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Dissolution processes, hydrolysis and condensation reactions during geopolymer synthesis: Part II. High Si/Al ratio systems

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Abstract The mechanisms of speciation of aluminate and silicate phases during dissolution and condensation stages of alumino-silicate geopolymer reactions characterised by Si/Al ≥ 3, have been investigated and the results compared to predictions of the partial charge model. Solid-state nuclear magnetic resonance (NMR) traces indicate that free $[Al(OH)_4]^-$ species, present in lower silicate formulations such as Si/Al ≤ 1, do not occur in the present systems, suggesting that the condensation reaction between $[Al(OH)_4]^-$ and silicate species is fairly quick and is consumed as soon as it is formed. This observation is also consistent with both calorimetric measurements and model predictions, as the condensation time increased exponentially with increased Si/Al ratio in the geopolymeric phase, indicating again that the high content of Al species in the gel phase greatly enhanced the condensation rate. The experimental observations suggest that the condensation process in these systems occurs in two stages: (a) quick condensation between aluminate and silicate species; followed by (b) a slow condensation stage solely involving silicate species.

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Introduction

The class of geopolymers referred to as poly(sialate) [1] systems are generally synthesized using straight alkaline hydroxide solution as the activator, while most conventional geopolymer systems are prepared by reacting aqueous alkaline silicates combined with alkaline hydroxide with alumino-silicate minerals such as metakaolin [2]. The key processes involved in the synthesis of geopolymers are: (a) dissolution of metakaolin or similar alumino-silicate precursors to provide the Al and all or part of the Si constituents needed; followed by (b) hydrolysis reaction to generate aluminum and silicate species; and finally (c) condensation of these species and/or silicates from the activator to build up geopolymeric network structures.

During the last decade, considerable research efforts have been directed to this area due to the wide range of potential applications of these materials, underpinned by Davidovits's pioneering work [2, 3]. For example, the dissolution of conventional precursor alumino-silicate minerals such as metakaolin, fly ash and other clays under alkaline conditions was studied by van Jaarsveld and van Deventer [5], Phair and van Deventer [6], and Palomo and Glasser [7]. In particular, the reaction between metakaolin and alkaline silicate solutions has been investigated by thermal analysis (DTA and TGA) [8, 9] FTIR and NMR [10, 11], among several others [3, 4]. However, to date little is known about the mechanisms and processes involved in dissolution, hydrolysis and condensation during geopolymer synthesis.

Part I of this paper reports on the mechanisms of hydrolysis and condensation that occur when synthesizing geopolymers using straight NaOH solution as the activator [12]. Part II reports our study of the chemical mechanisms involved in processing geopolymers using alkaline-rich sodium silicate solutions, which correspond to the family of geopolymers characterised by high Si/Al ratios, i.e., Si/Al ≥ 3, and conventionally referred to as poly(sialate-siloxo) and poly(sialate-disiloxo). The theoretical basis for the study is derived from the partial charge model (PCM) [13], and is here supplemented with experimental data to gain further understanding of the solution chemistry and reaction processes that control geopolymer formation. These findings further provide some insight into the actual chemical composition of the gel phase of geopolymers, in contrast to the widely practiced determination of the chemical formulae of this family of materials from reactants based on feedstock concentrations.

Mechanisms of dissolution, hydrolysis and condensation in synthesizing geopolymers from alkaline-activated sodium silicate solutions

Mechanisms of dissolution and hydrolysis of metakaolin in alkaline-activated sodium silicate solutions

The solubilisation of aluminate and silicate species in alkaline environments was previously assessed by PCM [14]. By considering only mass and charge balances, it was demonstrated that the dissolution and hydrolysis of alumino-silicate mineral raw materials under alkaline conditions can be schematically expressed by the following reactions:

$$Al_2O_3 + 3\,H_2O + 2\,OH^- \rightarrow 2\,[Al(OH)_4]^- \tag{1}$$

$$SiO_2 + H_2O + OH^- \rightarrow [SiO(OH)_3]^- \tag{2}$$

$$SiO_2 + 2\,OH^- \rightarrow [SiO_2(OH)_2]^{2-} \tag{3}$$

According to reactions (1)–(3), the alkalinity ($[OH]^-$ concentration) has an important influence on the dissolution rate of metakaolin. On the other hand, the dissolution rate of metakaolin is also dependent on the temperature of dissolution and the chemical reactivity of the feedstock itself.

