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The Effect of the SiO_2/Na_2O Ratio in the Structural Modification of Metakaolin-Based Geopolymers Studied by XRD, FTIR and MAS-NMR

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Abstract

A series of metakaolin-based geopolymers with different SiO_2/Na_2O compositions were synthesized to investigate the influence of the activator on the molecular nature and microstructure of the geopolymers. The structures and microstructures of the resulting products were systematically studied by means of XRD, FTIR, MASNMR, and SEM. The results show that the chemical composition of the activator and hence the ratios SiO_2/Na_2O and SiO_2/Al_2O_3 exert a significant effect on the structure of the geopolymers. The XRD diffractograms indicated that the higher the concentration of silicate species in the activating solution, the higher the amorphous content of the geopolymer. Zeolite formation was observed in samples with low SiO_2/Na_2O ratios. The MAS NMR spectra of the cured materials showed that as the reaction progressed, the coordination of Al in the metakaolin changed almost completely to IV but the SiO_2/Na_2O ratio affects the position of the $Q^4(mAl)$ peaks.

Keywords: Geopolymer, alkali activation, NMR spectroscopy, composition design, metakaolin

I. Introduction

Inorganic polymers (geopolymers) are novel X-ray amorphous materials consisting of a network of SiO_4 and AlO_4 tetrahedra linked randomly by sharing their oxygen atoms [1]. In this configuration, each AlO_4 tetrahedron introduces a negative charge, which is balanced by an alkali metal cation. Geopolymer synthesis involves reactions between a reactive solid aluminosilicate powder such as dehydroxylated kaolinite (metakaolin) and a concentrated caustic alkali metal silicate solution yielding a tri-dimensional poly(sialate) at ambient temperatures [1,2]. Geopolymers can be formed by alkaline activation of an aluminosilicate precursor; the activation process initiates a polycondensation reaction leading to the formation of a cementitious geopolymer material [3]. Geopolymerization is a complex multiphase process, involving a series of dissolution reorientation-solidification reactions analogous to those observed in zeolite synthesis from solid precursors [4]. In principle, almost any positive ion can be used to act as the charge-balancing ion, but in practice, the activating solution most often utilized is sodium silicate solution because it is cheaper and produced in substantially larger quantities than potassium silicate. However, potassium silicate and calcium hydroxide and mixtures of

these activating solutions have also been used to initiate the geopolymerization [5, 6, 7].

Although geopolymer technology is gradually finding commercial applications, a more complete understanding of the chemistry responsible for the formation and hardening of the gel is critical to commercial development and application of these binders. A variety of analytical techniques have been used to understand and control geopolymer behavior, but much about these materials is still not well understood. The molecular structure and hence the properties of geopolymers depend on parameters such as the chemical and mineralogical compositions of the raw material, its dissolution properties, the composition and amount of alkali activator, and the curing conditions. Of these parameters, the chemical composition of both raw material and activating solution is very important in determining the molecular structure of the final product. The chemical composition of such cementitious systems can be uniquely defined by the molar ratios of SiO_2/Al_2O_3, SiO_2/Na_2O, Na_2O/Al_2O_3, and H_2O/Al_2O_3 [1, 8, 9].

Owing to the complex nature of the raw materials usually present in the starting mixture, the exact effect of the initial composition on the synthesis of inorganic polymers and their final structure warrants further study, which can be conveniently carried out using spectroscopic techniques such as solid-state nuclear magnetic resonance

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spectroscopy (MAS NMR) to determine the coordination state and atomic environment of the silicate and aluminate units in the X-ray amorphous gel structure of the geopolymer [10]. Previous MAS NMR studies of the effect of various synthesis parameters on the formation of geopolymers from aluminosilicates such as metakaolin have tended to ignore small changes in the ^{27}Al chemical shift, simply using the spectra to indicate the completeness of the reaction and the absence of unreacted octahedral aluminium [11]. Likewise, although the ^{29}Si MAS NMR spectra of geopolymers are broad and featureless [11], they have been interpreted by previous workers by estimating the centre-of-gravity of possible components [12], or deconvoluted using simplified fitting rationales adopting arbitrarily chosen peak parameters- [13]. More recently, Urbanova *et al.* [14] used factor analysis to extract structural information from ^{27}Al and ^{29}Si MAS NMR spectra of samples of differing composition without resorting to spectral deconvolution; this procedure revealed differences in the spectral line shapes. This paper reports the effect of the SiO_2/Na_2O molar ratio on the geopolymer structure, as revealed by a detailed line shape analysis of the solid-state MAS NMR spectra of alkali-activated metakaolin-based geopolymers, in conjunction with X-ray diffraction, Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

