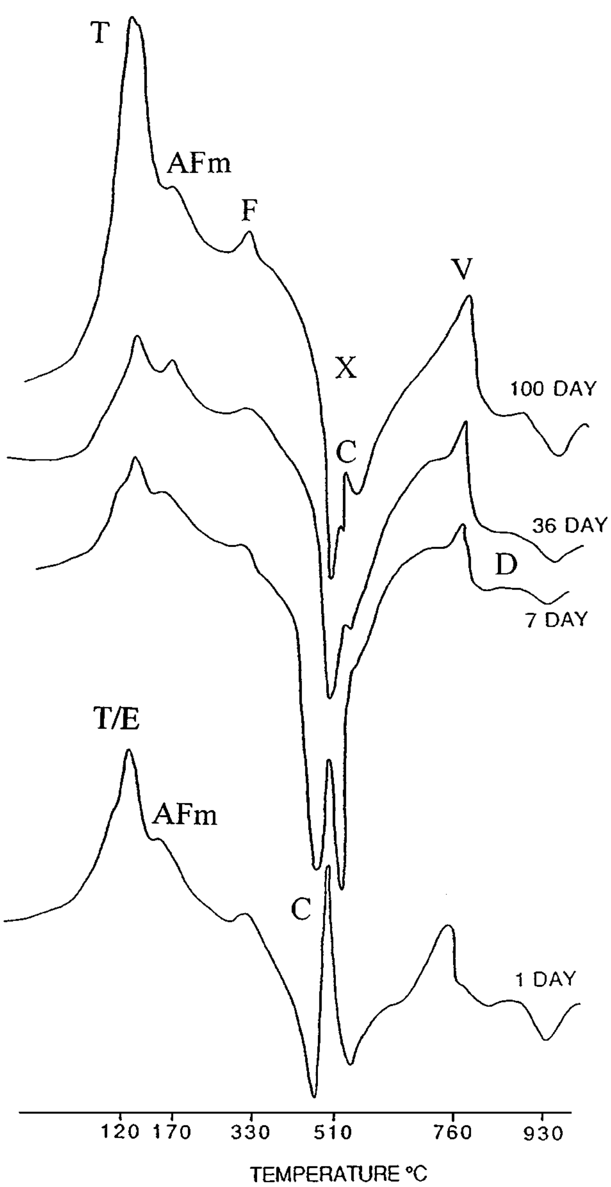

Figure 4 DTA traces of the hydration products of a blend of 80% ordinary Portland cement and 20% metakaolin with 1.0% chloride ion addition.

obtained using a rotor speed of 4–5 kHz. At this frequency overlap of some spinning side bands with the main transition may occur.

3. Results and discussion

3.1. Differential thermal analysis

The common features of all samples (Figs 1–4) are calcium silicate hydrate, CSH, gel (occurring in the region of 120°C), calcium hydroxide (at around 500°C), and vaterite (μ-calcium carbonate, which is centred around 760°C). CSH gel, one of the major strength rendering components of hydrated cement, is a product of reaction of the calcium silicate phases, alite and belite, present in anhydrous cement and is known to be one of the products of pozzolanic reaction of metakaolin, calcium hydroxide and water [1–3]. Calcium hydroxide is mainly liberated from the hydration of alite and vaterite is present as a consequence of atmospheric carbonation.

The presence of hydrated gehlenite, $2CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}8H_2O$, in the metakaolin-blended sample after one day indicates the occurrence of pozzolanic reaction as early as 24 hours into hydration (Fig. 2). Following the 24 h hydration period, similar quantities of calcium hydroxide (in the form of portlandite) are seen to be present in both sample-types irrespective of their metakaolin content (1 day DTA curves shown in Figs 1 and 2). After seven days a relative reduction in the magnitude of the calcium hydroxide peak of the blended sample is observed. This reduction in calcium hydroxide content and the presence of hydrated gehlenite indicate that the extent of pozzolanic reaction is significant after one week into the curing period. Comparison of the calcium hydroxide peaks of the blended and unblended samples in Figs 1 and 2 illustrates the extent of pozzolanic reaction after the various curing periods. After a 36 day curing period very little calcium hydroxide remains in the blended sample.

