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Structural studies of geopolymers by ^{29}Si and ^{27}Al MAS-NMR

PUYAM S. SINGH*, TIM BASTOW, MARK TRIGG
CSIRO Manufacturing and Infrastructure Technology, Normanby Rd Clayton, Private Bag 33, Clayton South MDC, Victoria Australia
E-mail: puyam@csmcri.org

A systematic study of geopolymers by ^{29}Si and ^{27}Al MAS NMR has been carried out in an attempt to understand polymer structural details. ^{27}Al MAS NMR data shows that transient aluminium species are formed during the reaction of metakaolin with NaOH. Interaction of silicate anions with the aluminium sites of metakaolin was evident during the synthesis of geopolymers as observed from low field shift of ^{29}Si MAS NMR resonance lines of silicate centres. As the reaction progresses, the coordination of aluminium (IV, V and VI) in metakaolin changes almost completely to IV. ^{29}Si MAS NMR of selected compositions of the ternary system of sodium silicate, metakaolin and aqueous alkali reveals that geopolymerisation occurs in a distinct compositional region. At high alkalinity [>30% (mol/mol) overall Na_2O content], connectivity of silicate anions is reduced, consistent with poor polymerisation. At low alkalinity [<10% (mol/mol) overall Na_2O content], a clear ^{29}Si NMR resonance line due to unconverted metakaolin is observed. NMR spectra were recorded from a series of samples with a fixed Na_2O content (20 mol%) and varied SiO_2/Al_2O_3 ratio to observe aluminium substitution in the cross-linked silicon tetrahedra of polymer network. Aluminium insertion into the silicate network is confirmed from the observed ^{29}Si NMR shift as a function of Si/Al ratio. The identification of the presence or absence of metakaolin in the cured geopolymer product is not possible even by ^{29}Si NMR as the signal from metakaolin is indistinguishable from a broad ^{29}Si NMR peak consisting of many resonance lines from the network of cross-linked silicon/aluminium tetrahedra. In an attempt to identify metakaolin signal, we prepared geopolymers with higher SiO_2/Al_2O_3 molar ratios. Since aluminium substitutions in the silicate tetrahedral network are decreased, this results in better-resolved ^{29}Si NMR lines. The ^{29}Si NMR signal due to metakaolin is then distinguishable in the spectra of cured products in a series of samples with 3 to 11 mol% metakaolin. These results indicate that a geopolymer structure is a network of silicon/aluminium tetrahedra with some presence of unreacted metakaolin. The silicon/aluminium tetrahedra might have connectivity ranging from 1 to 4.

1. Introduction

High-resolution ^{29}Si and ^{27}Al magic angle spinning NMR have proved to be a very informative technique for structural studies of silicates and aluminosilicates, for a deeper understanding of their structural properties as well as the process of formation [1]. ^{29}Si MAS-NMR is capable of distinguishing SiO_4 tetrahedra of connectivity ranging from 0 to 4, represented by the symbol Q^m, where m is the number of bridging oxygen [1]. ^{27}Al MAS-NMR can provide additional information since well-resolved peaks are observed for different oxygen coordinations around the Al atom.

^{29}Si NMR is capable of distinguishing different cross-linked Si tetrahedra and is a sensitive technique for determination of the substitution of Al for Si tetrahedra by the characteristic ^{29}Si line shifts. The technique, however fails when spectra exhibit relatively broad peaks without observable separation. This might occur in the spectra of samples that consist of Q^2, Q^3, Q^4 silicate tetrahedra and aluminium substituted silicate tetrahedra as there are relatively small differences in chemical shifts of Q^2, Q^3, Q^4 silicate tetrahedra and aluminium substituted silicate tetrahedra.

The geopolymer type of Na_2O, SiO_2 and Al_2O_3 is composed of sialate (—Si—O—Al—O—) and siloxo (—Si—O—) units [2] where Na^+ cations balance the negative charges on either bridging oxygens created by formation of Al—O—Si bonds or

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*Author to whom all correspondence should be addressed.
Present address: Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364002, Gujarat, India.

non-bridging oxygens [3]. Depending on Si/Al ratio, sialate and silioxo units proportions are determined. For geopolymer with Si/Al = 1, it consist of sialate units only; for Si/Al = 2 it is sialate-siloxo (—Si—O—Al—O—Si—O) units; for Si/Al = 3, it is sialate-disiloxo (—Si—O—Al—O—Si—O—Si—O—) and so on. Geopolymer is a viable alternative for cements and plastics. It has been reported that Si/Al ratio can be varied from 1 to 35. By changing the Si/Al ratio, it is possible to produce products ranging from concretes to fiber composites [4–7]. The geopolymer based concrete is acid resistant and geopolymer composites provide a heat resistant substitute for flammable plastics.

It was seen in our previous NMR study [8] of geopolymer formation process that geopolymerisation requires silicate anions of higher connectivity, and metakaolin in a presence of an adequate amount of alkali. Highly charged, silicate anions such as $HSiO_4^{3-}$ do not readily complex with aluminate species to form Al—O—Si linkages [9]. In highly alkaline environments the formation of highly charged, un-reactive, smaller silicate anions is favoured [10]. The commercial sodium silicate solution that consists of mainly silicate chains is a good silicate source for geopolymerisation. As the percentage of Na_2O (oxide basis) of the sodium silicate solutions ($2SiO_2{\cdot}Na_2O$) is 33.3 mol%, which is more than the total amount of alkali required for geopolymerisation, a large amount of metakaolin is needed to bring down the total alkali content for polymerisation to occur. However the formation of reactive aluminate species from metakaolin requires a large amount of alkali. The reactive aluminate species are formed during metakaolin reaction with alkali and they can't be separated or stored. As this is the case, the reaction can not be examined separately either by reducing alkali content of sodium silicate solutions or pre-making reactive aluminate species from metakaolin. In addition, geopolymerisation occurs in a highly concentrated solution and the reactions between silicate and aluminate species are rapid. It is difficult to follow such system and details of geopolymer structure are still not fully understood. For this purpose, 3 series of samples with number of compositions of various oxide molar ratios were selected.

A series of samples, denoted IP1-9, of selected compositions in the SiO_2—Al_2O_3—Na_2O geopolymer system prepared from sodium silicate solution [$Na_2O{\cdot}2SiO_2{\cdot}12{\cdot}7H_2O$], metakaolin [$Al_2O_3{\cdot}2SiO_2$] and aqueous alkali [NaOH] reactants, were investigated to examine the reactivity of the starting components as well as structural details of products. Another series of samples, denoted NA1-6, with different Si/Al ratios at a fixed Na_2O content have been selected to examine Al incorporation into the structure. A further series of samples, denoted S2-5, prepared using colloidal silica as an additional reactant to obtain higher Si/Al ratios, was also examined.

2. Experimental

2.1. Materials

The raw materials were kaolin (Imerys Minerals Australia Pty. Ltd.), NaOH pellets (Merck Pty. Ltd.), colloidal silica (Ludox HS-40) (Aldrich) and sodium silicate solution ($2SiO_2{\cdot}Na_2O{\cdot}12{\cdot}7H_2O$) (PQ Corp.). Metakaolin was prepared by heating kaolin at 750°C for 10 h.

