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Communication

Outstanding problems posed by nonpolymeric particulates in the synthesis of a well-structured geopolymeric material

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Abstract

In the conventional geopolymer synthesis of ternary reactants system of silicate anions [$Na_2O{\cdot}2SiO_2$], metakaolin [$Al_2O_3{\cdot}2SiO_2$] and aqueous alkali [Na_2O], the SiO_2/Al_2O_3 molar ratio can only be varied from ~ 2 to 8. For geopolymerisation to occur, the minimum mole percentage of metakaolin reactant is about 25% and the maximum mole percentage of Na_2O content is about 30%. As the reduction of metakaolin and increase of alkali content is limited, the total conversion of metakaolin into polymeric material is uncertain. The identification of the presence or absence of metakaolin in the cured geopolymer product is not possible in this synthesis of a ternary reactant system even by ^{29}Si NMR, as the signal due to metakaolin is indistinguishable from a broad ^{29}Si NMR peak consisting of many resonance lines of polymer network of cross-linked Si/Al tetrahedra.

With our modified synthesis method employing colloidal SiO_2 as an additional component, the metakaolin content is decreased while keeping an optimum amount of Na_2O, thereby increasing the compositional SiO_2/Al_2O_3 molar ratio. In this case, the signals related to Al-substituted SiO_4 tetrahedra are reduced, indicating the reduction of Al-substituted SiO_4 tetrahedra in the polymer network, resulting in better-resolved ^{29}Si NMR lines. 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. ^{29}Si NMR signal related to metakaolin was only absent in the spectra of cured product when metakaolin reactant content is ≤ 5 mol%; that is, the compositional SiO_2/Al_2O_3 molar ratio is ≥ 20.

Keywords: Metakaolin; Silica; Alkali; NMR; Structure

1. Introduction

Geopolymers or inorganic polymers [1] are emerging as a new class of engineering materials that offer the potential to fulfil important requirements that are not met by organic polymers. Geopolymers may also prove to be useful as major components for production of acid-, heat- and fire-resistant building materials with high compressive strengths up to about 80 MPa, and in waste encapsulation by incorporating toxic wastes into the polymer chain. Geopolymers are an attractive low-cost alternative for cements and plastics which can be synthesised at ambient conditions. Geopolymers with a range of chemical, physical and mechanical properties have been synthesised [1]. The reactants of conventional geopolymer synthesis are usually metakaolin particles and premade reactive silicate anions in aqueous alkali solution. The cured polymer is X-ray amorphous with a ^{29}Si NMR spectrum which exhibits a relatively broad peak without observable splitting, consistent with a three-dimensional disordered structure similar to that of glass. The geopolymer system of type $Na_2O-SiO_2-Al_2O_3$ are composed of sialate siloxo units [–Si–O–Al–O–Si–O–] [1] where Na cations balance negative charges of bridging oxygen created by formation of Al–O–Si bonds or nonbridging oxygen [2]. The key to polymer formation depends on the presence of weakly charged silicate anions, and uncomplexed aluminate species from the reaction of metakaolin. Highly charged silicate anions, such as $HSiO_4^{3-}$, do not readily complex with aluminate species to form Al–O–Si linkages [3]. In highly alkaline environments, the formation of highly charged, unreactive, smaller silicate anions are favoured [4]. As the percentage of alkali in premade silicate anions in aqueous alkali solutions (i.e., $Na_2O/SiO_2 = 1/2$) is high, a large amount of metakaolin is needed to bring down the total alkali content for polymerisation to occur. However, the formation of

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reactive aluminate species from metakaolin requires a large amount of alkali. Therefore, there is a limit in the ratio of metakaolin to alkali content in the conventional synthesis methods for a complete reaction of metakaolin particles into polymeric species. As a result, the polymerisation process is limited, and typically, the resultant product contains non-polymeric particulates that are usually derived from starting metakaolin particles. Therefore, to synthesise a well-structured geopolymeric material without nonpolymeric particulates is a matter of considerable importance.

