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The composition range of aluminosilicate geopolymers

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Abstract

Aluminosilicate geopolymers with SiO_2/Al_2O_3 ratios ranging from 0.5 to 300 have been prepared from mixtures of dehydroxylated kaolinite with either ρ-Al_2O_3 or fine Aerosil SiO_2, with the ratios Na_2O/SiO_2 and H_2O/SiO_2 kept constant throughout the series. All the compositions hardened at ambient temperature, but the high-alumina compositions were of low strength and did not display typical XRD and NMR geopolymer characteristics, by contrast with the compositions of S/A between 2 and 300 which showed typical amorphous geopolymer XRD traces and ^{27}Al, ^{29}Si and ^{23}Na NMR spectra. The samples with increasing SiO_2 content ($S/A > 24$) showed increasingly elastic behaviour, deforming rather than crushing in brittle fashion, and upon heating at 100–250 °C, their hydration water was expelled as bubbles, forming stable foamed materials at about 300 °C.

Keywords: Amorphous materials; Nuclear magnetic resonance spectroscopy; Mechanical properties; Geopolymers; Aluminiumsilicates

1. Introduction

As originally formalised by Davidovits,[1] aluminosilicate geopolymers consist of tetrahedral AlO_4 and SiO_4 units polycondensed at ambient temperatures under highly alkaline conditions into three-dimensional structures with charge stabilisation provided by alkaline earth ions. Davidovits[1] described three basic units for polymerisation, $[O–Si–O–Al–O]M^+$ (sialate), $[O–Si–O–Al–O–Si–O]M^+$ (sialate siloxo) and $[O–Si–O–Al–O–Si–O–Si–O]M^+$ (sialate disiloxo), corresponding to Si/Al ratios of 1, 2 and 3, respectively. Subsequently there has been much discussion regarding the possibility of aluminosilicate geopolymer formation with other Si/Al ratios, including non-integer ratios. For such discussion to be meaningful, a working definition of a geopolymer must be established. MacKenzie[2] have suggested a number of possible defining criteria for geopolymerisation, including development of strength at ambient temperatures, lack of long-range atomic order, the presence of solely tetrahedral Al–O and Si–O units (as determined by solid-state MAS NMR) and thermal stability at high temperatures.

The present study explores the possibility of geopolymer formation in aluminosilicates with a wide range of Si/Al compositions. Starting from dehydroxylated kaolinite (metakaolinite), both the alumina- and silica-rich compositions were explored, obtained by adding either amorphous Al_2O_3 or very fine amorphous SiO_2 to the mixture. The above-mentioned criteria (strength development at ambient temperature, X-ray and NMR characteristics and thermal stability) were used to test whether geopolymerisation had occurred in the samples.

2. Experimental

The starting materials were dehydroxylated kaolinite (Metamax metakaolinite, Engelhard Corp.), amorphous Al_2O_3 (Alphabond 300, Alcoa), fine amorphous silica

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(Aerosil 200, Degussa AG) and NaOH pellets (Scharlau Chemicals analytical grade). The alumina was chosen because it has the characteristics of ρ-alumina (it is X-ray amorphous and is shown by ^{27}Al MAS NMR (Fig. 2A) to contain a mixture of 4-, 5- and 6-coordinated Al, thus making it not unlike the Al coordination in metakaolinite. Although the fineness of Aerosil silica has the disadvantage of increasing the water demand, it was chosen for these experiments for the enhanced reactivity expected to result from its amorphous state.

The geopolymer samples were prepared by pre-dissolving the amount of NaOH necessary to maintain an $H_2O:Na_2O$ molar ratio of 11 throughout the series of compositions. The metakaolinite and either alumina or silica in the required proportions was dry-blended in a jar and the solid was then slowly added to the liquid with vigorous hand mixing. Aerosil has a high water demand and generally the mass of added water was approximately equal to the required amount of Aerosil for any given $SiO_2:Al_2O_3$ ratio. Thus, while the $H_2O:Na_2O$ ratio remained constant, the $H_2O:SiO_2$ and $H_2O:Al_2O_3$ ratios changed. Possible water loss during mixing resulting from the exothermic reaction between the Aerosil/metakaolinite and NaOH was not determined in these experiments.