A sample, designated MK was made by reaction of metakaolin and NaOH. A geopolymer sample of a composition selected from reference 11, designated REF, was prepared at room temperature from a mixture of metakaolin and sodium silicate ($2SiO_2{\cdot}Na_2O{\cdot}12{\cdot}7H_2O$) solution. In the reference REF sample, extra water added is 15.8 wt.%. The total water content in all the following samples prepared was kept nearly same with that of REF sample by adjusting on extra water added. Samples designated as IP1-9 of various reactants compositions from the ternary system of sodium silicate solution [$Na_2O{\cdot}2SiO_2{\cdot}12{\cdot}7H_2O$], metakaolin [$Al_2O_3{\cdot}2SiO_2$] and aqueous alkali [NaOH] were prepared at room temperature (Fig. 1a). The molar ratio of reactants and their product compositions for the samples studied are given in Table I.

In Table I, the molar ratio of reactants and their product compositions are also given for another series of samples (NA1-6) from the same ternary reactant system (Fig. 1b). The composition of sample NA6 is the same as that of sample IP6. The NA samples, which have systematic variation in SiO_2/Al_2O_3 ratios at a fixed Na_2O

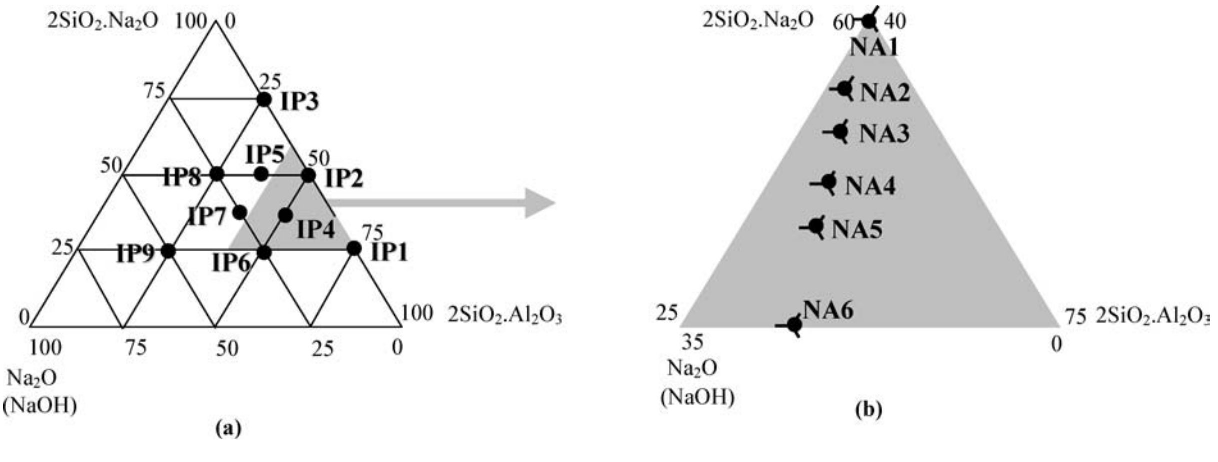

Figure 1 Compositions of samples investigated in the [($Na_2O{\cdot}2SiO_2$)-($Al_2O_3{\cdot}2SiO_2$)-(Na_2O)] system, as described in Table I.

TABLE I Molar ratio of reactants and their product composition for the samples studied

	Reactants[a] (mol%)				Oxides composition (mol%)			
Sample	$SiO_2 \cdot 2.2H_2O$ (Ludox HS-40)	$2SiO_2 \cdot Na_2O \cdot 12.7H_2O$ (Sodium silicate solution)	$2SiO_2 \cdot Al_2O_3$ (Metakaolin)	Na_2O[b]	SiO_2	Al_2O_3	Na_2O	SiO_2/Al_2O_3
MK	0	0	46.7	26.7	56	28	16	2
REF	0	43.8	44.4	5.9	65	16	19	4.1
IP1	0	25	75	0	66.7	25	8.3	2.7
IP2	0	50	50	0	66.7	16.7	16.6	4
IP3	0	75	25	0	66.7	8.3	25	8
IP4	0	37.5	50	12.5	63.6	18.2	18.2	3.5
IP5	0	50	37.5	12.5	63.6	13.7	22.7	4.6
IP6	0	25	50	25	60	20	20	3
IP7	0	37.5	37.5	25	60	15	25	4
IP8	0	50	25	25	60	10	30	6
IP9	0	25	25	50	50	12.5	37.5	4
NA1	0	60	40	0	66.7	13.3	20	5.02
NA2	0	51.9	42.3	5.8	65.3	14.7	20	4.44
NA3	0	46.3	43.9	9.8	64.3	15.7	20	4.10
NA4	0	40.9	45.5	13.6	63.3	16.7	20	3.79
NA5	0	35.8	46.9	17.3	62.3	17.7	20	3.52
NA6	0	25	50	25	60	20	20	3.00
S2	56.8	17	11.4	14.8	72.7	7.3	20	10
S3	66.7	10	6.7	16.7	75	5	20	15
S4	70.8	7.1	4.7	17.4	76.2	3.8	20	20
S5	74.2	4.5	3	18.4	77.4	2.6	20	30

[a] Extra water added is not tabulated.

[b] Na_2O amount is calculated from NaOH added.

content, are chosen from the geopolymer formation region.

Geopolymer samples designated S2, S3, S4 and S5 are also prepared from quaternary system of colloidal silica, sodium silicate solution [$Na_2O \cdot 2SiO_2 \cdot 12 \cdot 7H_2O$], metakaolin [$Al_2O_3 \cdot 2SiO_2$] and aqueous alkali [NaOH] of a synthesis method described elsewhere [8]. The molar ratio of reactants and their product compositions for these samples are also given in Table I.

2.2. MAS-NMR measurements

The ^{27}Al and ^{29}Si NMR spectra were obtained using a Bruker Avance 400 spectrometer, operating at 104.23 MHz for ^{27}Al and 79.46 MHz for ^{29}Si. The samples were loaded in 4 mm zirconia rotors with an accessible volume of 0.115 cm^3, and rotation frequencies of 10 and 12 kHz were used for the ^{27}Al (400 accumulations) and ^{29}Si (1800 accumulations) MAS spectra respectively with a delay time of 2 s for both isotopes. No proton decoupling was used. The chemical shifts were measured with respect to zero reference from tetramethyl silane (TMS) for ^{29}Si and $Al(H_2O)_6^{3+}$ for ^{27}Al.

3. Results and discussion

As shown in Fig. 2a, kaolin exhibits a 1:1 layer structure that is formed by pairing silicate tetrahedral and hydroxylated aluminium octahedral layers [12]. It exhibits one sharp ^{29}Si resonance peak at -91.5 ppm with full width at half maximum (FWHM) of–3 ppm assigned to Q^3 silicate tetrahedral layers and one ^{27}Al resonance peak at 0 ppm assigned to hydroxylated aluminium octahedral layers [1]. Metakaolin, a dehydoxylated kaolin prepared by heating kaolin at 750°C for 10 h (Fig. 2b), shows a broad ^{29}Si resonance peak at -103 ppm with FWHM of $\sim$20 ppm assigned to Q^3 sheets and three ^{27}Al resonances at 10 ppm (AlO_6), 28 (AlO_5) and 58 ppm (AlO_4) [3, 13]. The broadness of the ^{29}Si peak of metakaolin is due to a range of Si—O—T (T=Si or Al) bond angles with Si—O sheet networks remain unchanged; the major change being a flattening of Si—O linked to Al sheet [13]. This flattening occurs during dehydroxylation.