We have previously reported a method of geopolymer synthesis by generation of reactive silicate anions from reactions of aqueous alkali with colloidal silica [5]. Because the extra alkali present in this reaction system is from an independent source, various colloidal silica to metakaolin ratios with an optimum amount of alkali can be used for this synthesis. Incorporating this methodology to the existing conventional synthesis, we have attempted here to synthesise a well-structured geopolymer free from nonpoylmeric particulates.

2. Experimental

2.1. Materials

The raw materials were kaolin (Imerys Minerals Australia), NaOH (Merck), colloidal silica (LUDOX HS-40, Aldrich) and sodium silicate solution ($2SiO_2{\cdot}Na_2O{\cdot}12.7H_2O$, O, PQ).

Metakaolin was prepared by heating kaolin at 750 °C for 10 h. Geopolymers of selected compositions were prepared at room temperature from a mixture of metakaolin, colloidal silica and sodium silicate solution in alkaline aqueous environments. The molar ratio of reactants and chemical composition for a series of samples are given in Table 1. Sample S1 is a standard geopolymer synthesis composition that is already reported [6].

2.2. MAS-NMR measurements

The ^{27}Al and ^{29}Si magic angle spinning (MAS) 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 ^{29}Si and ^{27}Al MAS spectra, respectively. The chemical shifts were measured with respect to zero reference from tetramethyl silane for ^{29}Si and $Al(H_2O)_6{}^{3+}$ for ^{27}Al. The spectra were acquired using a

Table 1
Molar ratio of reactants and their product composition for the samples studied

Sample	Reactants (mol/mol)				Chemical composition (mol%)			SiO_2/Al_2O_3 (mol/mol)
	SiO_2 (colloidal)	$2SiO_2{\cdot}Na_2O$	$2SiO_2{\cdot}Al_2O_3$	Na_2O	SiO_2	Al_2O_3	Na_2O	
S1	–	1	1	0.27	64	16	20	4
S2	5	1.5	1	1.3	72.7	7.3	20	10
S3	10	1.5	1	2.5	75	5	20	15
S4	15	1.5	1	3.7	76.2	3.8	20	20
S5	25	1.5	1	6.2	77.4	2.6	20	30