Samples were cast into 30 mm diameter × 40 mm high cylinders for determination of the crushing strength, allowed to attain crushing strength at 40 °C for 1 h then cured at 90 °C overnight. After demoulding, the samples were crushed using an Instron Model TTKM 25 tonne Universal Tester with a crosshead speed of 10 mm min^{-1}. The reported crushing strengths, which are the mean of at least two or three replicates, depend on the sample shape and size, and while they provide a comparison between the present samples, they do not represent absolute strengths. The fragments from the crushing tests were powdered and examined by XRD (Philips PW 1700 computer-controlled goniometer with graphite monochromator and Co Kα radiation). The ^{27}Al, ^{29}Si and ^{23}Na MAS NMR spectra were acquired at 11.7 T using a Varian Unity 500 spectrometer and 5 mm Doty MAS probe spun at 10–12 kHz, under the following conditions:

- ^{27}Al: spectrometer frequency 130.244 MHz with a 1 μs (π/10 pulse for solution) and a 1 s delay, spectra referenced to $Al(H_2O)_6{}^{3+}$.
- ^{29}Si: spectrometer frequency 99.926 MHz with a 6 μs (π/10) pulse and a 100 s delay, spectra referenced to tetramethylsilane (TMS).
- ^{23}Na: spectrometer frequency 132.225 MHz with a 1 μs (π/10 pulse for solution) and a 1 s delay, spectra referenced to 1 M aqueous NaCl.

The thermal behaviour (up to 800 °C) of ∼0.5 mm sample fragments was examined in situ using a Nikon type XP microscope equipped with a hot stage (ULVAC Co., type MS-EIS) and a video camera to record the sample changes in real time as a function of heating temperature. The samples were heated at a rate of 10 °C min^{-1} in ambient atmosphere and viewed at a magnification of 100×.

3. Results and discussion

In the following discussion we have followed Barbosa et al.[3] by defining the sample compositions in terms of *molar ratios* of SiO_2 to Al_2O_3 (*S*/*A*). On this basis, a geopolymer made from metakaolinite alone would be described as having an *S*/*A* value of 2 (although in atomistic terms it would be a polysialate with Si/Al = 1). The present samples cover both the high-alumina range (to *S*/*A* = 0.5) and the high-silica range (to *S*/*A* = 300).

3.1. The high-alumina range (from S/A = 2 to 0.5)

All the samples set and hardened, with crushing strengths shown in Table 1. However, their X-ray traces (Fig. 1) show the as-prepared samples not to be characteristically X-ray amorphous, but to contain significant amounts of crystalline phases. This is most clearly seen in the *S*/*A* = 0.5 sample (Fig. 1A) in which the crystalline phases are gibbsite ($Al(OH)_3$, (PDF no. 70-2038)), a zeolite-type sodium aluminosilicate hydrate (PDF no. 31-1271) and thermonatrite, $Na_2CO_3{\cdot}H_2O$ (PDF no. 8-0448), the latter formed by atmospheric carbonation of excess NaOH. There is no evidence of an amorphous component in sample *S*/*A* = 0.5, but as the proportion of SiO_2 is increased to *S*/*A* = 1, an amorphous hump appears in the XRD trace, characteristic of a geopolymer, but with some of the crystalline peaks of thermonatrite and

Table 1
Composition and properties of the present series of geopolymers, prepared with Na_2O/SiO_2 fixed at 0.3 and H_2O/SiO_2 fixed at 11

SiO_2/Al_2O_3	Na_2O/Al_2O_3	H_2O/Al_2O_3	Relative crushing strength (MPa)	XRD phases[b]
0.5	0.66	7.2	0.7	g, z, t
1	0.66	7.2	1.0	am, z, t
2	0.88	9.7	7.8	am, z? (tr)
4	1.1	12.6	5.7	am
6	1.3	14	6.5	am
8	2.4	24	8.7	am
16	5	54	10.9	am
24	6.5	72	2.8	am
36	9	102	3.5	am
48	13	145	Nd[a]	am
60	16	175	Nd	am
72	21	233	Nd	am
85	21	231	Nd	am
100	30	326	Nd	am
150	45	490	Nd	am
200	59	653	Nd	am
300	87	960	Nd	am

b = broad, tr = trace, sh = shoulder.