3.1. Reaction of metakaolin with NaOH

The reaction of metakaolin with NaOH was examined to assist in understanding the process of geopolymerisation. Metakaolin was mixed with NaOH solution in the molar ratio of met kaolin:NaOH:H_2O = 1:1.14:9.25 (mol/mol) (Sample MK). After curing the sample for 2 h at room temperature it shows a dominant ^{29}Si resonance at -103 ppm with a shoulder around -87 ppm and ^{27}Al peaks at 76, 58, 28 and 10 ppm (Fig. 3). After curing for 24 h at room temperature, the spectrum shows two well-resolved ^{29}Si peaks at -103 and -87 ppm and a single ^{27}Al resonance at 58 ppm. The ^{27}Al resonance at 76 ppm has completely disappeared while few traces of ^{27}Al resonances at 28 and 10 ppm are obvious as there is a small hump in this shift range. Subsequent curing of the sample at 80°C for 16 h results in a further decrease of this ^{27}Al hump and increased intensity of ^{29}Si resonance at -87 ppm while the ^{27}Al resonance at 58 ppm remains unchanged.

The ^{27}Al resonance at 76 ppm suggests formation of transient soluble sodium aluminate ($NaAlO_2$) species or sodium aluminium hydroxide ($Na_2Al_2O(OH)_6$) [14]. Or, it may be due to AlO_4 tetrahedra linked to Q^3SiO_4 [$AlO_4(Q^3SiO_4)$] as these units have ^{27}Al chemical shift ranges between 70 and 80 ppm [1].

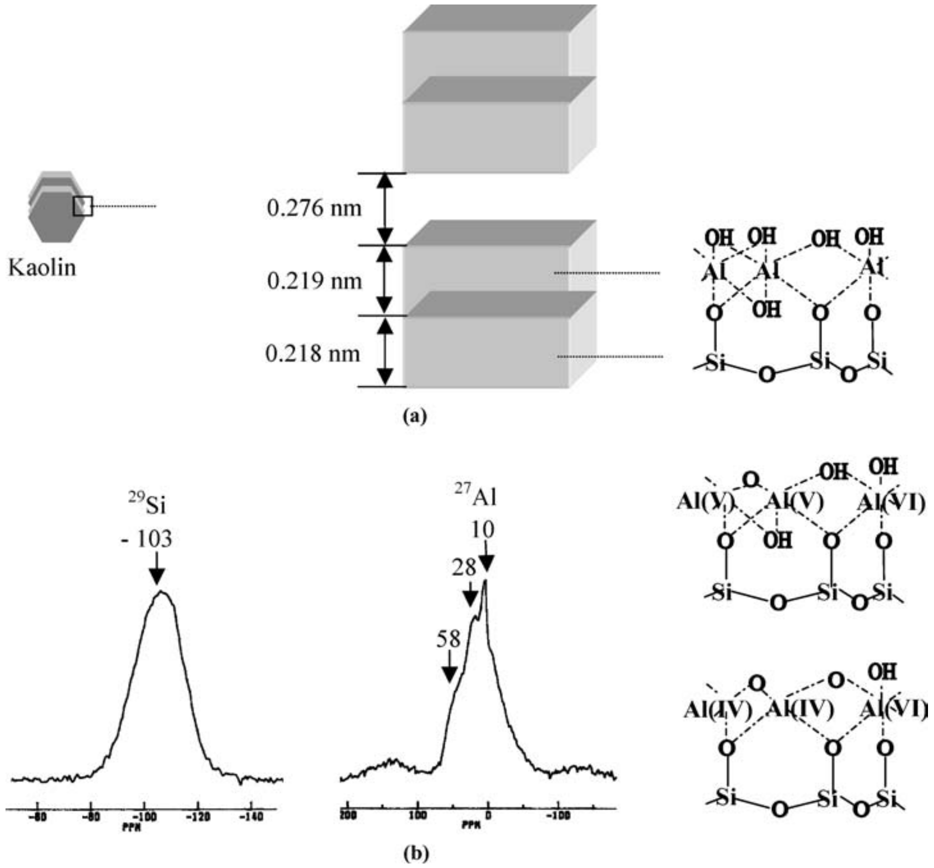

Figure 2 (a) Structure of kaolin based on reference 8 (b) ^{29}Si and ^{27}AlMAS NMR spectra of metakaolin studied here and a part of its amorphous structure based on reference 9, showing Al (IV, V, VI) coordination.

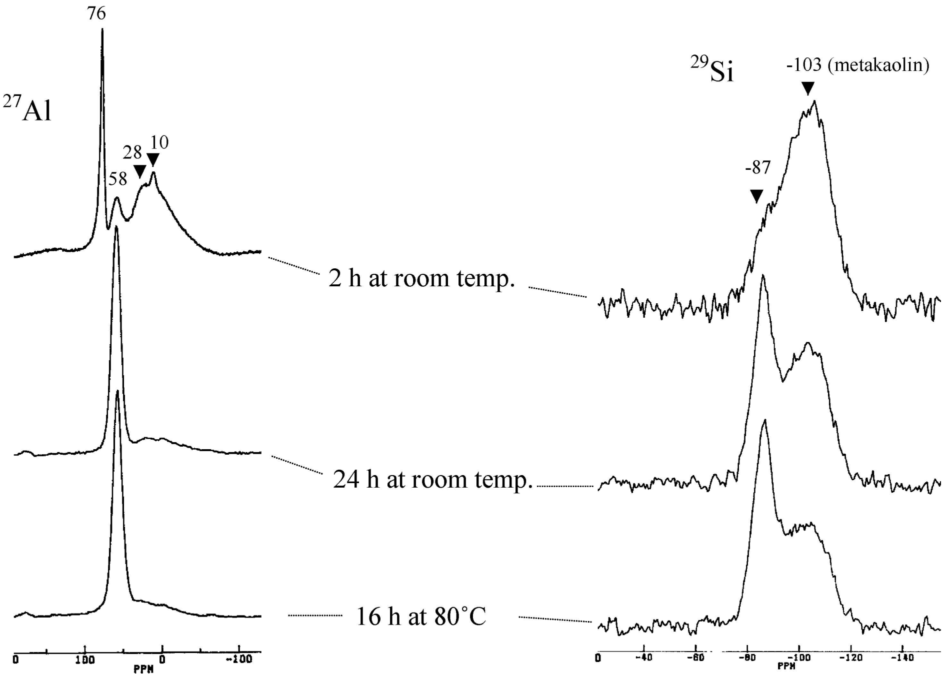

Figure 3 ^{27}Al and ^{29}Si MAS NMR spectra of metakaolin after reaction with NaOH.

These results might indicate formation of transient, soluble sodium aluminium hydroxide or structurally deformed aluminium sites that later transformed to tetra-coordinated aluminium sites resulting from a partial dissolution of aluminium sites of the metakaolin. Therefore, the product structure consists of silicates related to unconverted metakaolin, and aluminium substituted silicate (aluminosilicate) units. This is shown schematically in Fig. 4.