The DTA data for each of the 36 and 100 day samples are similar indicating that the majority of the hydration chemistry occurs before 36 days. This conclusion is supported by the findings of a pore solution investigation which revealed little change in the pore solution compositions (of both the blended and unblended samples) between 36 and 100 days [11].

Fig. 3 shows the effect of additions of sodium chloride on a number of constituents of the solid phase of OPC. Primarily, the formation of Friedel's salt, $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$, begins to occur at some point between one and seven days.

Hydrated gehlenite is absent from the DTA data of the metakaolin-blended samples which contain internal chloride ions (Fig. 4) This suggests that the presence of chloride ions diverts the hydration of calcium aluminate species which would otherwise participate in the formation of hydrated gehlenite. AFm (Al_2O_3-Fe_2O_3-mono) phases are of the general formula $[Ca_2(Al,Fe)(OH)_6].X.xH_2O$ where X denotes one formula unit of an anion carrying a single charge or half that of a doubly charged anion [18]. AFm phases are based upon hexagonal structural elements in which the principal layer, $[Ca_2Al(OH)_6]^+$, alternates with interlayers containing X anions and water molecules. Simple AFm structures are stacked such that octahedral interstices are formed by three water molecules from each of the adjacent layers. In tetracalcium aluminate hydrate each cavity contains an OH^- ion and a water molecule. Friedel's salt is formed when Cl^- ions occupy each of these octahedral interlayer cavities between the AFm principal layers. Friedel's salt is also formed when Cl^- ions from the pore solution are exchanged for OH^- ions in the interlayer interstices of tetracalcium aluminate hydrate and its derivatives [19].

There is little restriction on the separation between adjacent layers which allows large anions to be present in the interlayer sites. The crystallographic data for hydrated gehlenite indicates that it is an AFm phase with an interlayer aluminosilicate anion of probable composition $[AlSiO_3(OH)_2{\cdot}4H_2O]^-$ [18]. It is therefore reasonable to assert that the calcium aluminate phases which would normally participate in the formation of hydrated gehlenite may be engaged in Friedel's salt formation in chloride-contaminated metakaolin-blended specimens. It is also suggested that the AFm layer system of hydrated gehlenite, despite the bulky interlayer anion, confers chloride binding capacity on the structure. This postulate is supported by evidence from X-ray diffraction analysis of phases in the system $Al_2Si_2O_7 : Ca(OH)_2 : H_2O : NaCl$ [20].

An unusual feature of the DTA curves of samples containing both metakaolin and sodium chloride is the presence of large exothermic troughs which appear in the same region as the calcium hydroxide peaks. The presence of the exothermic trough is undoubtedly related to the combined effect of metakaolin and sodium chloride on the solid phase but does not necessarily represent a discrete phase in the matrix.

3.2. Nuclear magnetic resonance spectroscopy

Previous investigations have shown that the major feature in the ^{29}Si MAS NMR spectrum of anhydrous OPC is a resonance with δ between -71 and -72 ppm corresponding to a Q^0 silicon environment [21–23]. (In the Q^n notation, Q refers to a silicate tetrahedron and n represents the number of adjacent tetrahedra to which it is bridged via oxygen.) This signal is believed to arise from the superposition of resonances from alite and belite. Pure $3CaO{\cdot}SiO_2$ is reported to give rise to between six and nine resonances in the region -68.5 to -74.5 ppm whereas $2CaO{\cdot}SiO_2$ exhibits a maximum at around -71.5 ppm [24–26]. The presence of 'impurities' and paramagnetic species in OPC (2.6% Fe_2O_3) broadens the lines so that the individual resonances cannot be resolved. The ^{29}Si MAS NMR spectrum of metakaolin has also been well documented and consists of a single broad resonance at around $\delta \sim -101$ ppm corresponding to a Q^4 resonance arising from amorphous or *pseudo*-amorphous silica [17, 27]. The aluminium spectrum of metakaolin has been found to contain three resonances corresponding with 4-, 5- and 6-coordinate aluminium environments [17, 21], although the presence and relative proportions of these species is dependant on the origin of the precursor kaolinite [27, 28].