[a] Not determined.

[b] Key: am = X-ray amorphous, G = $Al(OH)_3$ (PDF no. 70-2038), Z = $1.08Na_2O{\cdot}Al_2O_3{\cdot}1.68SiO_2{\cdot}1.8H_2O$ (PDF no. 31-1271), T = $Na_2CO_3{\cdot}H_2O$ (PDF no. 8-448).

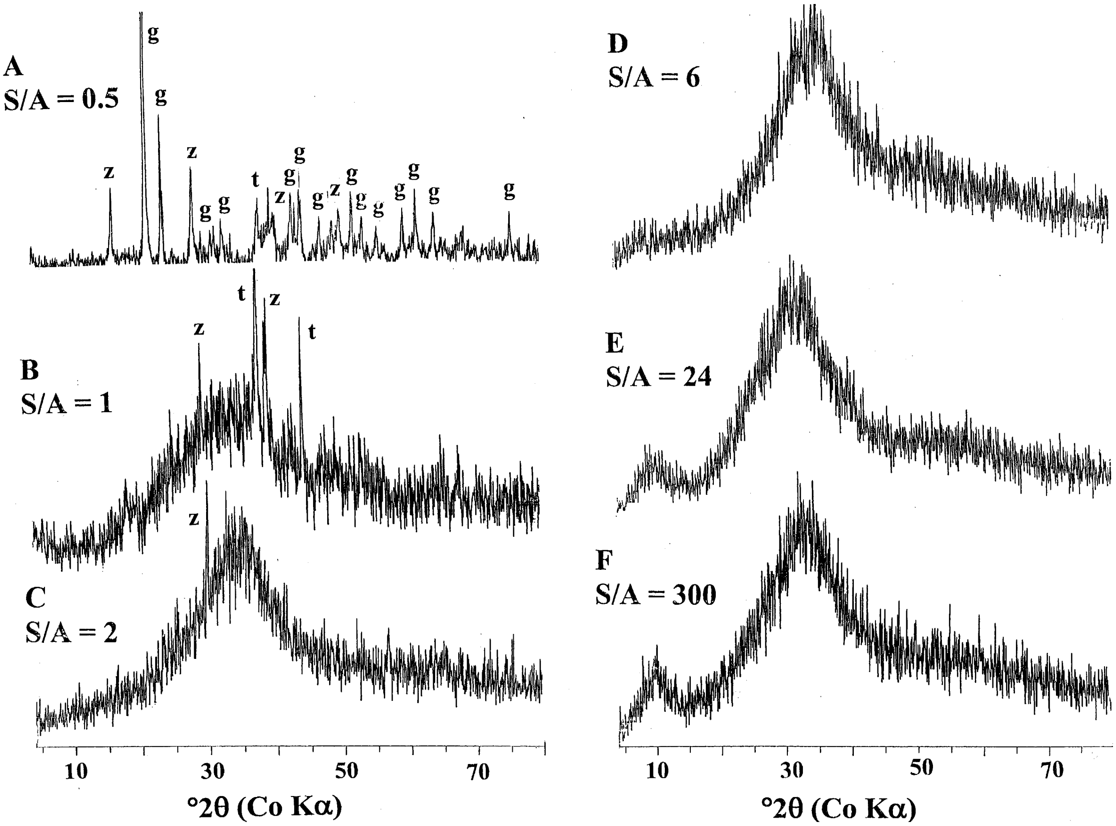

Fig. 1. XRD trace of selected geopolymers. Trace D is typical of samples with *S/A* of 4–16. Trace E is typical of samples with *S/A* of 24–200.

the hydrated sodium aluminosilicate zeolite superimposed (Fig. 1B). The amorphous geopolymer XRD feature is predominant in sample *S/A* = 2 (Fig. 1C), the single sharp peak in this diffractogram arising from the zeolite-type phase.