3.2. Reaction of metakaolin with silicate anions during geopolymerisation

Fig. 5a shows ^{29}Si spectra with ^{29}Si lines at −70, −79, −85 and −95 ppm, assigned to Q^0, Q^1, Q^2, Q^3 silicate

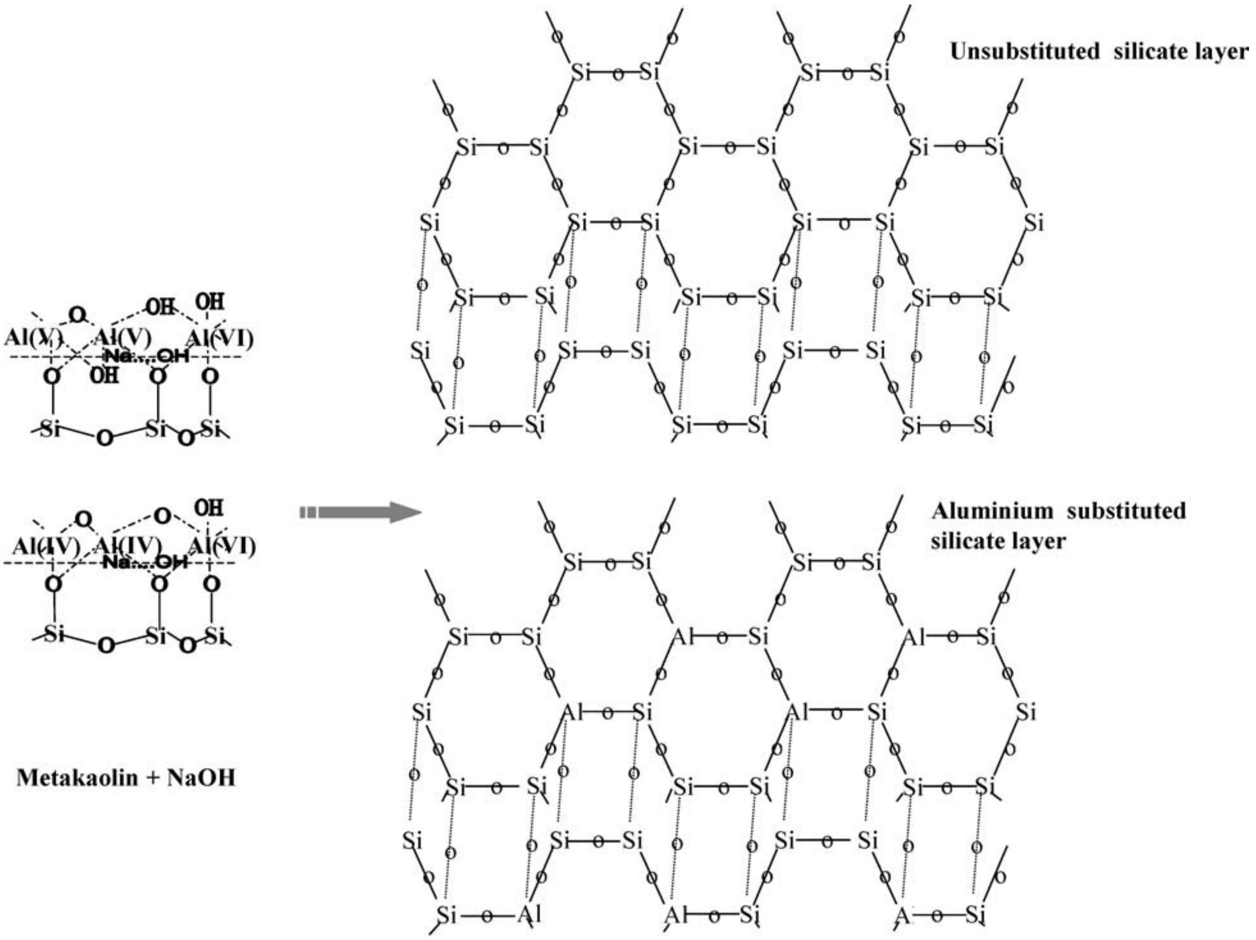

Figure 4 A schematic figure of some parts of amorphous structure formed when metakaoilin is reacted with aqueous NaOH solution, showing aluminium substituted and unsubstituted silicate layer. Na and H connectivity with oxygen are omitted for clarity.

units respectively, of geopolymer solution of Sample REF taken after 2, 5 and 21 h of reaction. Small peaks at around −81 ppm are due to Q^2c that is, Q^2 units in trimeric rings. It has been identified by ^{29}Si NMR that, 1 type of Q^0, 5 types of Q^1, 14 types of Q^2 and 18 types of Q^3 units are present in sodium silicate solution only [1]. However, the resonance lines for each type of Q unit are so close to one another that, for solid state NMR measurement conditions there is only one observable representative line of each Q unit.

All the spectra of the geopolymer solution of sample REF (Fig. 5a) during 2–21 h of reaction have similar ^{29}Si chemical shifts of Q^0, Q^1, Q^2 and Q^3 lines. The spectra show about 2 ppm low field shifts of Q^0, Q^1, Q^2, Q^3 lines compared with those of sodium silicate solution. The replacement of one silicon with one aluminium at a given site causes a downfield shift of about 5 ppm. This suggests only some types of the Q^0, Q^1, Q^2, Q^3 units have reacted with aluminium species derived from metakaolin suggesting incomplete reaction at this time. The ^{29}Si peak of metakaolin has been broadened suggesting a change in structure. The areas due to Q^0, Q^1, Q^2, Q^3 silicate units and unconverted metakaolin are integrated from the spectra and Q^0: Q^1: Q^2: Q^3: metakaolin ratios are found as $3 \pm 1{:}12 \pm 1{:}27 \pm 1{:}22 \pm 1$ for 2, 5 and 21 h reaction. These essentially unchanged population densities of Q species and metakaolin-derived sites indicate that full polymerisation of silicate species for this sample was not achieved after 21 h of reaction at room temperature.

After 45 h of curing at room temperature the sample shows relatively broader ^{29}Si lines of Q^2 and Q^3; the peak for Q^1 is much decreased and the line due to metakaolin-derived sites are now almost indistinguishable in the spectrum (Fig. 5b). In addition, various ^{29}Si chemical shifts of Q^4_n units, where 'n' is the number of Al atoms connected by oxygen bridges with SiO_4 tetrahedra and ranging from 1 to 4, could be observed in the cured product as a result of reaction between silicates and aluminium sites of metakaolin. The fully cured sample after 120 h shows a broad peak without distinct sub-peaks (Fig. 5b), which is typical of a geopolymer ^{29}Si NMR peak [2]. Typical ^{29}Si chemical shift ranges of Q^2, Q^3, Q^4 and aluminium substituted Q^4 silicate structural units are shown by bars on the bottom of the Fig. 5b, and all structural units fall within the broad peak of the cured product.

Unfortunately as the broad peak due to unconverted metakaolin sites in the cured geopolymer falls in the same as ^{29}Si chemical shift range as silicate and aluminosilicate structural units of the product, it is difficult to separate this signal from those of newly formed products.

The ^{27}Al peaks for the REF sample cured for 2 h are significantly different from that of the parent metakaolin (Fig. 6). The intensity of line at 58 ppm increases whereas the intensity of lines at 28 and 10 ppm decrease. At 5 h of curing, there is further decrease