The ^{27}Al NMR spectrum of anhydrous OPC, used in this study, in which there are two sharp resonances in the tetrahedral region and a very broad underlying resonance, is shown in Fig. 5. The coordination environment of aluminium in anhydrous OPC clinker is variable; anhydrous clinker which contains both octahedral and tetrahedral sites and that which contains tetrahedral sites alone is reported [25, 27]. Researchers have assigned the tetrahedral Al signal to aluminium species in tricalcium aluminate and tetracalcium aluminoferrite [27]. However, work of Skibsted *et al.* [29] provides compelling evidence for the view that the two sharp resonances in the tetrahedral region arise from Al for Si substitution in the alite and belite phases; the very broad resonance underlying the sharp signals arises in all probability from the tricalcium aluminate phase which may be broadened due to paramagnetic impurities, e.g. iron(III). The tetracalcium aluminoferrate phase ($4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$) present in anhydrous cement clinker is paramagnetic and it is questioned if this material is detectable in the experiment.

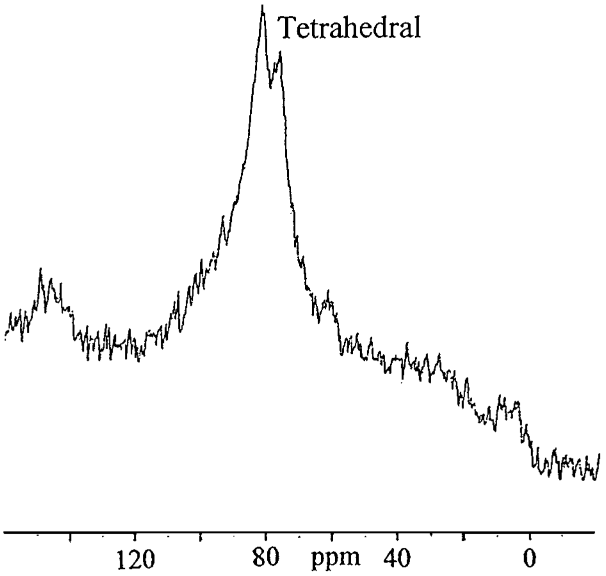

Figure 5 ^{27}Al NMR spectrum of anhydrous ordinary Portland cement.

The assignment of ^{29}Si and ^{27}Al resonances to the species from which they have arisen is based on established chemical shift range catagories for minerals and cements [30–33]. The ^{29}Si spectra of OPC at various stages of curing, shown in Fig. 6A to D, indicate the increase in the Q^1/Q^0 (i.e. the signals initially at -79 and -71 ppm) ratio as hydration proceeds. Following 36 days, in addition to the signals at -71 and -79, a new resonance at -85 ppm, corresponding to Q^2 silicate species is discernible and persists in the 100 day spectrum. The Q^2/Q^1 ratio after 100 days hydration is 0.5, which indicates that the average chain length of the siloxane chains of CSH gel, after this time, is approximately 3. An average chain length of 3 units is consistent with that of other specimens of similar composition and age [34].

The resonance centred around -101 ppm in Fig. 7A is assigned to amorphous silica (Q^4) of metakaolin. Comparison of the two such signals in Fig. 7A and B demonstrates the reaction of the silica species of metakaolin as hydration proceeds and the pozzolanic reaction takes place. The depolymerisation of the silica (Q^4) is denoted by the 'spreading' of the signal through the Q^3 range into the Q^2 and Q^1 regions of the spectrum. Depolymerisation occurs as the siloxane linkages between the silicate species are cleaved in the highly alkaline conditions associated with the cementitious system. This process continues until some point up to 36 days into hydration, by which time all of the silica derived from the metakaolin has reacted. No further significant changes are detectable by ^{29}Si NMR between 36 and 100 days.

The mechanism of pozzolanic reaction of metakaolin differs from that of finely divided silica which has been shown to break down directly in the formation of Q^1 and Q^2 hydrated products [34, 35]. The time-scales of the pozzolanic reactions of silica and metakaolin, in similar states of division, are, however, comparable [34, 35].