Comparison of the ^{27}Al MAS NMR spectra of the highest-alumina sample *S/A* = 0.5 (Fig. 2B) with that of the ρ-alumina starting material (Fig. 2A) shows the reaction with sodium hydroxide has led to the appearance of a new, sharp tetrahedral resonance at 60 ppm, apparently formed at the expense of some of the octahedral resonance at 8 ppm and the small resonance at 35 ppm sometimes ascribed to 5-coordinated Al–O.[4] The presence of gibbsite in this sample is reflected by its octahedral peak at 8 ppm (which also coincides with but is narrower than the original octahedral component of the ρ-alumina). The metakaolinite starting material has a ^{27}Al spectrum containing broad overlapping 4-, 5- and 6-fold Al–O resonances at about 60, 30 and 3 ppm, respectively;[4] the intense feature at 30 ppm is absent from Fig. 2B, suggesting that this site, which is common to both the metakaolinite and ρ-alumina starting materials, is vulnerable to reaction with NaOH. The more intense tetrahedral resonance in this spectrum at 60 ppm is narrower than in typical geopolymers, consistent with its location in the crystalline zeolite-type phase. Increasing the *S/A* ratio to 1 produces a broader tetrahedral ^{27}Al peak more typical of a conventional geopolymer but about 10 ppm downfield from the typical geopolymer position (Fig. 2C). The persistence of the octahedral resonance at 8 ppm is a further indication that this is not a normal geopolymer. The ^{27}Al NMR spectrum of sample *S/A* = 2 (Fig. 2D) shows the single tetrahedral resonance characteristic of a geopolymer, but differs slightly in being narrower and located about 4–5 ppm downfield.

The ^{29}Si spectra of these samples are shown in Fig. 3. The low-silica samples *S/A* = 0.5 (Fig. 3A) and *S/A* = 1 (Fig. 3B) show a two resonances, the narrower of which (at −83 to −86 ppm) correspond to a framework structure substantially saturated by Al as in a zeolite. The broader peak, at −106 ppm in sample *S/A* = 1 corresponds to a silicate unit considerably less saturated by Al while the peak at −118 ppm in sample *S/A* = 0.5 indicates the presence of silica with no bonded Al atoms. The presence of these discrete silica units in such highly aluminous compositions is unexpected, and seems to indicate incomplete reaction in these samples. The ^{29}Si spectrum of sample *S/A* = 2 (Fig. 3C) shows only a small trace of incompletely reacted silica, but the major resonance at −89 ppm is narrower than in a typical geopolymer, and is displaced towards the position of a more aluminous structure.

The ^{23}Na spectra of the two most Al-rich compositions (Fig. 4A and B) differ from the typical single-resonance geopolymer spectrum in showing two well-resolved peaks which probably arise from two discrete Na sites rather than from a single distorted site with a quadrupolar lineshape. The presence of narrow resonances from two Na sites is consistent with the presence of two crystalline Na-containing phases

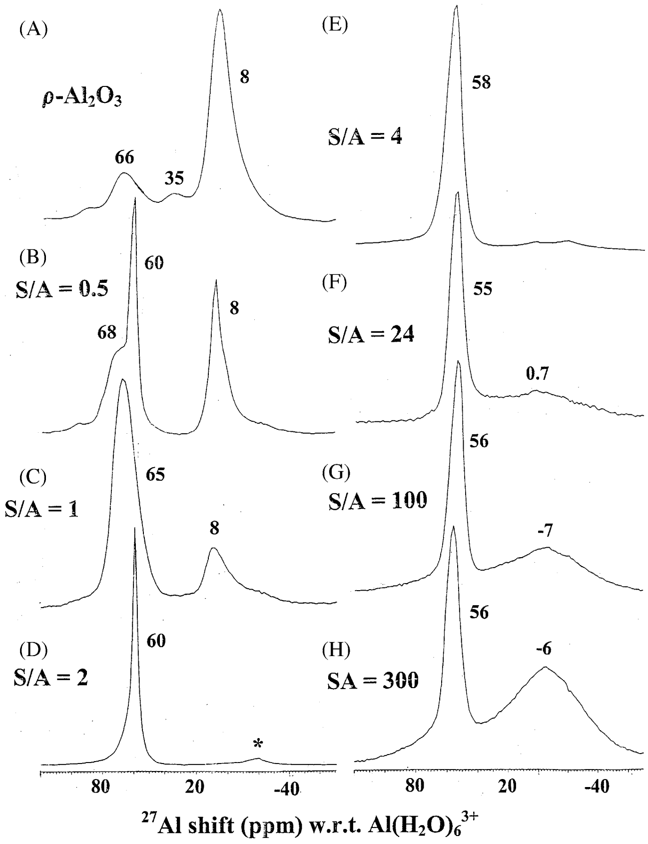

Fig. 2. 11.7 T ^{27}Al MAS NMR spectra of selected geopolymers. Spectrum E is typical of samples with *S/A* of 4–16.