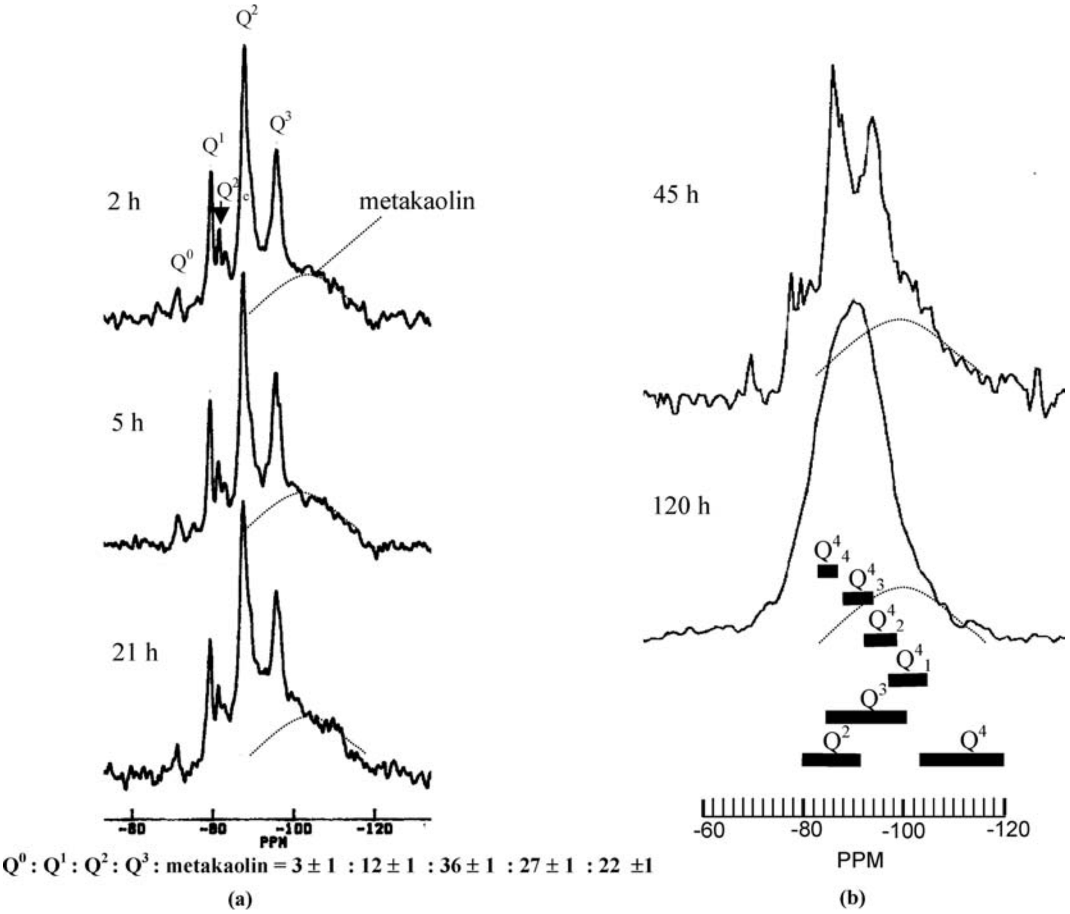

Figure 5 (a) ^{29}Si MAS NMR spectra from the early stages (2, 5, 21 h), and (b) the later stages (45, 120 h) of a geopolymer formation process from a reaction of metakaolin, aqueous NaOH and silicate anions at room temperature (Sample REF); Q^2_c denotes Q^2 units in trimeric rings. Typical ^{29}Si chemical shift ranges Q^2, Q^3, Q^4 and substituted $Q^4_{(1-4)}$ structural units are shown by bars on the bottom of the figure.

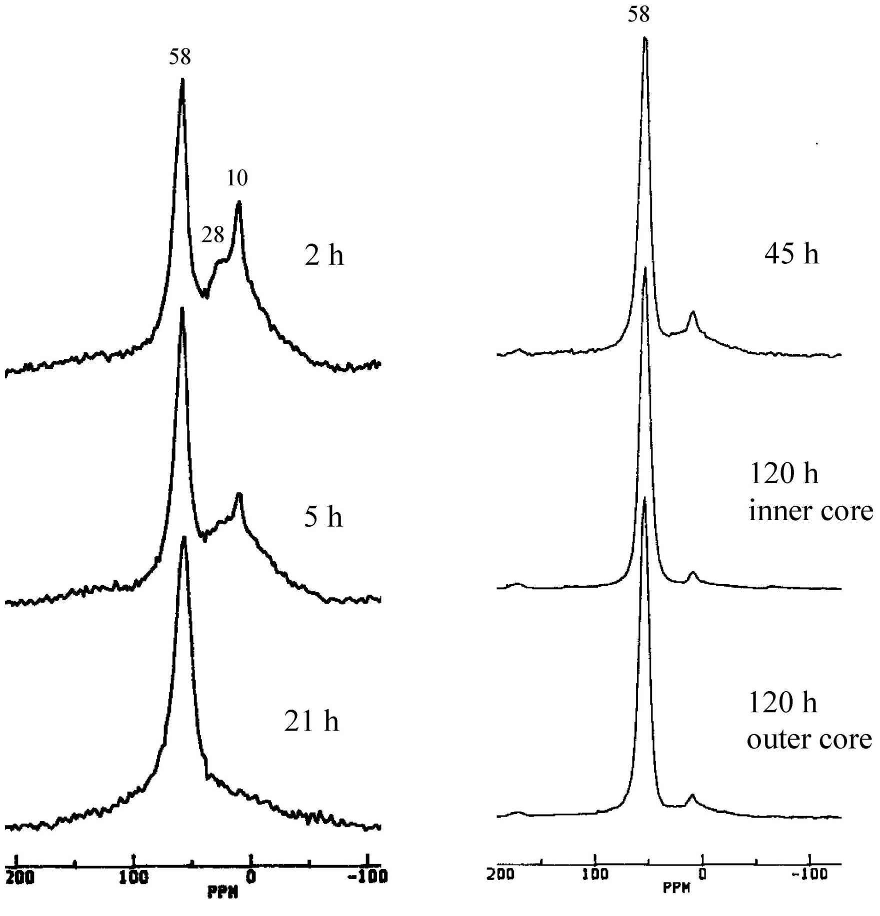

Figure 6 ^{27}Al MAS NMR spectra of Sample REF cured at room temperature.

in intensity of lines at 28 and 10 ppm, and at 21 h, it shows only one peak at 58 ppm with a broad baseline assigned to various tetra-coordinated aluminium. The samples after 45 h and 120 h of curing at room temperature show a sharper ^{27}Al NMR line width. This also suggests continuing reactions between metakaolin, silicate anions and NaOH. ^{27}Al NMR was also taken from outer and inner surface of the sample cured for 120 h, and show similar spectrum indicating homogeneous distribution of aluminium coordination in the sample.

3.3. Composition and network structure of geopolymer

Fig. 7 shows the ^{29}Si MAS-NMR spectra from the IP series of samples (IP1 – IP9) measured at 2 days and 2 weeks of reaction at room temperature. Sample IP1 exhibits ^{29}Si lines at −79.5, −87.8, −96.4 and −103 due to Q^1, Q^2, Q^3 units and unconverted metakaolin respectively. These signals of ^{29}Si lines are still observed even after 2 weeks of reaction indicating incomplete geopolymerisation. The molar ratio of metakaolin to silicate anions of Sample IP1 is 3:1 giving 8.3 mol% overall Na_2O content (Table I). This amount of alkali present is probably not enough for a complete geopolymerisation process. On the other hand, Sample IP9 was prepared with a high amount of Na_2O (37.5 mol%) and 1:1 molar ratio of metakaolin /silicate anions. The extra Na_2O was from added NaOH. In this case, only major ^{29}Si lines at −79 and −86 ppm due to Q^1, Q^2 with minor peaks at −81 ppm due to Q^2c units were observed both at 2 days and 2 weeks of reaction. No distinct peak at −96 and −103 ppm were visible. This indicates amount of Q^3 peak present is relatively less, and that metakaolin is almost completely reacted during the process. The total absence of unconverted metakaolin in the sample cannot be ruled out, as metakaolin peak is broad. The product consists of silicate and aluminosilicate units mainly with 1 and 2 connectivity in presence of a small proportion of 3 connectvity, indicating a more open structure.