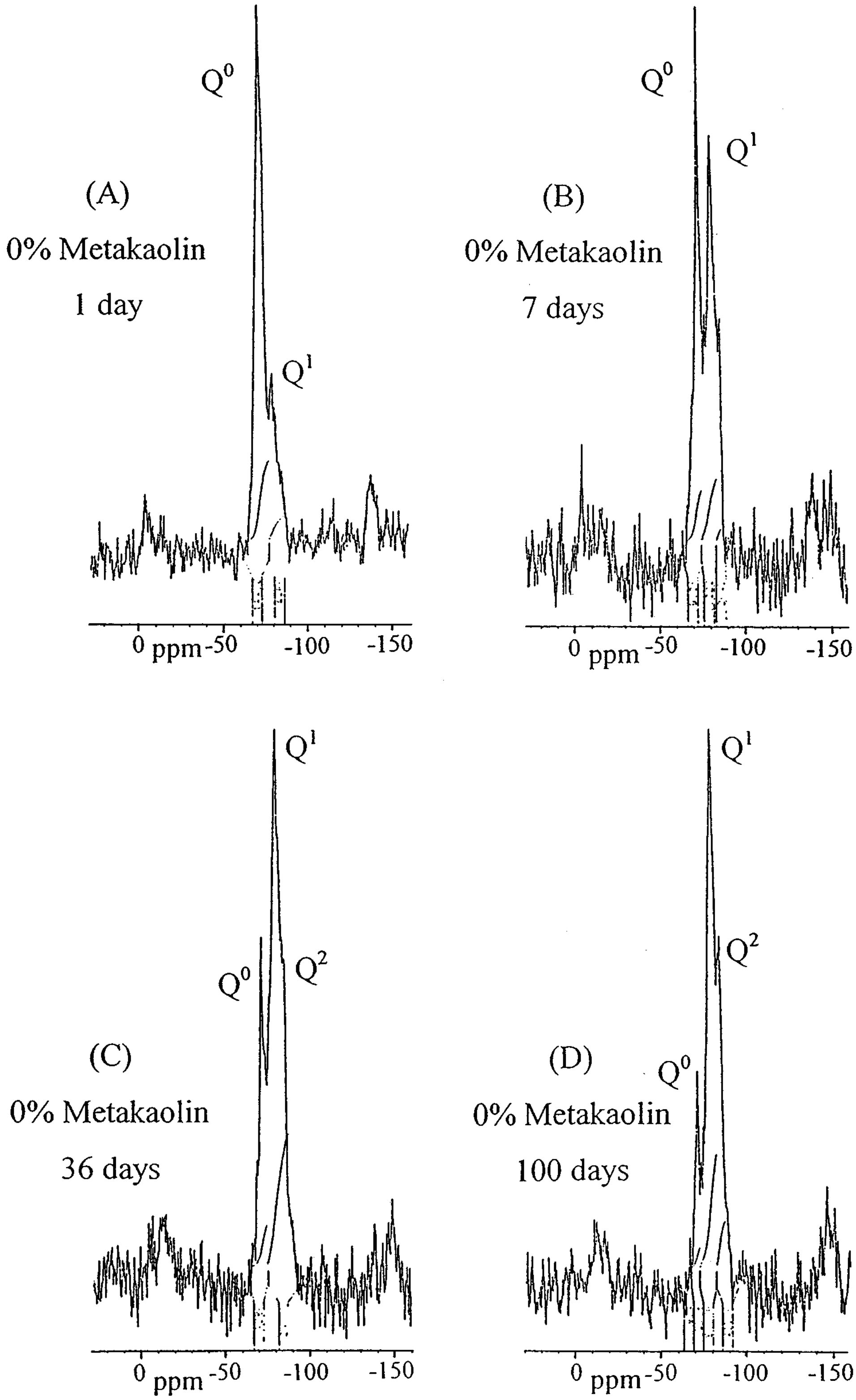

Figure 6 ^{29}Si MAS NMR spectra of the hydration products of ordinary Portland cement after 1, 7, 36 and 100 days.

The presence of the reactive Q^3 intermediate during the pozzolanic reaction of metakaolin may arise from sites of superior reactivity afforded by the interface of the silicate and aluminate layers within the metakaolin structure.