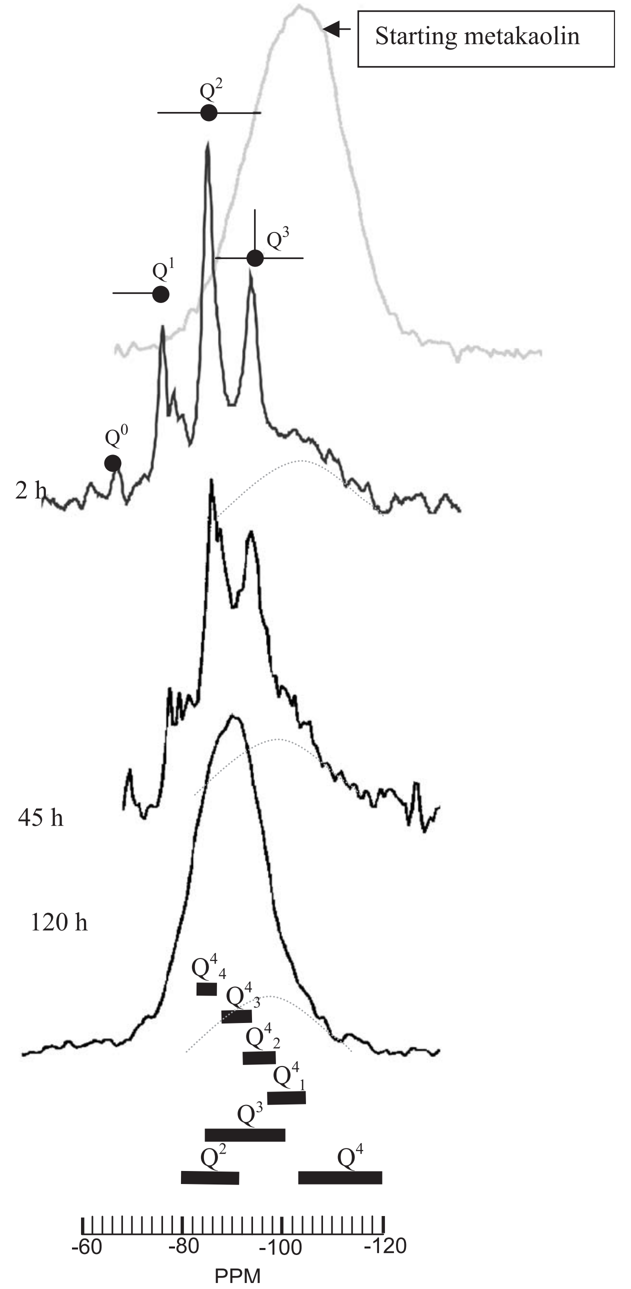

Fig. 1. ^{29}Si MAS-NMR spectra from the stages of a geopolymer formation process from the conventional method (Sample S1). ^{29}Si MAS NMR spectrum of starting metakaolin is given on top as grey line. Silicon atoms of silicate anions and their connectivity are marked by black dots and solid lines, respectively, oxygen atoms connectivity with Al or Na are omitted for clarity. 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.

pulse length of 2 μs and a repetition time of 2 s for both isotopes.

3. Results and discussion

^{29}Si MAS-NMR is capable of distinguishing SiO_4 tetrahedra of cross-linked density ranging from 0 to 4, which then provide valuable information on the type of the various cross-linked SiO_4 tetrahedra. They are represented by SiO_2 tetrahedra of the type Q^m with three or less bridging oxygen ($m = 0$ to 4). Using the Q^m nomenclature, Q means silicon in fourfold coordination with oxygen and m indicates the number of bridging oxygen.

Geopolymerisation of Sample S1 is from a reaction of metakaolin particles and premade reactive silicate anions in