II. Experimental Procedure

(1) Materials

Metakaolin was obtained by calcining kaolin at 750 °C for 24 h. The chemical composition of the resulting metakaolin determined with XRF was $2.25SiO_2 \cdot Al_2O_3$ with small amount of alpha quartz as an impurity (Fig. 1). NaOH pellets (98 % pure) and sodium silicate solution with a molar ratio SiO_2/Na_2O of 3.4 (Merck) were used as the alkaline reagents.
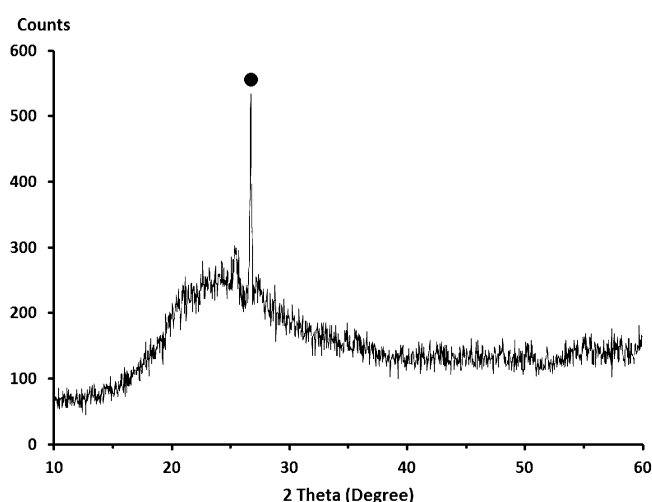

Fig. 1: XRD diffraction trace of metakaolin. The marked peak is from a quartz impurity (JCPDF file no. 33 – 1161).

(2) Processing and composition design

To study the effect of the SiO_2/Al_2O_3 molar ratio on the composition and structural development of the geopolymers, sodium silicate and sodium hydroxide were introduced in different proportions into the metakaolin-

based geopolymers. Activating solutions were prepared with various SiO_2/Na_2O ratios to produce the series of geopolymer compositions listed in Table 1. Solid NaOH was first dissolved in the sodium silicate solution, followed by the addition of water as required. The solution was cooled to room temperature before being mixed with metakaolin so as to produce a series of samples with $Na_2O/Al_2O_3 = 1$ and SiO_2/Na_2O varying from 2.25 to 4.00. The samples were cast in 25-mm-diameter airtight cylindrical polyethylene molds and vibrated for 10 mins to remove entrapped air. All samples were then cured at 60 °C for 24 h.

Table 1: Molar composition of the activating solution and the corresponding geopolymer samples.

Sample no	Activating solution SiO_2/Na_2O	Geopolymer SiO_2/Al_2O_3	Geopolymer SiO_2/Na_2O	Geopolymer H_2O/Na_2O
1	0.00	2.25	2.25	10
2	0.25	2.50	2.50	10
3	0.75	3.00	3.00	10
4	1.25	3.50	3.50	10
5	1.75	4.00	4.00	10

(3) Characterization Methods

The mineralogical, structural and microstructural characteristics of the samples were investigated with XRD, FTIR, ^{27}Al and ^{29}Si MAS NMR and SEM. XRD patterns of powdered samples were recorded on a Siemens D500 diffractometer using CuKα radiation with a scanning rate of 1°/min in the range 10 – 90° (2θ). FTIR spectra were obtained on a Shimadzu FTIR-8400S spectrometer over the range 400 – 40000 cm^{-1} at a resolution of 1 cm^{-1}. Powdered samples were also examined with ^{29}Si and ^{27}Al solid-state MAS NMR at 11.7 T using a Bruker Avance III 500 spectrometer operating at a ^{29}Si frequency of 99.29 MHz with a 5-mm Doty MAS probe and a zirconia rotor spun at ~ 6 kHz. The excitation pulse for ^{29}Si was 7 µs with a recycle time of 30 s and the spectra were referenced with respect to tetramethyl silane (TMS). The 11.7 T ^{27}Al solid-state spectra were acquired at an operating frequency of 130.24 MHz using a 4-mm Doty MAS probe with a silicon nitride rotor spun at 10 – 12 kHz, a 1 µs pulse and a 1 s recycle time. The spectra were referenced with respect to $Al(H_2O)_6^{3+}$. The development of microstructure in the geopolymer matrix was observed using a Tescan VEGA SEM. The images were obtained from solid polished samples coated with Au, at an accelerating voltage of 30 kV and working distance of 12 mm. The samples for SEM were prepared by cutting with a diamond saw (using an oil-based blade lubricant), grinding in water and polishing using consecutively finer media, prior to final preparation with 1200 grit SiC abrasive paper. After they had been polished, the samples were dried in the oven at 60 °C and then coated with Au before imaging.