The relative increase in the intensities of Q^1 and Q^2 signals with curing time of the ^{29}Si NMR spectra of samples containing 20% metakaolin, shown in Fig. 7, demonstrates the progression of hydration. Throughout hydration the proportion of Q^1 and Q^2 silicon species of the hydrated product relative to the Q^0 silicon species of the unreacted clinker is notably greater for the blended cement (Figs 6 and 7). This effect is particularly pronounced in the 1 and 7 day samples containing 0% and 20% metakaolin (Figs 6 and 7, spectra A and B) and indicates that the initial rate of hydration of the metakaolin-blended OPC paste is greater than that of its unblended counterpart; there is also a more rapid development of the Q^2 silicon signal at −86 ppm. This initial accelerating effect has also been observed by

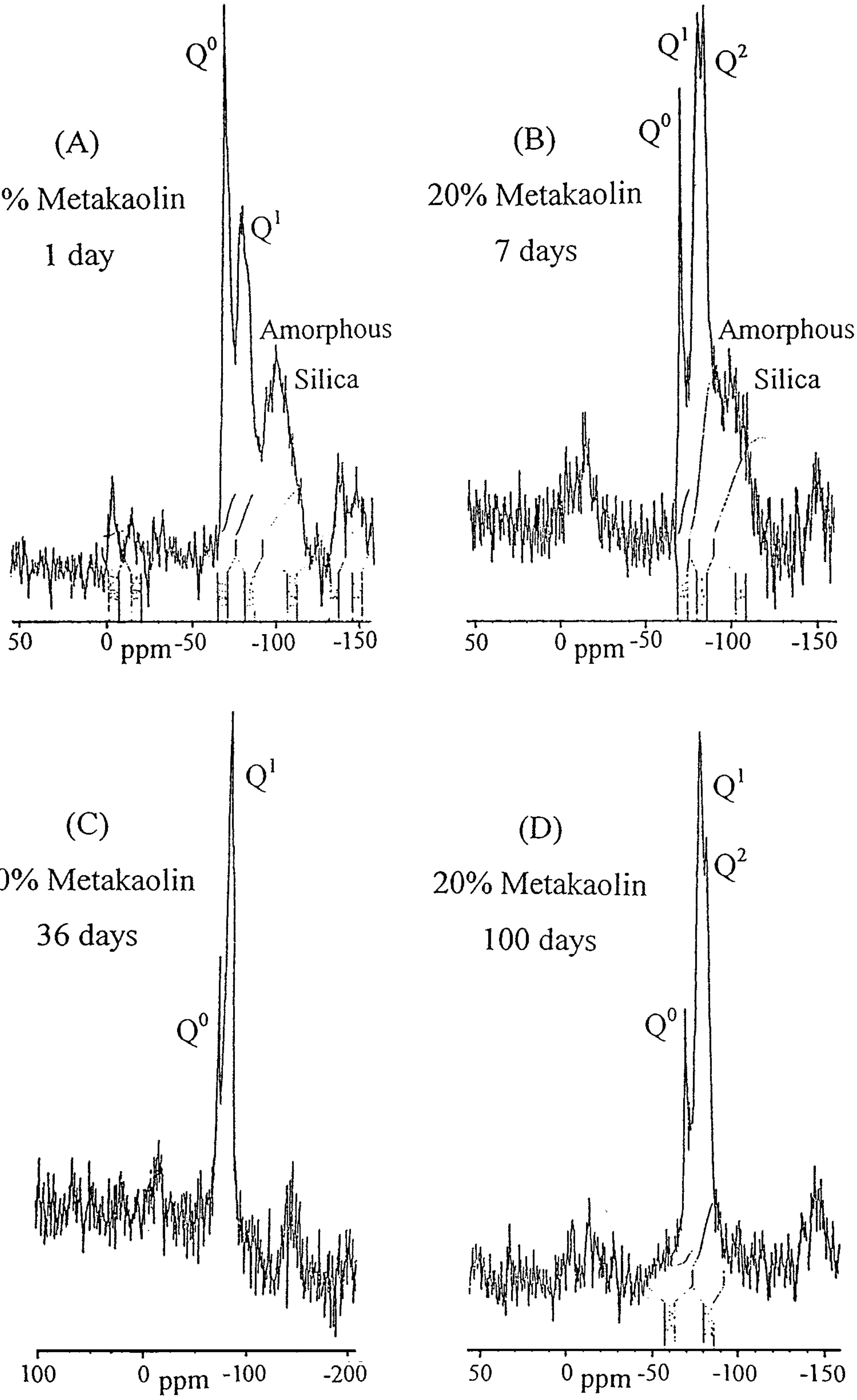

Figure 7 ^{29}Si MAS NMR spectra of the hydration products of a blend of 80% ordinary Portland cement and 20% metakaolin after 1, 7, 36 and 100 days.