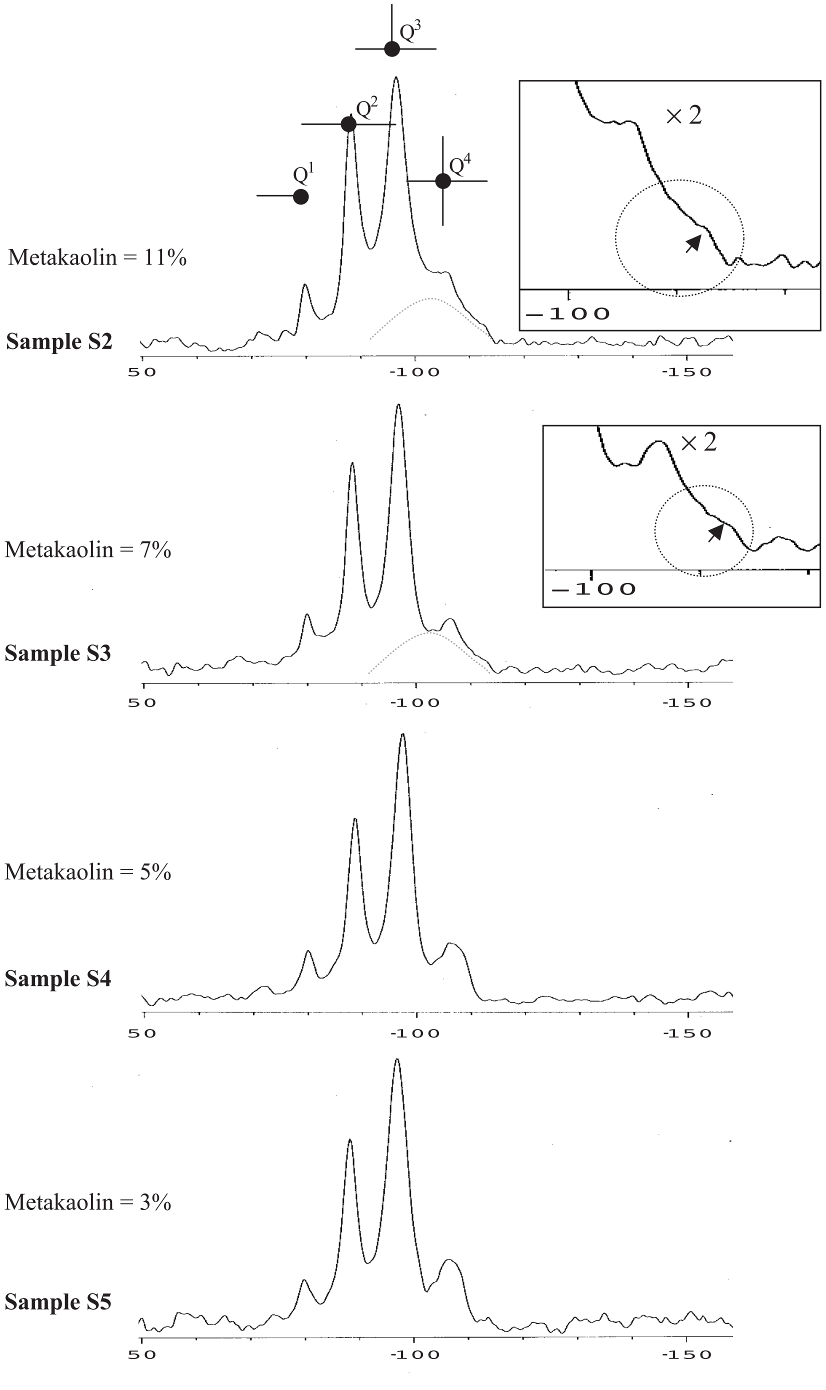

Fig. 2. ^{29}Si MAS-NMR spectra of cured samples prepared by our modified method. Silicon atoms of silicate anions and their connectivity are marked by black dots and solid lines, respectively, oxygen atoms connectivity with Al or Na are omitted for clarity.

aqueous alkali solution at room temperature according to the method of conventional synthesis. Initially, before geopolymerisation, metakaolin shows a broad ^{29}Si resonance peak at -103 ppm with full width at half maximum (FWHM) of ~ 20 ppm shown as grey lines on top of Fig. 1, and ^{29}Si lines at -72, -81, -89 and -97 ppm, assigned to Q^0, Q^1, Q^2, Q^3 silicate units of silicate anions [7].

After 2 h of geopolymerisation, the ^{29}Si lines of Q^0, Q^1, Q^2 and Q^3 silicate units were detected at -70, -79, -85 and -95 ppm, respectively, which are lower than the shift values for the starting premade reactive silicate solutions and the intensity of ^{29}Si line of starting metakaolin has been very much decreased and broadened (Fig. 1).

The peak position and degree of broadness of ^{29}Si resonance lines depends on the nature of geopolymerisation. The replacement of Si with Al of a given silicate unit causes low field shift [7]. Although there is evidence of reaction between silicate anions and metakaolin, as indicated by low field shifts of silicate units, the metakaolin peak still observed at 2 h of reaction are shown as dotted lines in Fig. 1.

The sample, after 45 h of curing at room temperature, shows relatively broader ^{29}Si lines of Q^2 and Q^3. The intensity of the ^{29}Si line of Q^1 units has decreased and the ^{29}Si line related to the metakaolin was not resolved.

In addition, various ^{29}Si chemical shifts of Q_n^4 units, where n is the number of Al atoms connected by oxygen bridges with SiO_4 tetrahedra ($n = 1-4$, refer to Fig. 1), could be observed in the cured product as a result of reaction between silicates and Al sites of metakaolin. A significant amount of Q_1^4, Q_2^4, Q_3^4 and Q_4^4 units could be in the structure of geopolymer product.

The fully cured sample after 120 h shows a broad ^{29}Si peak without observable splitting (Fig. 1). Typical ^{29}Si chemical shift ranges of Q^2, Q^3, Q^4 and substituted Q_1^4, Q_2^4, Q_3^4 and Q_4^4 structural units are shown by bars on the bottom of Fig. 1, almost all fall within the broad peak of the cured product.