III. Results and Discussion

(1) X-ray diffraction analysis

The XRD diffraction patterns (Fig. 2) indicate that the original metakaolin is basically amorphous and only contains quartz as minor crystalline phase (Fig. 2f). The XRD traces of the geopolymers show an obvious shift in the amorphous feature of the geopolymers; the crystalline phase originally present in metakaolin has been slightly shifted towards higher values (from ~ 23° to ~ 28° 2θ). As shown by the broad diffraction peaks, all the geopolymers are X-ray amorphous with a clear lack of long range order [1]. However, there are obvious differences in the degree of crystallinity and the crystal phases formed in the different samples. The XRD patterns of the samples synthesized with low SiO_2/Na_2O ratios ($SiO_2/Na_2O \leq 2.50$) show a number of intense diffraction peaks which are associated with the crystallization of zeolite-type materials. The formation of zeolites in samples synthesized without silicate species in the activating solution has been reported previously [1, 15]. The XRD patterns indicate that the higher the concentration of silicate species in the activating solution, the greater the amorphous content of the geopolymer products.
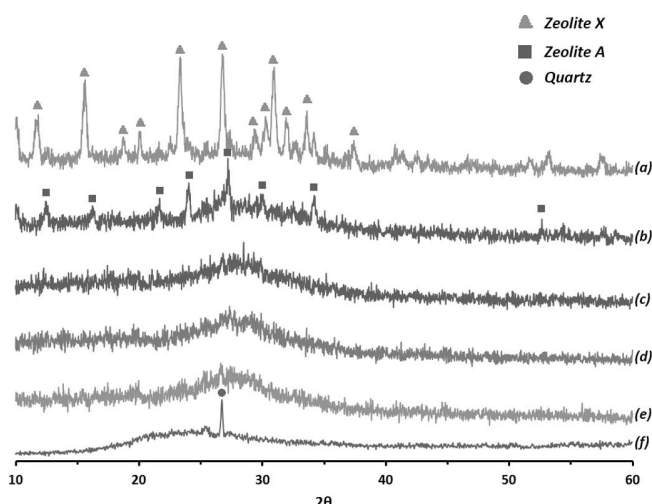

Fig. 2: XRD diffractograms of samples with different SiO_2/Na_2O molar ratios after curing; (a) 2.25, (b) 2.50, (c) 3.00, (d) 3.50, (e) 4.00 and (f) metakaolin. Zeolite X (PDF # 38 – 0237), Zeolite A (PDF # 38 – 0241)

In the geopolymerization process, the alkali activator performs different functions. The metakaolin particles are dissolved by the alkali solution while the soluble silicate accelerates the polymerization by providing self-polymerizing species and by initiating polymerization between the silicate oligomers [16]. Therefore, increasing the SiO_2/Na_2O ratio in the alkali solution should result in the formation of larger molecular units in the material.

(2) FTIR analysis

The IR spectra of metakaolin and different geopolymer pastes are shown in Fig. 3. According to these spectra it can be concluded that:

(a) The strong characteristic band at 1090 cm⁻¹ in the spectrum of metakaolin is shifted by about 110 cm⁻¹ to lower wavenumbers after alkali activation. This shift indi-

cates the formation of a new structure different from metakaolin, as was also observed in the XRD patterns. The 1090 cm⁻¹ band is related to the Si-O vibration. The large shift towards low wavenumbers can be attributed to the replacement of SiO_4 tetrahedra by AlO_4 tetrahedra, which alters the local chemical environment of the Si-O bonds [11].