Pietersen *et al.* [22] and has been attributed to the effective increase in water:cement ratio of blended cements. After 100 days hydration the Q^2/Q^1 ratio of the blended samples is considerably higher than that of the unblended OPC paste suggesting a longer than average silicate chain length. However, an estimate of average silicate chain length was made impossible by the poor resolution of the Q^1 and Q^2 signals.

Comparison of Figs 5 and 8A to D, which show the ^{27}Al MAS NMR spectra for anhydrous and hydrating cement respectively, indicates a change in environment of the aluminium species present in cement on hydration. Initially 4-coordinate aluminium species are present in the anhydrous cement. However, as little as 24 h into hydration essentially all of the 4-coordinate species appear to have been transformed into

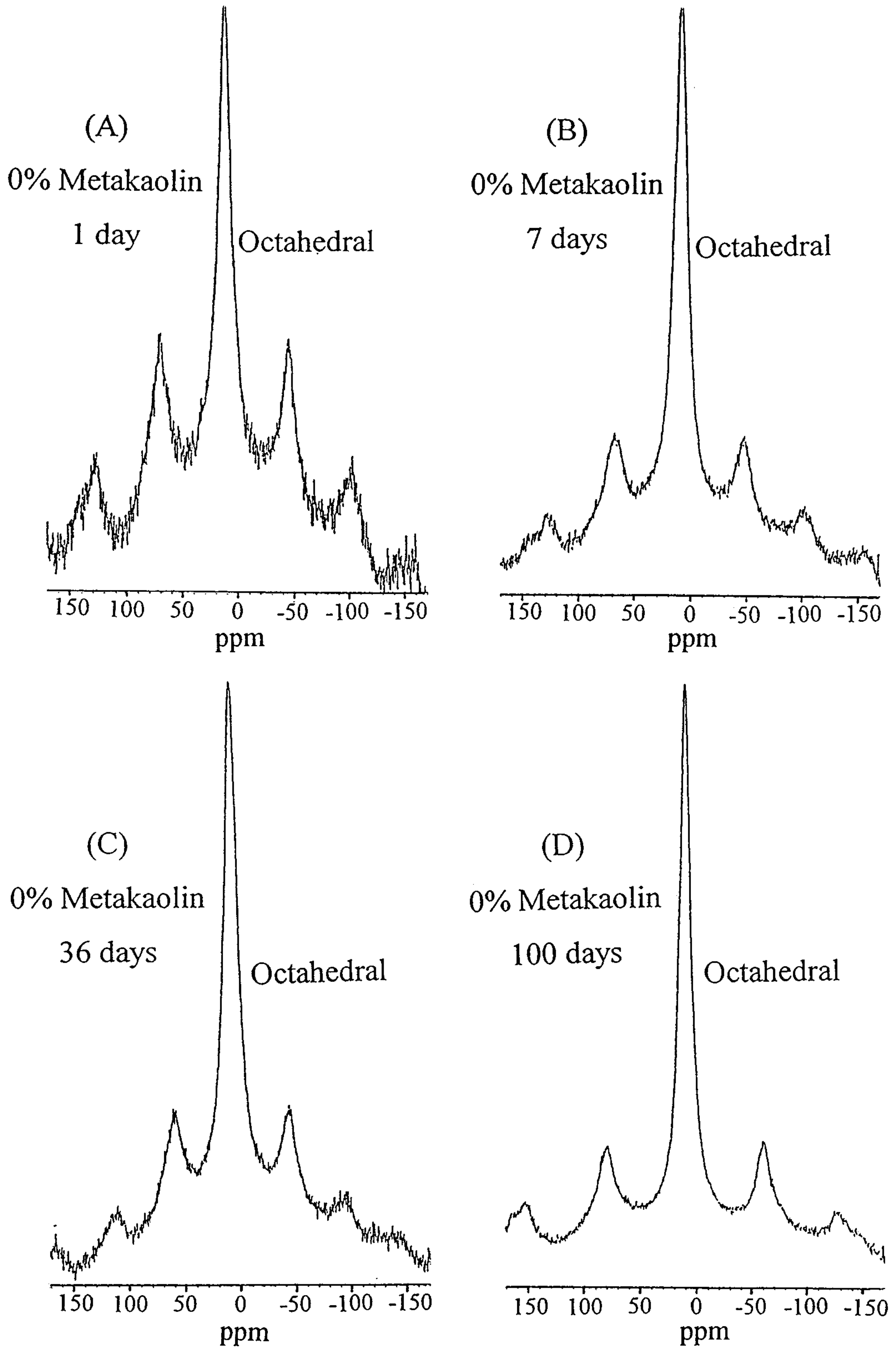

Figure 8 ^{27}Al NMR spectra of the hydration products of ordinary Portland cement after 1, 7, 36 and 100 days.

6-coordinate species. Some 4-coordinate aluminium may still exist which has been masked by the spinning side bands from the 6-coordinate species, but this seems unlikely since the spinning side bands on either side of the 6-coordinate signal are of similar intensity.

After one day of hydration the chemical shift value for the 6-coordinate aluminium species is 13 ppm (Fig. 8A). This value differs from those of the more mature samples which occur at around 7.5 to 8 ppm (Fig. 8B to D) and is indicative of a change in the chemical environment of the aluminium species.

An interesting feature of the ^{27}Al spectra of 20% metakaolin-blended samples presented in Fig. 9 is the rapid disappearance of the 5-coordinate aluminium species. After a curing period of 7 days a negligible concentration of 5-coordinate aluminium remains. Rocha *et al.* [17] used ^{27}Al NMR to assess the hydrothermal rehydration (at 155°C and 200°C) of metakaolin