Condensation of aluminate and silicate species in highly alkaline sodium silicate solutions

The condensation reactions between aluminate and silicate species from the dissolution of metakaolin were reported in Part I of the paper [12], which demonstrates that specie concentration and alkalinity of the reaction medium have a great influence on the condensation between silicate species themselves, and between aluminate and silicate species. According to the PCM [13], the condensation between aluminate and silicate species from sodium silicate solution are different from that between aluminate and monomeric silicate species, since the silicate species of sodium silicate are mostly oligomeric.

Silicate speciation and their condensation with $[Al(OH)_4]^-$ have been discussed exclusively by using the PCM in our previous work [13]. In summary, it is concluded that monomeric silicate anions tend to condense to form oligomeric species in concentrated alkaline silicate solutions, which further conform to a cyclic configuration due to the influence of partial charge distribution, the number of hydroxyl groups, and electrostatic and steric effects. The added $[Al(OH)_4]^-$ anions in alkaline silicate solutions generally tend to promote the condensation process, because Al atoms in $[Al(OH)_4]^-$ units have a higher partial charge, larger atomic size and four hydroxyl groups, therefore they are more reactive compared to corresponding silicate units. The condensation products between aluminate and silicate species are mostly found to have cyclic structures, corresponding to the formation of cyclic silicate species [15]. Thus, the solid-state geopolymer structure is expected to be initiated by condensation between $[Al(OH)_4]^-$ anions and mainly oligomeric silicate species. This condensation process results in numerous alumino-silicate oligomers, and consequently the network structure gradually forms by further condensation between oligomers. These condensation reactions are very important in synthesizing the so-called poly(sialate-siloxo) and poly(sialate-disiloxo) geopolymers, because the solubility of silicate component in metakaolin during synthesis is typically fairly low [12], consequently the structure of sodium silicates has a great influence on the structure and condensation process of geopolymers.

Experimental

Chemical analysis

The dissolution rates of metakaolin in NaOH solutions was investigated by reacting 10 g metakaolin (kaolin calcined at 850 °C for 5 h) with 15 ml NaOH solutions of different concentration for 1 h respectively at room temperature. Thereafter, the liquors were separated from solids by filtration under reduced pressure. The Al and Si compositions of the liquors were analysed by inductively coupled plasma optical emission spectroscopy.

Calorimetric measurement

For these experiments, 2.0 g metakaolin was mixed with 3.0 ml of activator, comprising of sodium silicate solution (SiO_2/Na_2O 3.22, ~63%wt H_2O, and SiO_2/Na_2O 2.0, 56%wt H_2O; supplied by PQ Australia Pty Ltd) and varying quantities of NaOH and H_2O, respectively. Mixing was carried out for five minutes before starting calorimetric measurements at 23 °C.

NMR measurements

Here, 2.0 g metakaolin was mixed with 3.0 ml sodium silicate solution, followed by the addition of respective amounts of NaOH and H_2O, to achieve various nominal bulk compositions. NMR measurements were conducted on samples with the following compositions:

(a) $1.2Na_2O.Al_2O_3.4SiO_2.20H_2O$.
(b) $1.0Na_2O.Al_2O_3.4SiO_2.15H_2O$.
(c) $1.3Na_2O.Al_2O_3.4SiO_2.15H_2O$.
(d) $1.55Na_2O.Al_2O_3.4SiO_2.15H_2O$.

The NMR spectra of unreacted metakaolin were also measured. The ^{27}Al and ^{29}Si NMR spectra were obtained using a Bruker Avance 400 spectrometer under the conditions reported in Part I [12]. The chemical shifts were measured with respect to zero reference from $Al(H_2O)_6^{3+}$ for ^{27}Al, and tetra methyl silane (TMS) for ^{29}Si.