(the zeolite-type phase and thermonatrite) in these samples. The ^{23}Na spectrum of sample *S/A* = 2 (Fig. 4C) is more typical of a geopolymer spectrum, but the relatively less negative shift of the single resonance suggests that the Na site is more heavily hydrated than in a normal geopolymer.[4]

Taken together, these results indicate that although the more highly aluminous compositions (*S/A* < 2) will set at ambient temperature, their strength is weak and they do not resemble normal geopolymers in other respects;

- (i) they contain substantial amounts of crystalline phases,
- (ii) their ^{27}Al NMR spectra reveal octahedral sites in addition to the solely tetrahedral sites of a typical geopolymer,
- (iii) their ^{29}Si NMR spectra indicate both Al-rich and Si-rich phases rather than the broad envelope of Si sites typical of the amorphous geopolymer structure,
- (iv) their ^{23}Na NMR spectra indicate more than one well-resolved Na sites corresponding to the presence of two crystalline hydrated Na compounds.

This tendency to form several discrete compounds rather than a single tetrahedral aluminosilicate geopolymer framework structure reflects the fact that the formation of the latter would violate Lowenstein's Rule in which the occurrence of adjacent Al–O–Al groups is unfavourable. Only in compositions *S/A* ≥ 2 (i.e. where the Si/Al atomic ratio ≥1) can

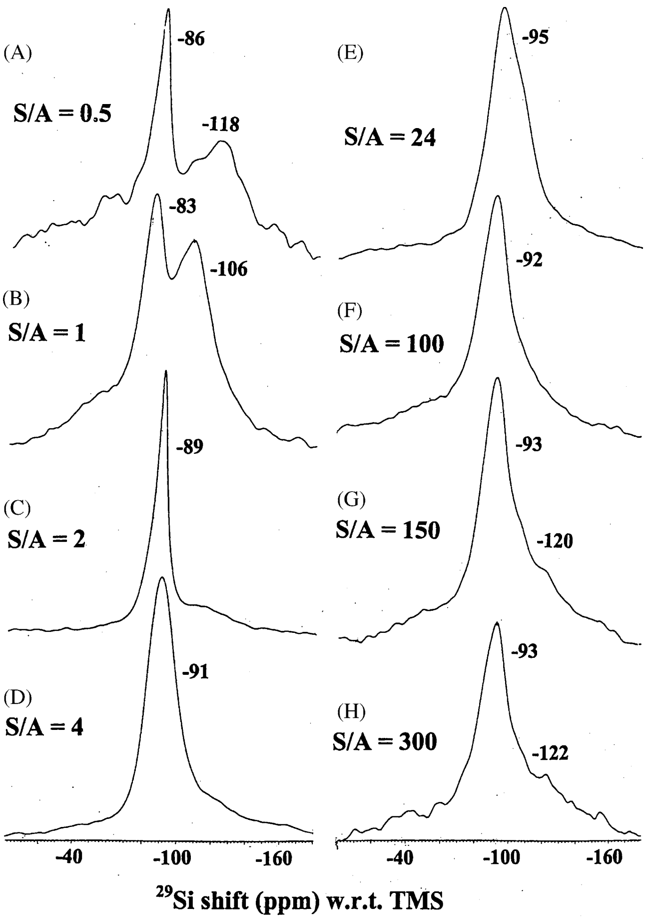

Fig. 3. 11.7 T ^{29}Si MAS NMR spectra of selected geopolymers. Spectrum D is typical of samples with *S/A* of 4–16.

Lowenstein's Rule be satisfied, as borne out by sample *S/A* = 2 which is much more typical of a "normal" geopolymer with respect to its crushing strength, amorphous XRD diffraction pattern and NMR spectra.

3.2. The high-silica range (from S/A = 2 to 300)

The setting and hardening properties of these samples show considerable variation with composition. Samples with *S/A* < 24 set normally, and possess comparable relative crushing strengths (Table 1). However, samples with *S/A* above ∼24, although setting, become increasingly rubbery in texture and in the manner of their failure; this militates against meaningful crushing strength measurements since the samples deform rather than fail.