(b) The intense band related to the Si-O vibration shifts to lower wave numbers with decreasing SiO_2/Na_2O molar ratios in the activating solution (Fig. 4). This may be caused by the presence of weaker Al-O bonds owing to silicon substitution by aluminum in the second coordination sphere. The peaks at around 1000 cm¹ are a major characteristic of geopolymer materials, representing the fusion of both Al-O and Si-O stretching, and can indicate the extent of aluminum incorporation with a lowering in the energy of the peak [17].

(c) In the metakaolin spectrum the broad band at about 3 450 cm⁻¹ results from absorbed atmospheric water. After the formation of the polymeric structure, the intensity of the bands at about 1 650 cm⁻¹ and 3 450 cm⁻¹ increases owing to the presence of additional water.

(d) A Si-O-Al vibration band at 810 cm⁻¹ and a Si-O bending vibration band at about 450 cm⁻¹ is observed in the metakaolin IR spectrum. In geopolymers the Si-O-Al band at 810 cm⁻¹ is replaced by several weaker bands in the range 600 – 800 cm⁻¹ which confirms the disruption of the Al environment during geopolymerization. More detailed information about Al behavior during this process is provided by ²⁷Al MAS NMR.

(e) The intensities and number of the bands in the range 600 – 800 cm⁻¹ in the IR spectrum of the geopolymers are considerably reduced by increasing the SiO_2/Na_2O ratio in the alkali solution, confirming that less soluble silicate species has produced a more organized structure. This was also indicated in the XRD patterns.

(3) MAS NMR spectroscopy

The ²⁷Al MAS NMR spectrum is a key factor in characterizing geopolymers and other amorphous aluminosilicates, since it provides direct information about the coordination state of the alumina units in the structure [10]. The ²⁷Al NMR spectrum of the metakaolin starting material (Fig. 5a) shows three broad peaks which can be fitted to Laurentzian line shapes at 58.3 ppm, 29.4 ppm and 2.2 ppm, corresponding to aluminium in tetrahedral, pentahedral and octahedral coordination respectively [10]. The significantly larger size of the pentahedral resonance shows this to be the most abundant Al coordination state in metakaolin, and the relative intensities of all the peaks in this spectrum are quite typical of metakaolin [10]. The ²⁹Si NMR of metakaolin (Fig. 5b) exhibits a broad asymmetric envelope containing shoulders which can be fitted to six Laurentzian line shapes spanning the range of $Q^4(mAl)$ sites, with maximum intensities at -94.2, -102.9 and -107 ppm corresponding to silicon sites with m = 0 – 2 [10].

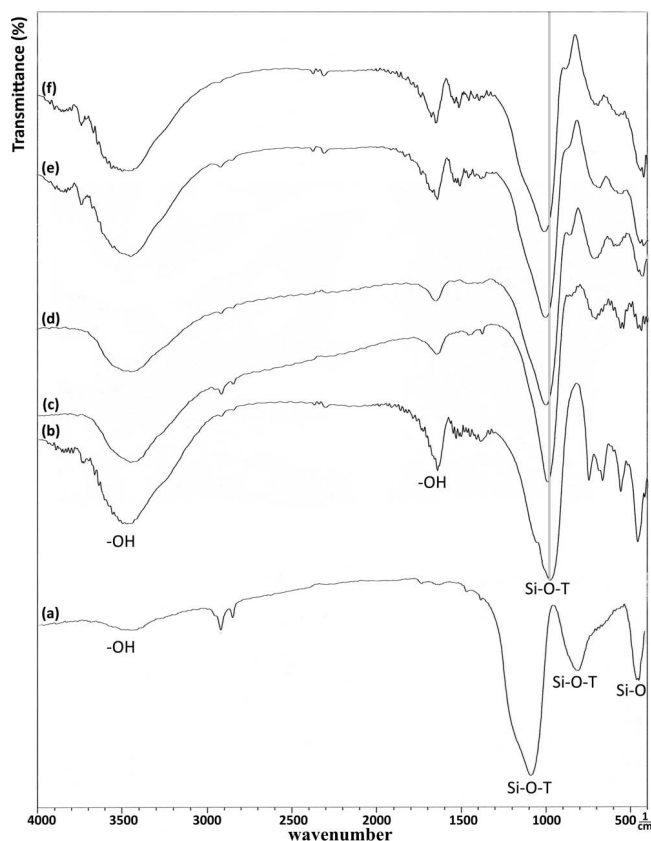**Fig. 3:** FTIR spectra of samples with different SiO_2/Na_2O molar ratios after curing; (a) 2.25, (b) 2.50, (c) 3.00, (d) 3.50, (e) 4.00 and (f) metakaolin.