Results

Chemical analysis

The solubility of metakaolin under various alkaline conditions is shown in Fig. 1. The Al and Si components of the metakaolin have different solubility tendencies under these alkaline conditions. The concentration of the Al component derived from metakaolin under relatively low alkaline conditions increased substantially with increased alkalinity, while it only increased slightly with alkalinity under high alkaline conditions. Thus, when the NaOH concentration in solution is below 3 M, the concentration of Al from metakaolin increased fairly rapidly with increased alkalinity, while the corresponding change within the range 3–8 M was relatively slow with increased alkalinity of the NaOH solution. On the other hand, the concentration of the Si component from metakaolin under different alkaline conditions seems to follow an exponential trend. The concentration of Si content in the liquid phase increased slightly with increased alkalinity under low alkaline conditions, rising rapidly with increased alkalinity in the high NaOH concentration range. In general, the Al component of metakaolin is dissolved more easily than the Si component in NaOH solutions with concentrations up to around 6 M. However, most of the metakaolin was not dissolved after reacting with the NaOH solutions based on experimental observations of solids separated from extracts. The chemical analysis results also suggest that the solubility of metakaolin is low, as shown in Fig. 1. Consistent with Fig. 1, the initial stage of dissolution of many alumino-silicate minerals and clays in alkaline solution display preferential release of aluminum up to very high pH range as pointed out by Provis et al. [16].

However, reprecipitation reactions also inevitably occur. The degree of the effect may be dependent on pH value and concentration of aluminate and silicate species. Higher pH conditions and low concentrations decrease reprecipitation rates. Hence the deliberate avoidance of activated alkaline silicate solution for metakaolin dissolution, as the concentration of silicate species would then be too high, and the error significant. It is however acknowledged that under the current high pH environment (pH above 14) and lower species concentration, monomeric alumino-silicate may be dominant, therefore, the level of precipitation may be relatively small, though unavoidable.

Calorimetric measurements

The effect of the alkalinity of the activator on the heat evolution during geopolymer synthesis was measured

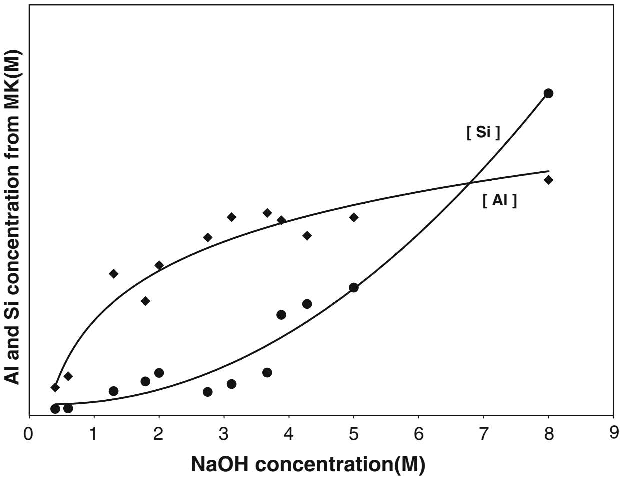

Fig. 1 Concentration of Al and Si dissolved from metakaolin under different alkaline conditions

by calorimeter, and the results are shown in Fig. 2. In general, the calorimetric curves show two stages: the first stage involved a high heat generation in a relatively short period, while the second stage was more prolonged but generated moderate heat. With an increase in alkalinity (the addition of NaOH to sodium silicate solution from 8, 13 and 18%, with respective nominal compositions of $1.0Na_2O.Al_2O_3.4SiO_2.15H_2O$, $1.3Na_2O.Al_2O_3.4SiO_2.15H_2O$ and $1.55Na_2O.Al_2O_3.4SiO_2.15H_2O$, respectively) in geopolymer synthesis, the second stage became more significant, while the reaction time appeared shortened.

Figure 3 shows calorimetric results of the influence of different activator precursors of a fixed composition of $1.2Na_2O.Al_2O_3.4.4\ SiO_2.18H_2O$. The three curves shown represent (a) fumed silica and NaOH solution; (b) sodium silicate solution of $SiO_2/Na_2O = 3.22$ with NaOH; and (c) straight sodium silicate solution ($SiO_2/Na_2O = 2.0$), on the heat evolution in geopolymer synthesis. Activator mixtures were prepared and equilibrated for 24 h before synthesis. The results clearly show that the sample composed of fumed silica and NaOH solution had the most significant second exothermic stage, while the sample made with straight sodium silicate solution ($SiO_2/Na_2O = 2.0$) gave the least heat evolution during the entire reaction time.