The XRD diffractograms, selected examples of which are shown in Fig. 1D–F, indicate that all the samples in the high-silica composition range are characteristically amorphous. In samples with *S/A* ≥ 24, an additional broad but weak feature appears at about 10° 2θ (Fig. 1D and E). Drying these samples at 90 °C removes this feature, suggesting that it is associated with an increasingly higher water content necessitated by the higher water demand of the increasing content of fine Aerosil silica.

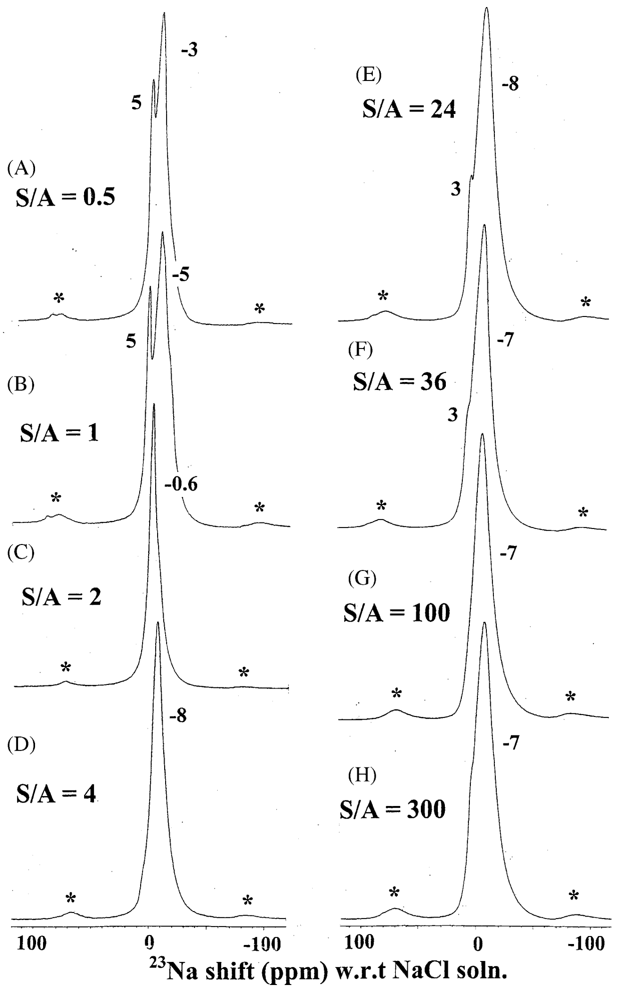

Fig. 4. 11.7 T ^{23}Na MAS NMR spectra of selected geopolymers. Spectrum D is typical of samples with *S*/*A* of 4–16.

The ^{27}Al MAS NMR spectra of these samples (Fig. 2E–H) are also typical of a normal geopolymer,[2] containing a predominant slightly broadened tetrahedral Al–O resonance at 55–58 ppm. The samples with $S/A \geq 24$ show an additional broad feature in the octahedral region, which becomes increasingly intense with increasing silica content (Fig. 2H). Since the alumina content of these samples becomes increasingly dilute at the higher silica concentrations, the stability of the tetrahedral aluminosilicate framework is not compromised by possible violation of Lowenstein's Rule, as in the samples of extremely low Si content. An alternative mechanism driving the Al component increasingly to adopt an octahedral environment may be associated with the higher water content associated with the high-Si samples, which may encourage the formation of hydrated Al species which are predominantly octahedral.

The ^{29}Si spectra of these samples (Fig. 3D–H) all show the characteristically broad geopolymer resonance[2] centred at about −91 to −95 ppm. The samples with the highest silica contents ($S/A \geq 150$) show an additional shoulder at about −120 ppm (Fig. 3G and H) indicating the presence of some uncombined silica, suggesting that these samples are approaching the composition limit at which the silica fully reacts. These spectra contain no clue to possible reasons for the increasing elasticity of the samples with increased silica content.