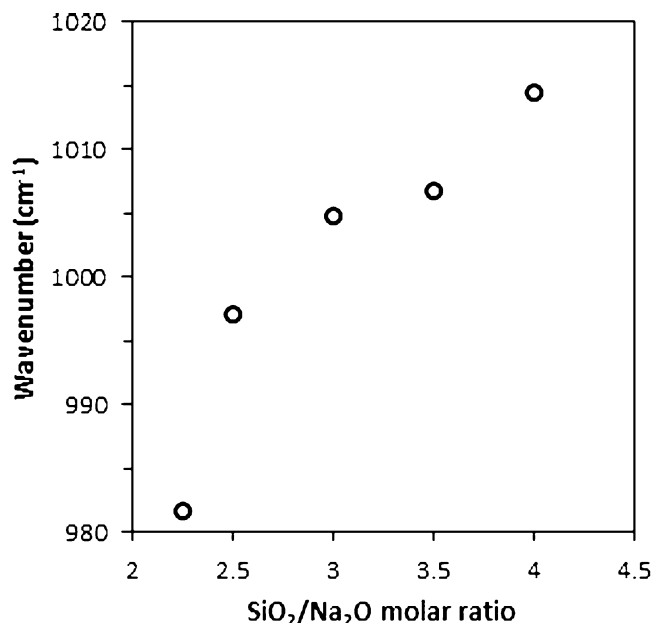**Fig. 4:** Variation of Si-O-T peak position with SiO_2/Na_2O molar ratio for geopolymers

When the geopolymers are produced by alkali activation, only one intense ^{27}Al MAS NMR peak at about 58 – 59 ppm is present (Fig. 6), indicating the conversion of the aluminum to fully tetrahedral coordination with four oxygen atoms. The lack of a resonance peak at 28 ppm in the geopolymer materials indicates that Al(V) is completely converted to Al(IV) during geopolymerization. In samples synthesized with SiO_2/Na_2O ratios ≤ 2.50, the

spectra are of slightly asymmetric shape (Fig. 6a, b), suggesting the presence of aluminum in more than one non-identical tetrahedral site. In the sample with $SiO_2/Na_2O =$ 2.25, the asymmetric component appears as a shoulder at about 65 ppm, moving to about 61 ppm in the sample with $SiO_2/Na_2O = 2.50$ before being incorporated into the main tetrahedral envelope at higher SiO_2/Na_2O ratios. The presence of asymmetric aluminium ^{27}Al MAS NMR peaks in geopolymers with low SiO_2/Na_2O ratios has not previously been reported, but may reflect the presence of the zeolite-type compounds with different Al-O bonds or different Al-O-Al angles seen in the XRD traces (Fig. 2). This result is consistent with a previously reported qualitative observation that lower-silica geopolymers are more likely to form zeolitic components [18]. The centre-of-gravity (COG) of the ^{27}Al peaks become slightly more negative with increasing values of the SiO_2/Na_2O molar ratio of the activating solution (Table 2). As this shift in the peak position is relatively small and the Al avoidance principle predicts that AlO_4 tetrahedra can be bonded only to SiO_4 tetrahedra, the Al peak position must be influenced by the changes in the second coordination sphere. The ^{27}Al NMR spectra were augmented by ^{29}Si MAS-NMR data to provide additional information on the molecular structure of the aluminosilicate network in the different geopolymer gel samples.
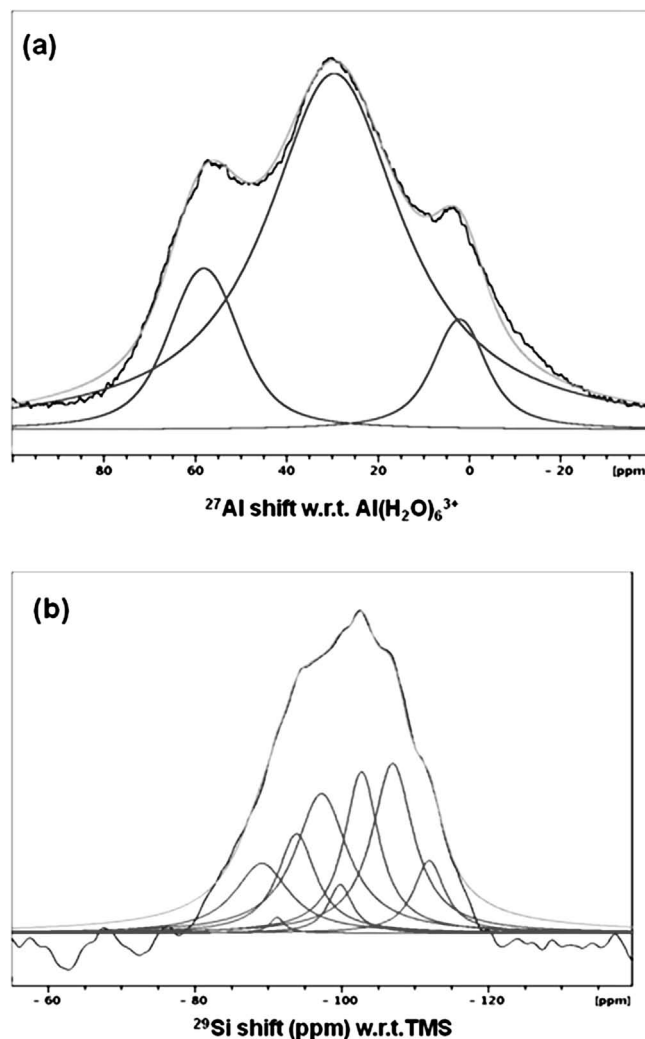