NMR measurements

Figure 4 shows the NMR spectra of the metakaolin powder used in the present study. There are two peaks at 28 and 10 ppm, with a shoulder at 58 ppm in the ^{27}Al NMR spectrum of metakaolin (Fig. 4b), while the ^{29}Si NMR spectrum of metakaolin gives a broad peak at –103 ppm (Fig. 4a). The ^{29}Si NMR spectrum of dried sodium silicate ($SiO_2/Na_2O = 2$) from solution shows five peaks at –72, –81, –89, –97 and –105 ppm, respectively (Fig. 5).

Figure 6a shows the ^{29}Si NMR spectra of samples of metakaolin with a nominal composition of

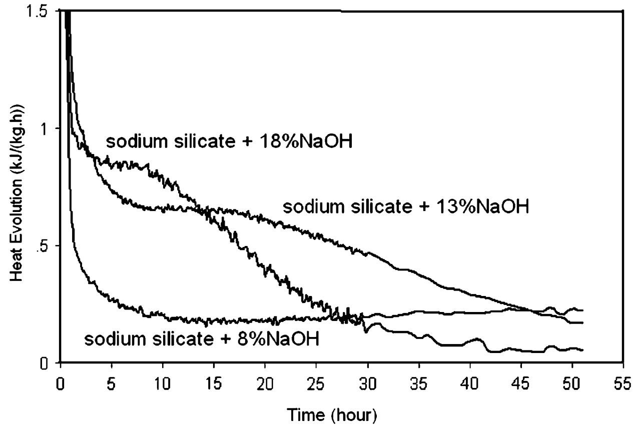

Fig. 2 Influence of the alkalinity of activators on the calorimetric results of geopolymers

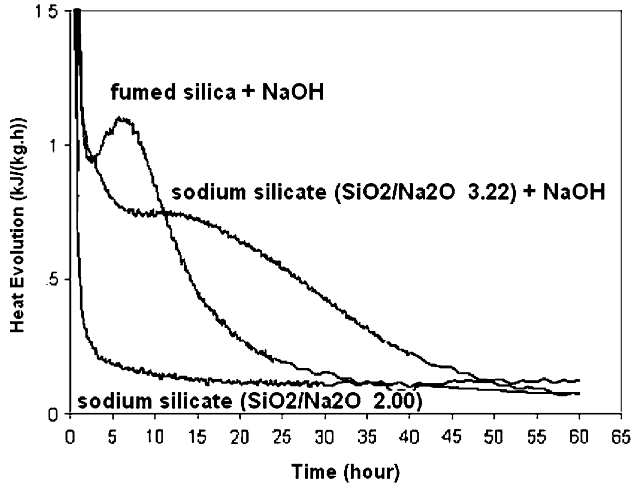

Fig. 3 Calorimetric results of the geopolymer with a nominal composition of $1.2Na_2O.Al_2O_3.4.4\ SiO_2.18H_2O$ from different precursors