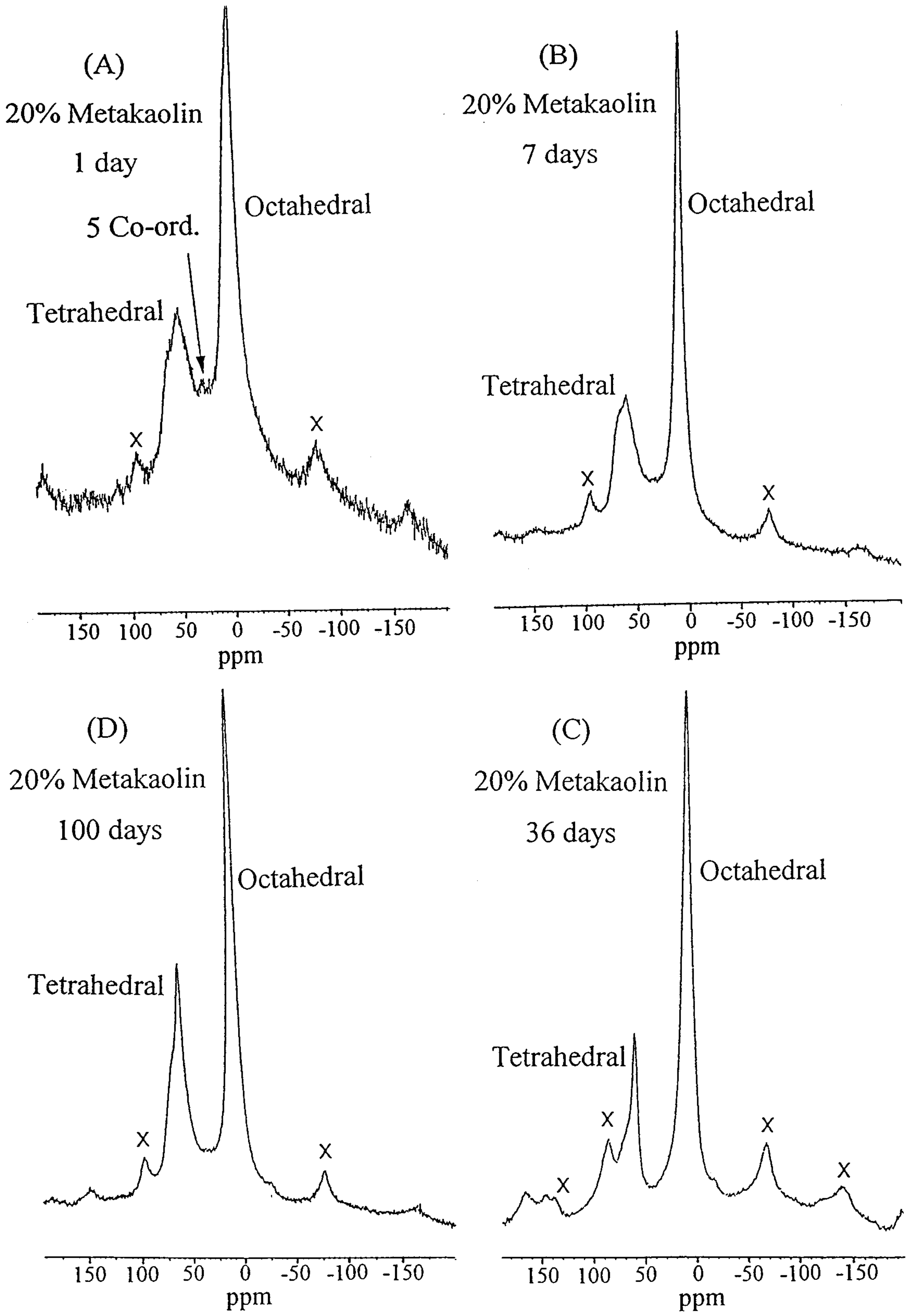

Figure 9 ^{27}Al NMR spectra of the hydration products of a blend of 80% ordinary Portland cement and 20% metakaolin after 1, 7, 36 and 100 days.

to kaolinite and discovered that the signal from the 5-coordinate aluminium decreased at a significantly faster rate than that of the 4-coordinate aluminium; also Akram and McWhinnie [28] have found that it is the 5-coordinate aluminium sites which are reactive when metakaolin is used as a component of moulds for the casting of metals. Hence, in previous investigations [17, 28] and the research reported here the 5-coordinate aluminium species is seen to be the initially reactive site. This is unsurprising since the symmetry of that environment is lower than those of the other aluminium species present. The fate of the 5-coordinate aluminium species cannot be ascertained by NMR alone as the integrals of resonances from quadrupolar nuclei in low symmetry environments are not in linear relation to the concentrations from which they arise. During the first 24 h curing period the formation of hydrated gehlenite has been noted by DTA (see previous section) although it does not necessarily follow that the 5-coordinate aluminium species is engaged in this reaction.

A proportion of 4-coordinate aluminium from the metakaolin is seen to remain throughout the 100 day curing period. The smoothing of the shoulder of the 4-coordinate aluminium resonance as hydration proceeds occurs as strained sites are relieved. In Fig. 9 the spinning side bands associated with the 6-coordinate species are marked with the symbol 'X' to distinguish them from those arising from other resonances. The narrowing line widths of all ^{27}Al resonances with the progression of hydration is indicative of increasing order in the products of reaction (Figs 8 and 9)