It is difficult to separate the signal due to nonpolymerised metakaolin as the peak due to metakaolin falls in the overlapping chemical shift ranges of Q^2, Q^3, Q^4, Q_1^4, Q_2^4, Q_3^4 and Q_4^4 units of the product.

Fig. 2 shows ^{29}Si MAS-NMR spectra of fully cured samples for 2 weeks at room temperature prepared by our modified method. In this method, a quaternary system of colloidal silica, silicate anions, metakaolin and aqueous alkali was employed. The metakaolin content in the samples was reduced while keeping alkali content the same by adding appropriate amount of colloidal silica and sodium hydroxide. By decreasing the amount of metakaolin, Al-substituted Q_1^4, Q_2^4, Q_3^4 and Q_4^4 structural units are less, resulting to clearer Si NMR resonance lines. Samples S2, S3, S4 and S5 have 11, 7, 5, 3 mol% of metakaolin, respectively, in starting reactants composition.

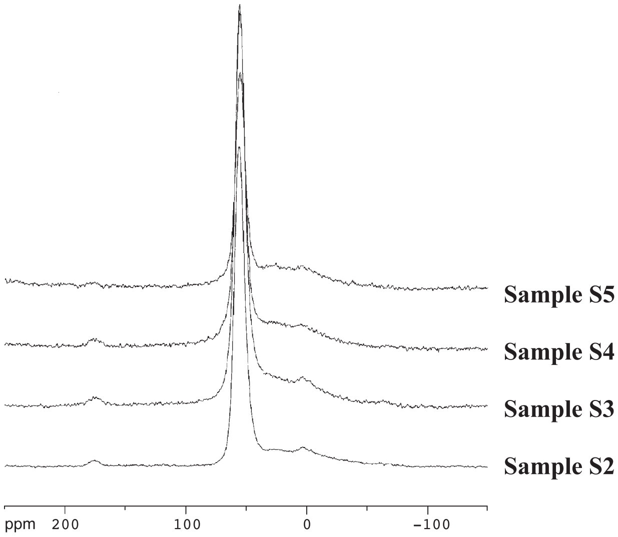

Fig. 3. ^{27}Al MAS-NMR spectra of cured samples prepared by our modified method.

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 small ^{29}Si resonance broad hump at about -110 ppm is present in both the spectra of Sample S2 and Sample S3 as shown more clearly in the insets of Fig. 2. This broad hump at about -110 ppm could originate from the broad peak of metakaolin. The reasonable outlines of the ^{29}Si line for metakaolin are shown as dotted lines in Fig. 2. The hump at about -110 ppm subsided under the relatively resolved peak from Q^4 when metakaolin content is ≤ 5 mol%; that is, the compositional SiO_2/Al_2O_3 molar ratio is ≥ 20 with same alkali content (Fig. 2; S4 and S5). This is an indication that, in the cured geopolymer products, even with 7 mol% of metakaolin reactant, that is, the SiO_2/Al_2O_3 molar ratio of 15, the metakaolin is not fully transformed to geopolymeric units. Fig. 3 shows ^{27}Al MAS-NMR spectra for Samples S2, S3, S4 and S5. The spectra are more or less identical with a predominant peak from AlO_4 at 56 ppm. There are small amounts of AlO_5 (~ 30 ppm) and AlO_6 (~ 3 ppm).

4. Conclusions

A modified synthesis method is described whereby a decrease of metakaolin content to a minimum for the total reaction of metakaolin particles, while still producing high reactivity of silicate anions for geopolymerisation to occur. From the results of this modified synthesis route, by comparing NMR spectra, it appears that geopolymer products synthesised from the conventional route may contain metakaolin-derived nonpolymeric particulates. As NMR indicates, the cured geopolymeric product by the modified method contains nonpolymeric metakaolin particulates even with SiO_2/Al_2O_3 molar ratio of 15.

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