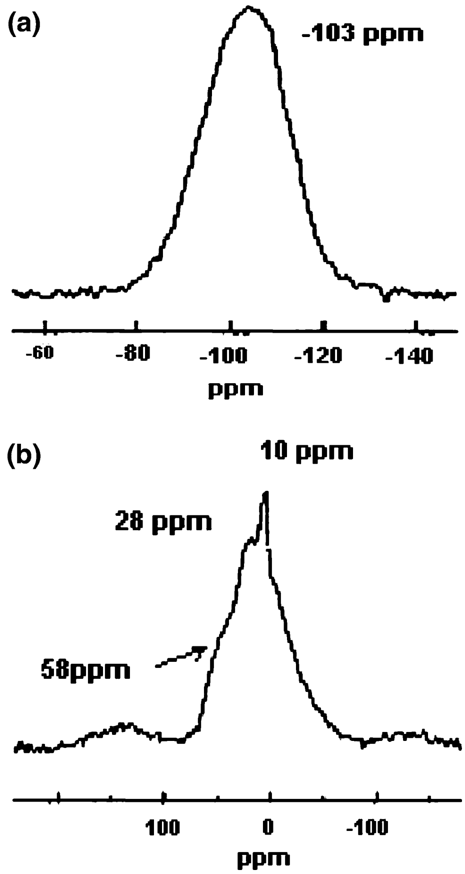

Fig. 4 NMR spectra of metakaolin: (**a**) ^{29}Si NMR; and (**b**) ^{27}Al NMR

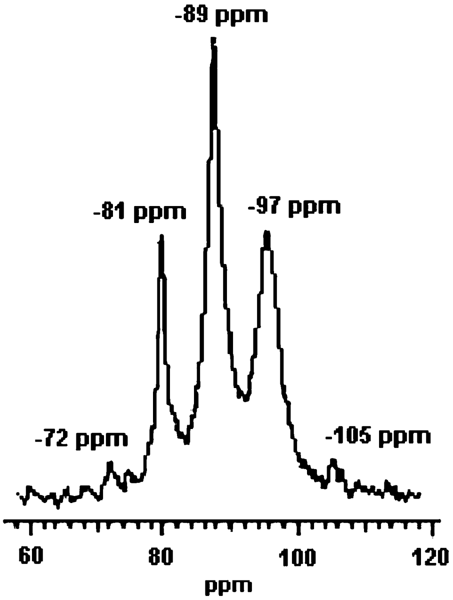

Fig. 5 ^{29}Si NMR spectrum of dried sodium silicate ($SiO_2/Na_2O = 2.0$)

$1.2Na_2O.Al_2O_3.4SiO_2.20H_2O$ for different durations at room temperature. There are mainly four peaks at –70, –79, –85 and –95 ppm, and a broad shoulder from –100 to –120 ppm in the samples with the reaction times of 2 and 21 h. The sample cured for 45 h shows further overlaps between the two peaks at –85 and –95 ppm, with the peak at –79 ppm weakening. The broad peak from –75 to –120 ppm is observed in the sample cured for 5 days, which is due to an overlapping of the peaks at –81, –89 and –94 ppm and the shoulder from –100 to –120 ppm.

The ^{27}Al NMR spectra of the same samples are shown in Fig. 6b. The peaks for the sample cured for 2 h are different from that of the parent metakaolin (Fig. 4b). The intensity of the peak at 58 ppm increased significantly, while the intensity of the peaks at 28 and 10 ppm decreased. The ^{27}Al NMR spectrum of the sample reacted for 21 h shows only one peak at 58 ppm, subsequently this peak became sharper with the reaction time extending to 5 days, and a small peak at 10 ppm was also observed.