Fig. 5: (a)^{27}Al and (b)^{29}Si MAS NMR spectra of metakaolin.

Table 2: ^{27}Al and curve-fitted ^{29}Si MAS NMR parameters of the geopolymer samples. Asterisks denote the major ^{29}Si resonances.

Sample	SiO$_2$/Na$_2$O	^{27}Al (ppm)	^{29}Si (ppm)	^{29}Si (ppm)	^{29}Si (ppm)	^{29}Si (ppm)
Metakaolin	0	58.3, 29.4, 2.2	-	-89.1, -91.0, -93.6*	-97.1, -99.6, -102.6*	-106.7, -111.7
1	2.25	59.1	-84.3*	-88.6	-	-
2	2.50	59.3	-83.8	-89.5*	-102.7	-
3	3.00	59.2	-78.6, -81.6, -83.9	-86.7*, -90.6,	-95.9	-
4	3.50	58.6	-81.8, -84.9	-88.2*, -93.1,	-96.7	-
5	4.00	58.5	-79.6, -82.3	-86.9, -91.1*, -94.8	-98.6, -102.0	-
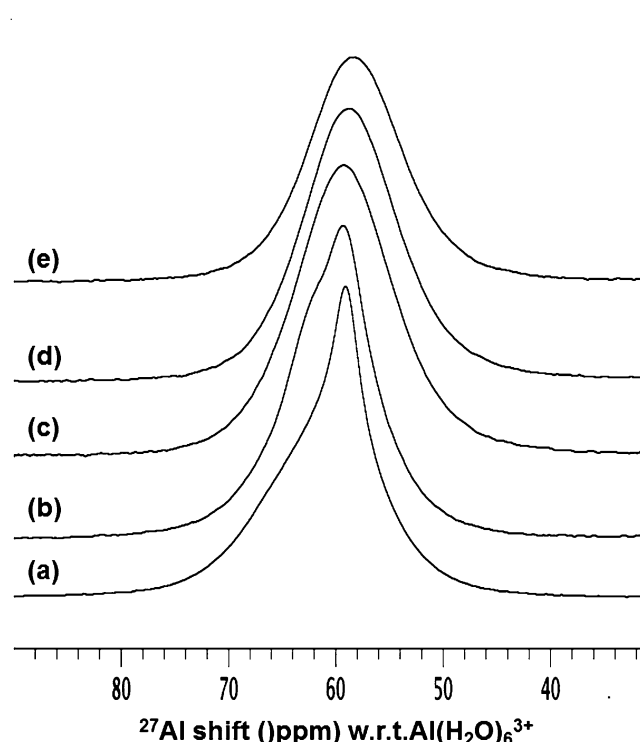
Fig. 6: ^{27}Al NMR of geopolymers synthesized with different SiO$_2$/Na$_2$O ratio; (a) 2.25, (b) 2.50, (c) 3.00, (d) 3.50, (e) 4.00.