The ^{23}Na NMR spectra of the samples in this composition range (Fig. 4D–H) show in general a single resonance at a position corresponding to the hydrated Na$^+$ of a typical geopolymer.[2] The spectra of samples with $S/A \geq 24$ show a hint of an additional more hydrated Na site in the form of a shoulder at about 3 ppm (Fig. 4E and F).

In summary, these results indicate that the samples of high-silica composition generally show typical geopolymer characteristics, being X-ray amorphous, with typical MAS NMR spectra indicating predominantly tetrahedral Al, a range of tetrahedral Si environments (but predominantly SiQ$_4$(3Al) and hydrated Na$^+$ essentially in a single site). The most startling difference between these samples and "normal" aluminosilicate geopolymers is the increased elasticity at the higher silica contents. The structural parameters give no hint of the reason for this unexpected departure from brittle mechanical behaviour, for which we presently have no satisfactory unexplanation. Associated with the increased silica content of these samples is increased water content, which may account for a concomitant progressive increase in octahedral Al and the appearance of an additional broad lower-angle feature in the X-ray diffractogram which disappears on drying at 90 °C.

3.3. *Effect of heat on these materials*

The thermal dehydration of these geopolymers was observed in situ using a hot-stage microscope equipped with a video camera to record changes in the sample in real time. The samples of low Si content are all thermally stable, showing no evidence of change up to 800 °C. In samples of $S/A \geq 2$, the loss of a small amount of water at 430–440 °C is preceded by the opening up of small grooves or cracks at about 200 °C. These observations are consistent with the water loss previously reported from a sample of $S/A = 3.3$;[5] thermal analysis and dilatometry of that compound indicated that about 12% of the hydration water was lost below about 230 °C with a further 3% gradually evolved up to 500 °C.[5] The thermal behaviour of the higher-silica samples ($S/A > 24$) is more dramatic, occurring by the formation and growth of bubbles which cause the samples to foam. The onset temperature of this phenomenon is related to the silica content of the samples, which determines both their softening temperature and their water content (since in all these samples the Na$_2$O/SiO$_2$ ratio was maintained at about 0.3 and the H$_2$O/Na$_2$O ratio was fixed at 11, both the sodium and water contents increase with increasing *S*/*A* ratio). In the sample $S/A = 100$, bubble formation was first observed at 225 °C, whereas in samples $S/A = 150$ and 300 this temperature decreased to 140 and 100 °C, respectively. The rate of bubble growth also became more rapid in the samples of higher silica