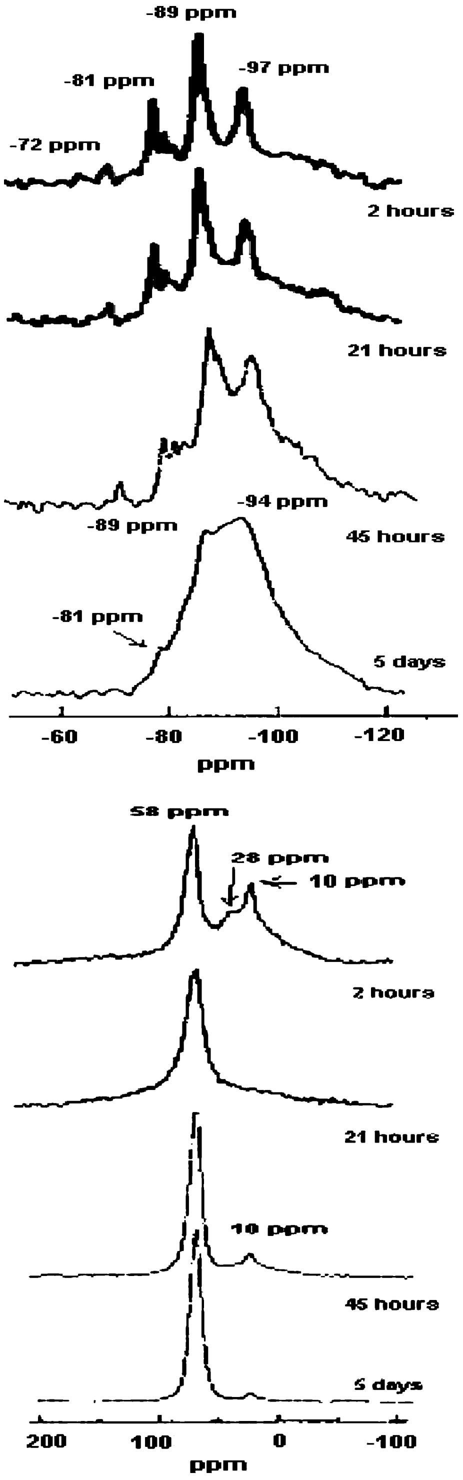

Fig. 6 NMR spectra of the geopolymer samples with a nominal composition of $1.2Na_2O.Al_2O_3.4SiO_2.20H_2O$ at room temperature for different cure durations: (**a**) ^{29}Si; and (**b**) ^{27}Al spectra

Discussion

Dissolution and hydrolysis process of geopolymer synthesis

According to the PCM predictions, as mentioned in Section 2.1, the resultant species from the dissolution of metakaolin are $[Al(OH)_4]^-$, $[SiO(OH)_3]^-$ and $[SiO_2(OH)_2]^{2-}$ [12]. Consistent with the PCM model, the 4-coordinated Al peak at 78 ppm, representing free $[Al(OH)_4]^-$ specie, was observed by NMR spectrometry in our previous study [12], although monomeric silicate species appeared to be elusive in the NMR spectrometry, due to their low concentration and rapid reactivity via condensation between aluminate and silicate species when only NaOH solution is used as the activator. Reactions (1)–(3) derived from the PCM indicate that the high $[OH]^-$ concentration leads to a high dissolution rate, which is also in accordance with the chemical analysis results shown in Fig. 1.

The observed dissolution trends of aluminate and silicate components from metakaolin, shown in Fig. 1, are important to provide guidance for geopolymeric setting. Especially, when alkaline silicate solutions are used as activator to furnish adequate silicate components. As shown by previous experimental results [15, 17, 18] and present estimates from the PCM model, $[Al(OH)_4]^-$ species largely regulate the condensation reaction rate and, consequently, setting rates. Figure 1 suggests that the concentration of $[Al(OH)_4]^-$ species in solution can be adjusted by pH value of the solution. Accordingly, lower pH solutions result in lower concentration of $[Al(OH)_4]^-$ species and longer setting time. The $[OH]^-$ concentration may not be in excess of 3 M in the present case since the concentration of $[Al(OH)_4]^-$ species could not increase significantly, while, at the same time, the higher pH value retards the condensation reaction between silicate species. Of course, the exact dissolution behavior is dependent on the properties of metakaolin used, and the large existence of 5-coordinated aluminate in metakaolin is beneficial to high dissolution rate.

A separate key factor is the coordination state of Al atoms present in metakaolin before and after reaction under alkaline conditions. Comparing the ^{27}Al NMR spectrum of metakaolin (Fig. 4b) with that of the sample with 2 h reaction time (Fig. 6b), 5- and 6-coordinated Al atoms changed to 4-coordinated Al atoms, consistent with other previous studies [9, 11], suggesting an initial occurrence of the dissolution and hydrolysis process. However, the peak at 78 ppm attributed to a free $[Al(OH)_4]^-$ specie, observed for NaOH activator systems [12], does not occur in the present sample, indicating that the condensation reaction between $[Al(OH)_4]^-$ and silicate species from the activator is fairly quick, and the free $[Al(OH)_4]^-$ specie was consumed as soon as it was formed. Consequently, it is unlikely to separate the dissolution and hydrolysis stages from the dominant condensation reactions in geopolymer synthesis, when alkaline sodium silicate is used as the activator. Under these circumstances, the dissolution and hydrolysis process in geopolymer synthesis may be best studied by investigating the solubility of metakaolin in NaOH solutions with equivalent alkalinity to the corresponding alkaline sodium silicate activators, since the dissolution and hydrolysis process resulted primarily from the alkalinity of the activator, according to Reactions (1)–(3). The results presented in Fig. 1 show the trends in the dissolution of metakaolin in various alkaline environments. They also suggest incomplete metakaolin dissolution, which was also indicated by the chemical analysis results, SEM and by ^{29}Si NMR spectrometric analysis [12, 19]. Any existence of residual unreacted metakaolin leads to deviations of the actual gel phase composition from the often-reported nominal gross compositions derived from reactant material compositions.