The Na_2O content is 16–20 mol% and molar ratio of $SiO_2/Al_2O_3$is 3–4 in Samples IP2, IP4 and IP6. ^{29}Si MAS-NMR spectra of these samples measured both at 2 days and 2 weeks of reaction exhibit a broad peak without distinct sub-peaks, similar to that of Sample REF. The peak position falls between −87 and −91 ppm and FWHM varies from 13 to 16 ppm. The absence of resolved ^{29}Si lines due to Q silicate units in the spectra of Sample IP2, IP4 and IP6 measured at 2 days of reaction indicates faster polymerisation reaction between silicate units and metakaolin as compared to that of Sample IP1.

The molar ratio of metakaolin to soluble silicate in Sample IP3 is 1:3 giving 25 mol% of overall Na_2O content with a SiO_2/Al_2O_3 molar ratio of 8. It exhibits well-resolved ^{29}Si lines at −79.5, −87.5, −95.8 related to Q^1, Q^2, Q^3 species and an overlapping broad peak due to unconverted metakaolin after 2 days of reaction. After 2 weeks of reaction only a broad peak centred at −94.5 ppm was detected. Sample IP7 also has 25 mol% of overall Na_2O content where the extra Na_2O is from added NaOH. However, the molar ratio of metakaolin to soluble silicate is 1:1 with a SiO_2/Al_2O_3 molar ratio of 4. In this case, weak ^{29}Si signals due to various Q^n species were clearly observed only at 2 days of reaction. After 2 weeks, only a broad peak centred at −87 ppm was observed. These differences, in particular the shift of peak position from −87 to −94.5 ppm may be due to the differences in the amount of aluminium inserted into the silicate network. This peak position at −87 ppm of IP7 reveals that a relatively larger proportion of aluminium is inserted into its silicate network than that of IP3. This can be expected as IP7 has the synthesis composition with higher Al_2O_3 content than IP3.

Sample IP5 is 22.7 mol% Na_2O, with a SiO_2/Al_2O_3 molar ratio of 4.6. The ^{29}Si lines at −79, −87, −95 ppm related to Q^1, Q^2, Q^3 species and a small peak at about −81 ppm due to Q^2c (that is, Q^2 units in trimeric rings) at 2 days of reaction, and a broad peak centred at −91.5 ppm at 2 weeks of reaction were observed. Sample IP8 with 30 mol% Na_2O content and a SiO_2/Al_2O_3 molar ratio of 6 exhibits ^{29}Si lines at −78.6 ppm and −86.7 ppm, and a smaller line at −81 ppm at 2 days of reaction. With continued reaction time only slight changes in the ^{29}Si lines were observed. Peaks were still present at −78.6 ppm and −86.2 ppm.

The structure of geopolymers can be explained based on the above NMR data. The geopolymers investigated in this work do not consist of a structure made up of only a single type of Q unit. Rather, as revealed from the NMR spectra, a geopolymer structure may consist of various Q unit types of connected SiO_4 and AlO_4 tetrahedra depending on chemical composition. The sets of Q units may be formed from Q^2 'chain or cycle like' structures, Q^3 'sheet like' and Q^4 'three-dimensional networks'. The following sets of Q units are possible structural units of geopolymers based on our present study.

(i) Sheet like networks containing Q^2 and Q^3 units formed by interconnecting some bridges of Q^2chains; (ii) Sheet like networks containing Q^2 and Q^3 units formed by interconnecting some bridges of Q^3 sheet like networks and Q^2 chains; (iii) Three dimensional networks containing Q^3 and Q^4 units by interconnecting some Q^3 sheet like networks; (iv) Three dimensional networks containing Q^3 and Q^4 units by interconnecting some Si—O—T defect sites of Q^4 three dimensional networks; (v) A complex network containing Q^2, Q^3 and Q^4 units formed by combination of the above structures.

3.4. Aluminium insertion into silicate network

As discussed earlier, downfield ^{29}Si chemical shifts in aluminosilicate are due to (i) lower network connectivity and (ii) aluminium substitution in silicate units. It is known from NMR studies of silicate glasses [1] that the connectivity of silicate networks is dependent on the amount of alkali present. Therefore, many different aluminium containing geopolymers with a fixed alkali content has probably similar network connectivity

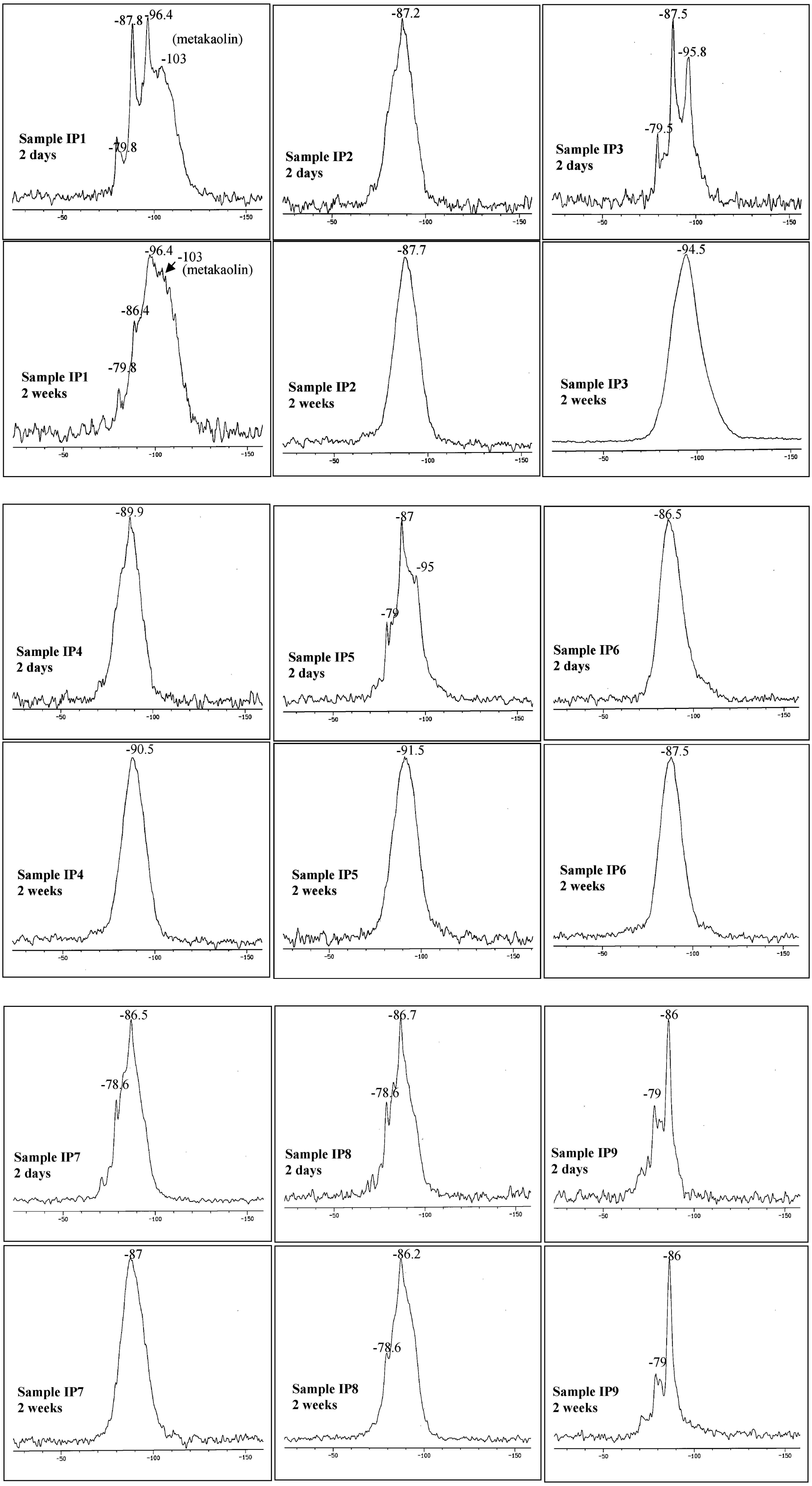

Figure 7 ^{29}Si MAS NMR spectra of IP samples from selected compositions in the [($Na_2O{\cdot}2SiO_2$)-($Al_2O_3{\cdot}2SiO_2$)-(Na_2O)] system.