4. Conclusions

The incorporation of 20% metakaolin into OPC paste of moderate alkali content (0.63% equivalent Na_2O) has been seen to result in changes in the chemical composition of the solid state phases of the hydrated material. The pozzolanic reaction has been demonstrated by DTA. Very little calcium hydroxide remained after a curing period of 100 days. Calcium hydroxide content is considered to be relevant to the stability of the passive Fe_2O_3 film that provides corrosion protection for embedded steel reinforcement [10].

It has been suggested that the increase in chloride binding capacity observed for metakaolin-blended cement paste samples [11] could be attributed to the participation of calcium aluminate species in the formation of Friedel's salt which would otherwise be engaged in the formation of hydrated gehlenite and tetracalcium aluminate hydrate.

The reactive centres of the pozzolan have been shown to be the 5-coordinate aluminium and the amorphous silica component. Spreading of the Q^4 resonance of amorphous silica of metakaolin through the Q^3 and into the Q^1 and Q^2 regions of the NMR spectrum during pozzolanic reaction has indicated a different reaction mechanism than that observed for finely divided Q^4 silica which breaks down directly to form Q^1 and Q^2 products [34, 35]. The accelerating effect of metakaolin has been observed by ^{29}Si MAS NMR and was denoted by a comparative increase in the intensity of the resonances arising from Q^1 and Q^2 species compared with that of Q^0 species for metakaolin-blended specimens, particularly during the early stages of hydration.

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