Condensation reactions during geopolymer synthesis

The condensation reactions in geopolymer synthesis mostly involve the condensation between aluminate and silicate species and between silicate species alone, since the apparent Si content in the gel phase is far higher than the Al content, when alkaline sodium silicates are used as activators. According to PCM predictions [13], the $[Al(OH)_4]^-$ specie in alkaline silicate solutions greatly enhances the condensation process because of its a higher partial charge, larger atomic size and four hydroxyl groups, while the condensation between silicate species themselves is relatively slow. Therefore, the condensation process in geopolymer synthesis appears to involve two steps: (a) quick condensation between aluminate and silicate species; and (b) slow condensation between silicate species.

When metakaolin reacts with the alkaline silicate activator for 2 h, the ^{27}Al NMR spectrum in Fig. 6b discloses that a large proportion of Al atoms change to the coordination number of 4 from 5- and 6-coordinated, with each $[AlO_4]$ unit coordinated with four Si atoms. The absence of a peak at 78 ppm due to free $[Al(OH)_4]^-$ indicates the rapid condensation between aluminate–silicate species, which strongly supports the above analysis.

By comparing the calorimetric results of the geopolymers with different compositions, the importance of Al species dissolved from metakaolin on the condensation reaction was also further established. In general, the first larger peak in the calorimetric curves of geopolymer synthesis (i.e. Fig. 2) was due to the dissolution and hydrolysis processes, although the condensation may also contribute to heat evolution to some extent, according to the NMR results (Fig. 6b), while the second peak was mostly attributable to the condensation reaction according to our previous study [12].

On the other hand, the condensation reactions between silicate species are relatively slow. The ^{29}Si NMR spectra of the 2 and 21-h samples (Fig. 6a) show similarity to that of sodium silicate (Fig. 5), except that there is a shoulder from –100 to –120 ppm, which is probably due to the influence of metakaolin (Fig. 4a). Considering peak shifts due to the formation of Si–O–Al link, which contribute around 5 ppm per Al substituent [20, 21], when the reaction time extended to 45 h, the peak intensity at –81 ppm due to Q^1 decreased, and the peaks due to Q^2 and Q^3 overlapped in the ^{29}Si NMR spectrum, indicating possible occurrence of condensation reactions. After metakaolin reacted with the activator for 5 days, the new peak at –94 ppm assigned to Q_4^4 appears stronger, overlapping with other peaks, i.e. the identifiable peaks at –89 and –81 ppm, to form a broad peak from about –75 to –120 ppm, suggesting the significant existence of alumino-silicate species. The continuous change of the ^{29}Si NMR spectra during the 5 days indicates that the time for completion of silicate condensation may be very long, in accordance with PCM predictions.

It is known that Al content increases with increasing alkalinity, as shown in Fig. 1 and indicated by reactions (1)–(3), therefore the alkalinity of the activator determines the rate of condensation between aluminate and silicate species, besides such factors as temperature and the nature of the feedstock. The calorimetric results shown in Fig. 2 support this conclusion, since the calorimetric curves of samples with high alkalinity clearly show quicker and more significant condensation. However, the likelihood of retardation of condensation reactions between silicate species at high alkalinity cannot be ruled out. This is because highly alkaline activators have high contents of the $[SiO(OH)_2]^{2-}$ specie and its derivatives, which do not favour rapid condensation leading to network structure formation, according to the PCM, as reported in our previous study [13].