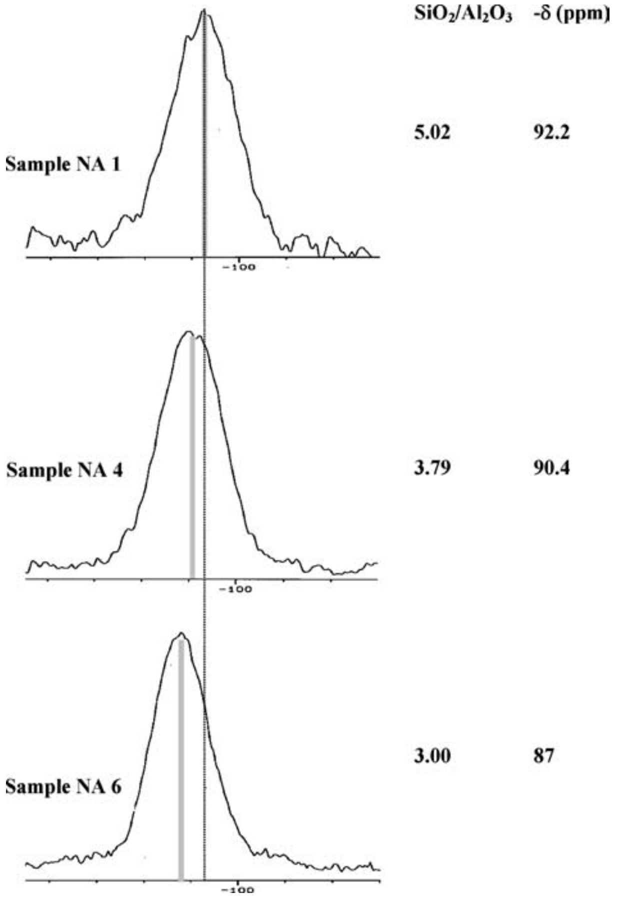

Figure 8 ^{29}Si MAS NMR spectra of cured NA samples from selected compositions in the [($Na_2O{\cdot}2SiO_2$)-($Al_2O_3{\cdot}2SiO_2$)-(Na_2O)] system.

compared to each other and the chemical shift variance of ^{29}Si line are probably due to degree of aluminium substitution in SiO_4 units. Sample NA series (NA1 to NA6) with a fixed Na_2O content (20 mol%) with various SiO_2/Al_2O_3 ratio were thus measured to observe aluminium substitution in the cross-linked silicate network. Spectra from the cured sample NA series with SiO_2/Al_2O_3 molar ratios varying from 5.02 to 3.00, have corresponding ^{29}Si NMR low field shifts from −92.2 ppm to −87 ppm (Fig. 8, Table II), which is consistent with aluminium insertion into silicate network during geopolymerisation.

^{27}Al MAS-NMR spectra were measured from cured samples for 2 weeks, however, few differences were observed in all the samples except sample IP1. This may be due to a quadrupolar broadening of ^{27}Al NMR peak masking small variations in chemical shifts of ^{27}Al NMR peaks. All the samples except for the sample IP1 exhibit a dominant ^{27}Al peak at 58 ppm due to tetrahedral aluminium sites (Fig. 9). A weak ^{27}Al NMR peak at about 10 ppm present in sample IP2, IP3 and IP9 is due to some presence of octahedral aluminium sites. Sample IP1 has a ^{27}Al line at 58 ppm along with 2 other lines at 28 and 10 ppm related to five-fold coordinated and octahedral aluminium sites. As also seen in ^{29}Si NMR above, the difference observed in ^{27}Al MAS-NMR of Sample IP1 is due to incomplete reaction of met kaolin.

TABLE II ^{29}Si NMR data of cured samples at room temperature for 2 weeks

	^{29}Si NMR data	
Sample	-δ (ppm)	Δν (ppm)
MK	87, 103	
REF	93	15
IP1	79.6, 86.4, 96.4, 103 (shoulder)	
IP2	87.7	14
IP3	94.5	17
IP4	90.5	16
IP5	91.5	16
IP6	87.5	13
IP7	88	15
IP8	78.6, 86.2	
IP9	79, 81, 86	
NA1	92.2	16
NA2	91.9	15
NA3	90.7	15
NA4	90.4	15
NA5	89.5	15
NA6	87.5	13
S2	80, 88, 97, 106, 110 (shoulder)	
S3	80, 88, 97, 106, 110 (shoulder)	
S4	80, 88, 97, 106	
S5	80, 88, 97, 106	

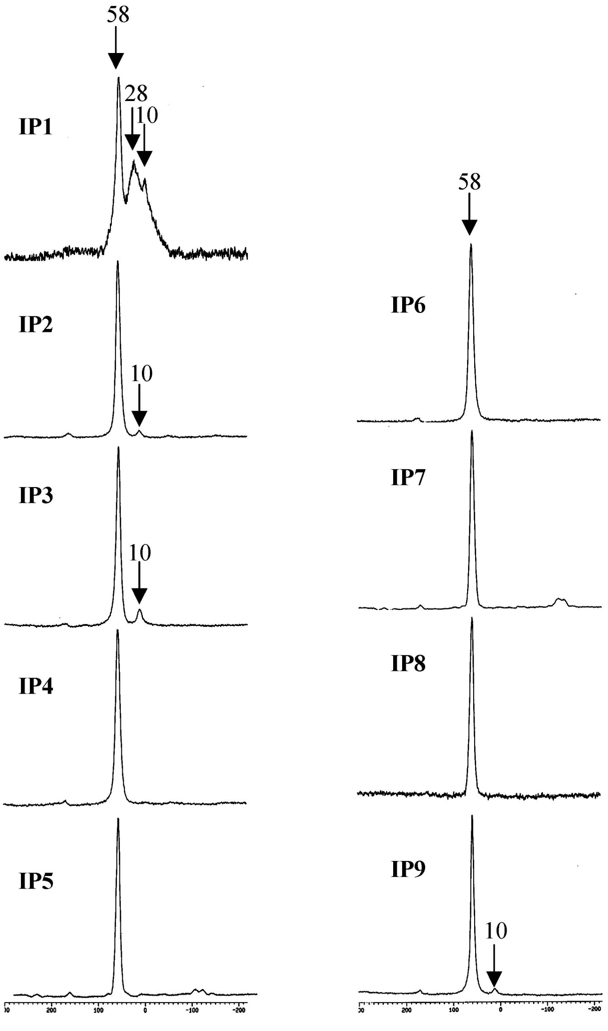

Figure 9 ^{27}Al MAS NMR spectra of cured IP samples for 2 weeks at room temperature from selected compositions in the [($Na_2O{\cdot}2SiO_2$)-($Al_2O_3{\cdot}2SiO_2$)-(Na_2O)] system, as described in Table I.