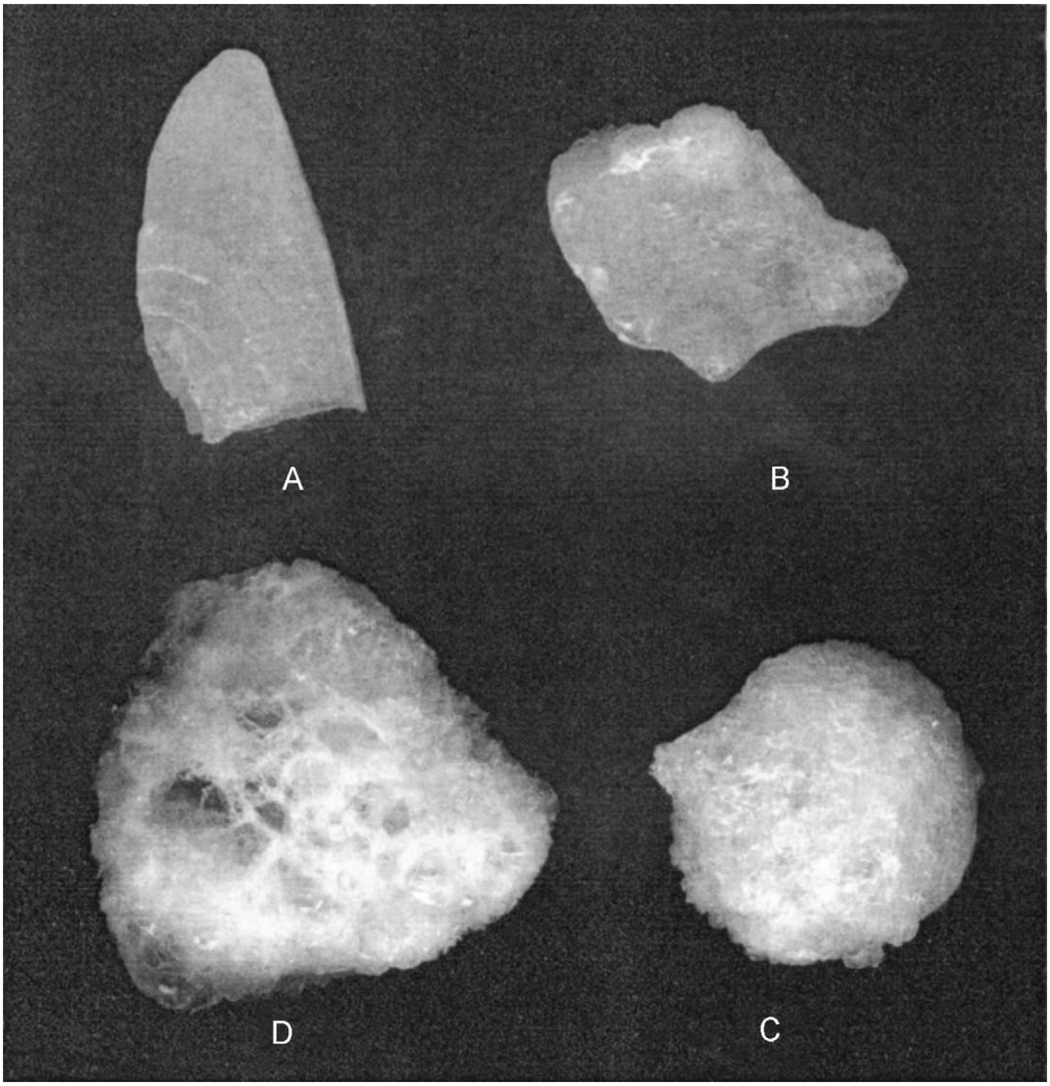

Fig. 5. Photographs of geopolymer *S*/*A* = 300 in various stages of foaming. (A) Unfoamed material showing striations typical of glassy fracture. (B) Heated to onset of bubble formation, visible in the upper right-hand region. (C) Bubble formation complete throughout the sample. (D) Sample expanded and bubbles burst to expose open pores.

content; in sample *S*/*A* = 300 bubble formation which started at 100 °C (Fig. 5B) had become widespread by 170 °C, with numbers of smaller bubbles rapidly coalescing, probably as a result of the decreased viscosity of this sample (Fig. 5C). The practical outcome of this self-foaming activity is the production of a stable foamed material at low temperatures; in the samples with $S/A \geq 100$, the foaming had ceased by 300 °C (Fig. 5D) and no further change was observed above this temperature. Foamed geopolymers prepared using a variety of foaming agents generally added prior to curing have already been reported as potential insulation materials,[6] but the present results suggest a means of utilising the compositional water as the foaming agent, allowing the foaming temperature (and potentially also the pore size distribution and shape) to be controlled by manipulation of the sample composition.

4. Conclusions

Aluminosilicate materials have been prepared with a wide range of SiO_2/Al_2O_3 ratios by the action of NaOH on mixtures of metakaolinite with either ρ-alumina (for compositions in the range *S*/*A* = 0.5–1) or fine Aerosil silica (for compositions in the range *S*/*A* = 4–300). The Na_2O/SiO_2 and H_2O/SiO_2 in all these samples were kept constant at about 0.3 and 11, respectively. All the samples hardened at ambient temperature, but the high-alumina compositions were of low strength, whereas above *S*/*A* = 24, the mechanical properties of the samples became increasingly elastic with increasing SiO_2 content, and deformed rather than failed in brittle fashion.

On the basis of XRD, ^{27}Al, ^{29}Si and ^{23}Na MAS NMR data, the high-alumina samples ($S/A < 2$) do not display typical geopolymer characteristics, but all the higher-silica samples (*S*/*A* up to 300) appear to be geopolymers.

The action of heat on the samples of higher silica content ($S/A > 24$) causes the formation of bubbles due to the removal of the hydration water resulting in the formation of a stable foamed material. The onset temperature of this foaming activity depends on the silica content, which in these samples controls both the sodium and water contents.

Acknowledgment

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6. See, for example, J. Davidovits, Fr. Patent No. 8117545, September 17, 1981.