The ^{29}Si NMR spectra of the different geopolymers (Fig. 7) contain broad peaks containing several shoulders reflecting the presence of a number of overlapping resonances in the range -78.6 to -102.7 ppm. Fig. 7 shows that these spectra can satisfactorily be fitted with several Laurentzian line shapes (Table 2). As the SiO$_2$/Na$_2$O ratio increases, the spectral envelope becomes more complex, necessitating a greater number of peaks required for a satisfactory fit (Fig. 7, Table 2). At the same time, the COG of the fitted spectral envelope moves from -84.1 ppm in the sample with SiO$_2$/Na$_2$O = 2.25 to -91.1 ppm in the sample with SiO$_2$/Na$_2$O = 4.00. The direction of this shift indicates that increasing the SiO$_2$/Na$_2$O molar ratio of the activating solution will decrease the number of neighboring aluminate tetrahedra; thus the Si nuclei will become less shielded (the chemical shifts become less negative). Replacement of next-nearest-neighbor Al by Si decreases the distance between the two tetrahedral cations, shielding the silicon nuclei [19].
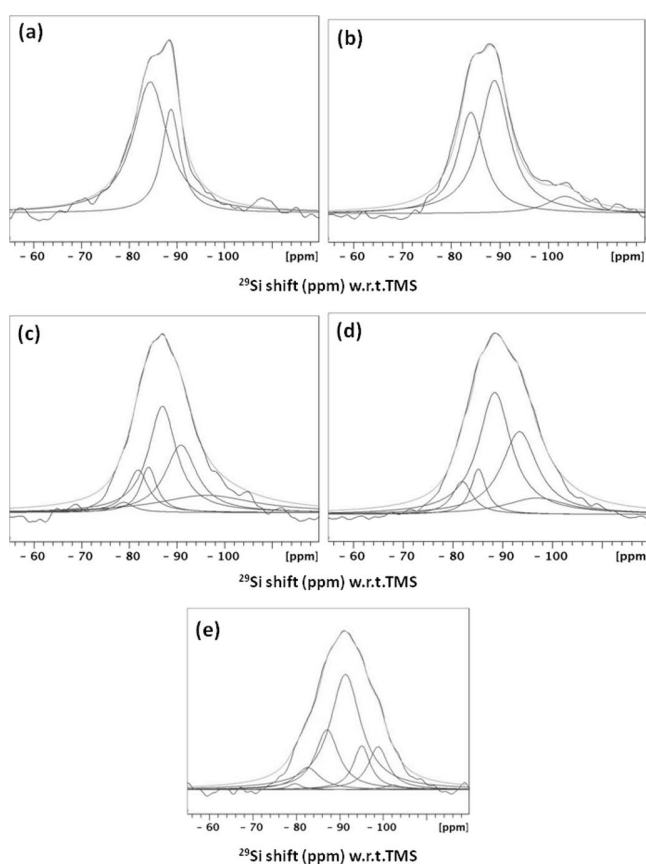
Fig. 7: ^{29}Si NMR of geopolymers synthesized with different SiO$_2$/Na$_2$O ratio; (a) 2.25, (b) 2.50, (c) 3.00, (d) 3.50, (e) 4.00.

The ^{29}Si peaks become less symmetric and broader as the molar ratio of the activating solution increases. The broad ^{29}Si resonances indicate that the Si and Al tetrahedra in geopolymer are not regularly oriented. The peak width and symmetry is influenced by the relative abundance of the various Q^4(mAl) units. Increasing the silicon atoms in the geopolymer structure will cause a wider distribution in the number of aluminum atoms around the SiO$_4$ tetrahedral and the polymeric structure will become more disordered.

Previous studies have shown that the chemical shift of ^{29}Si in an amorphous or highly disordered state in geopolymers increases by approximately 5 ppm compared with a zeolite of the same chemical composition [20].