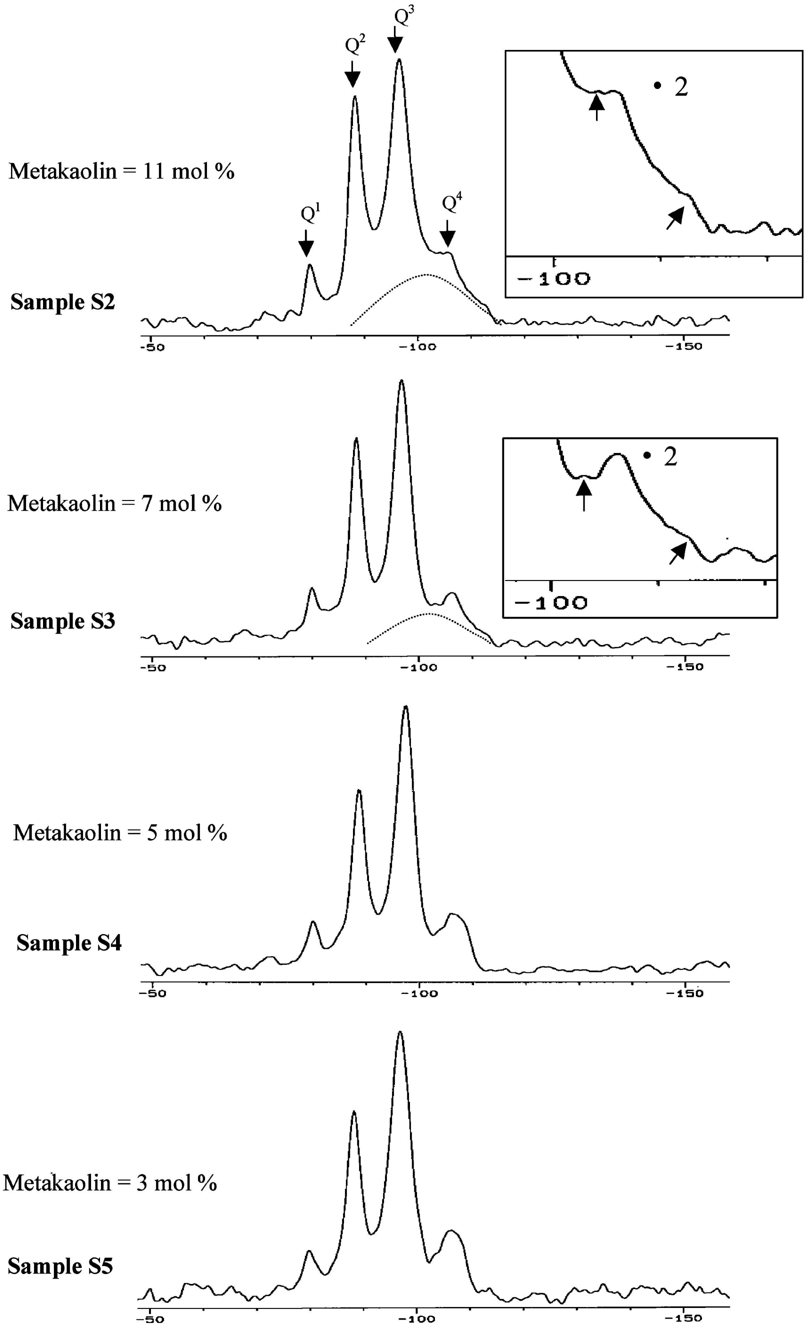

Figure 10 ^{29}Si MAS-NMR spectra of cured samples prepared by our modified method.

3.5. Samples with high SiO_2/Al_2O_3 ratio

Fig. 10 shows ^{29}Si MAS-NMR spectra of fully cured samples after two weeks at room temperature prepared by our modified method [8]. In this method a quaternary system of colloidal silica, sodium silicate solution, metakaolin and aqueous alkali was employed. The metakaolin content in the sample was reduced while keeping alkali content the same by adding appropriate amount of colloidal silica and sodium hydroxide (Table I). By decreasing the amount of metakaolin, the formation of substituted Q^4_1, Q^4_2, $Q^4_3$and Q^4_4 structural units by reaction between aluminium sites of metakaolin and Q^4 silicate units is reduced, thus resulting in more resolved ^{29}Si NMR resonance lines. Samples S2, S3, S4 and S5 had 11, 7, 5, 3 mol% of metakaolin respectively in starting reactants composition.

All the samples show four sharp ^{29}Si resonance peaks at −80, −88, −97 and −106 ppm indicative of Q^1, Q^2, Q^3 and Q^4 respectively. A broad, low amplitude ^{29}Si resonance at about −110 ppm is present in both the spectra of Sample S2 and Sample S3 as shown more clearly in insets of the Fig. 10. These broad humps at about −110 ppm could originate from the broad peak of metakaolin (shown as dotted lines in Fig. 10). Since these humps almost disappear under the relatively resolved peak intensities of $Q^4$when the metakaolin content is $\leq$5 mol% and the SiO_2/Al_2O_3 molar ratio is $\geq$20 as seen from the spectra of Sample S4 and S5. This may indicate that, in the cured geopolymer products even with 7 mol% of metakaolin reactant and a SiO_2/Al_2O_3 molar ratio of 15, the metakaolin is not fully transformed to geopolymeric units.

4. Conclusion

The ternary system of sodium silicate solution [$Na_2O \cdot 2SiO_2 \cdot 12 \cdot 7H_2O$], metakaolin [$Al_2O_3 \cdot 2SiO_2$] and aqueous alkali [NaOH] was investigated to study the geopolymer formation region and geopolymer networks. The geopolymers investigated in this work reveal that a geopolymer structure may be a complex network consisting of chains, sheet-like and three-dimensional networks made up of various Q unit types of connected SiO_4 and AlO_4 tetrahedra. Within the geopolymer formation region the Si/Al ratio was systematically varied with a fixed overall Na_2O percentage (20 mol%) and the ^{29}Si NMR shift observed as a function of the Si/Al ratio confirming aluminium insertion into the silicate network. Although an alkaline environment is required for metakaolin to be reacted, a very high alkaline environment [>30 mol% overall Na_2O content] reduces connectivity of silicate anions, which then results in poor polymerisation. On the other hand a large amount of metakaolin is needed for geopolymerisation, the minimum percentage (mole/mole) of metakaolin reactant required in such systems is around 25%. The identification of the presence or absence of starting metakaolin in the cured geopolymer product is not possible in this synthesis even by ^{29}Si NMR as the signal related to metakaolin is indistinguishable from a broad ^{29}Si NMR peak consisting of many resonance lines of a polymerised network of cross-linked Si/Al tetrahedra.

With our modified synthesis method employing colloidal SiO_2 as an additional component, metakaolin content is decreased while keeping an optimal amount of Na_2O content thereby increasing the compositional SiO_2/Al_2O_3 molar ratio. The ^{29}Si NMR signal related to metakaolin is then distinguishable in the spectra of cured products by observing a series of samples with 11, 7, 5 and 3 mol% of metakaolin reactant. No distinct ^{29}Si NMR signal related to metakaolin was observed in the spectra of cured product when the metakaolin content is ≤ 5 mol% and the SiO_2/Al_2O_3 molar ratio is ≥ 20. From the results of this modified synthesis route, it appears that geopolymer products synthesised from the conventional route with metakaolin reactant content ≥ 20 mol% will also contain unconverted metakaolin particles.

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