^{29}Si spectra of samples synthesized with SiO$_2$/Na$_2$O ratios ≤ 2.50 show sharp resonances assigned to Q^4(4Al) and Q^4(3Al) units, confirming that SiO$_4$ and AlO$_4$ tetrahedra are connected to each other alternatively. Samples synthesized with SiO$_2$/Na$_2$O ratio ≥ 3.00 have their major peak at about -90 ppm arising from silicon atoms in Q^4(3Al) units, but shoulders on the major peak suggest that Q^4(2Al) and Q^4(4Al) units are also present in their structure.
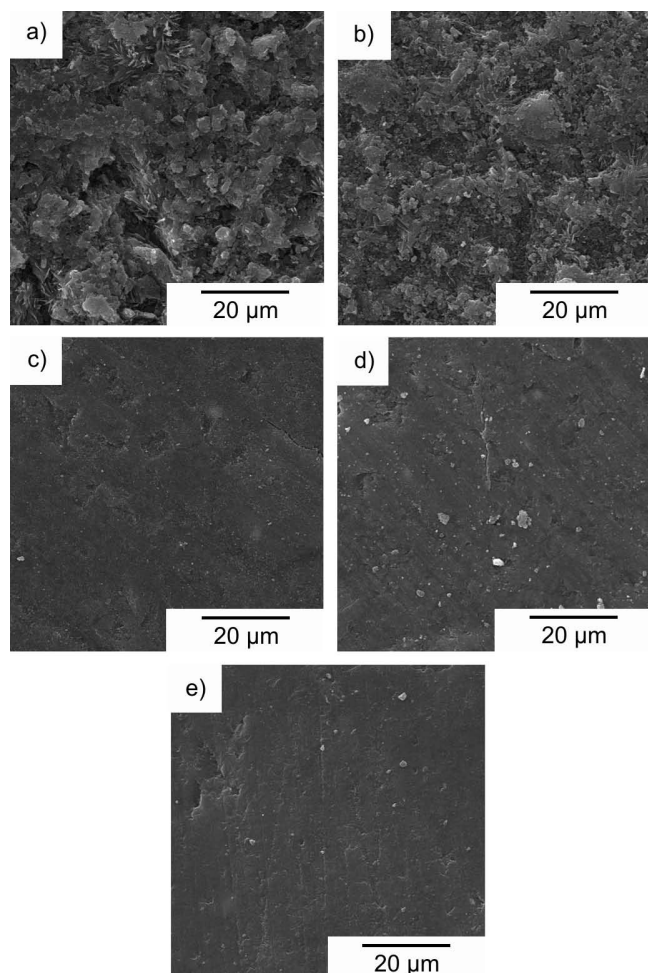

Fig. 8 : SEM micrograph of geopolymers synthesized with different SiO$_2$/Na$_2$O ratio; (a) 2.25, (b) 2.50, (c) 3.00, (d) 3.50, (e) 4.00

(4) Microstructure development

SEM images of samples of SiO$_2$/Na$_2$O ratios 2.25, 2.5, 3, 3.5 and 4 are presented in Fig. 8, showing an obvious change in microstructure and homogeneity of the samples as the SiO$_2$/Na$_2$O ratio increases. The microstructures of geopolymers of composition SiO$_2$/Na$_2$O ≥ 3.00 do not change significantly with increasing SiO$_2$/Na$_2$O ratio, but the fineness of the texture and the density of the geopolymer increases markedly from SiO$_2$/Na$_2$O = 2.50 to 3.00. Fig. 8 shows that the microstructures of samples with SiO$_2$/Na$_2$O ≤ 2.50 are entirely non-uniform, consisting of loose grains of different shapes and sizes and containing continuous pores. The sharp peaks found in the XRD patterns of these samples may be due to presence of these grains. The microstructures of geopolymers with higher SiO$_2$/Na$_2$O ratios are clearly more homogeneous and dense.

IV. Conclusion

The effect of the composition of the activating solution on the formation and structure of geopolymer gels with a range of compositions has been investigated by a range of analytical techniques. The structure of geopolymers produced by polycondensation of metakaolin in sodium silicate solutions is dependent on, among other factors, the SiO$_2$/Na$_2$O molar ratio. The reaction product of metakaolin activated with sodium silicate and NaOH solutions is an amorphous hydrated sodium aluminosilicate in which a Q^4(3Al) type three-dimensional structure predominates. The alkali activation of metakaolin with sodium silicate and NaOH produces materials with higher degree of polymerization than activation with NaOH alone.

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