The composition of the activator cannot be properly represented by widely used formulations, such as $1.0Na_2O.\ Al_2O_3.\ 4SiO_2$, since the sodium content does not reflect the $[OH]^-$ concentration in sodium silicate activator solutions and, in fact, the alkalinity of an activator is mainly determined by the NaOH added, considering that the pH value of commercial sodium silicate solutions is comparatively low (pH 11–13). Figure 3 provides clear evidence that the activators derived from different precursors have a great influence on condensation, even though they have the same nominal composition. Metakaolin reacted with the activator made by mixing fumed silica with NaOH and H_2O, showed a significant second exothermic peak because of the very high alkalinity of the activator, which efficiently dissolved the metakaolin and provided enough Al content for condensation with silicate species dissolved from fumed SiO_2. When the low modulus (Si_2O/Na_2O) sodium silicate solution was used as the activator, the lower pH value did not generate sufficient amounts of Al ions for significant condensation to occur, therefore its second exothermic peak was comparatively small and broad. Incomplete dissolution of metakaolin may result in deviation of the composition of the geopolymeric gel phase from the nominal composition derived from the bulk precursor compositions. This deviation is expected to be very significant when fly ash feedstock is used, due to its relatively poor dissolution characteristics, even under very high alkaline conditions [22].

The ^{29}Si NMR spectrum of sodium silicate shown in Fig. 5 displays three strong peaks at –81, –89 and –97 ppm, which are assigned to Q^1, Q^2 and Q^3, respectively [23]; exponent indicating number of bridging oxygen. A weak peak at –72 ppm can be seen, which is due to Q^0, suggesting that few monomeric silicate species exist in sodium silicate ($SiO_2/Na_2O = 2$ with pH = 12.8). There also exists one weak peak at –105 ppm attributable to Q^4. These results indicate that most of the tetrahedral $[SiO_4]$ units in silicate species have one, two or three Si atoms around them as secondary coordination. The lack of Q^4 species suggests that silicate oligomers in sodium silicates are formed from $[SiO(OH)_3]^-$ and $[SiO(OH)_2]^{2-}$ species, consistent with the PCM predictions [13].

On the other hand, the oligomeric silicate species and the condensation products between aluminate and silicate species are mostly found to have cyclic structures, according to previous studies on zeolite [15], therefore the basic structural units in geopolymers are expected to have cyclic structures.

Several pertinent issues can also be addressed based on the present experimental results.

Firstly, the ^{29}Si NMR spectra of the 2 and 21-h samples (Fig. 6a) show similarities to those of sodium silicate (Fig. 5). This similarity suggests that the addition of NaOH in sodium silicate solution has little effect on the structure of silicate species, which is in disagreement with Harris and Newman's study [23] that showed the intensity increase of the peaks of Q^0, Q^1 and Q^2. Harris and Newman's results can be explained by the PCM in that highly alkaline solutions lead to the formation of monomeric and smaller oligomers, due to the tendency to form larger amount of $[SiO(OH)_2]^{2-}$ species [13]. The discordance with the findings of the present study may be due to the difference of the reaction time between the two studies, since the process of dismantling larger oligomers in sodium silicate solutions could be slow.

Secondly, the ^{29}Si NMR result of the sample reacted for 2 h may not provide sufficient information on the dissolution and hydrolysis of metakaolin during the geopolymer synthesis process when alkaline sodium silicates are used as activators. The ^{29}Si NMR spectrum of the sample with 21 h reaction time (Fig. 6a) is somewhat similar to that of sodium silicate, moreover, the peaks attributable to alumino-silicate condensation are still unidentifiable in the samples after 45 h reaction time. These observations suggest that the ^{29}Si NMR spectrometry may not be totally effective in studying the change of the coordination environment around [SiO_4] tetrahedral units, and hence the final structure of geopolymers. This is because the strong Q^2 and Q^3 peaks from primary sodium silicate solution have a large masking effect on the less strong peaks of other species in the early stage of geopolymer synthesis. On the other hand, almost all alumino-silicate and silicate species able to be represented by Q_n^m have peaks in the range of –70 to –120 ppm, and these peaks tend to further overlap with each other due to the multiphase nature of the mixture of metakaolin and activator in the later stage of geopolymer synthesis.

Conclusions

The mechanism of speciation of aluminate and silicate phases of alumino-silicate mineral raw materials in highly alkaline solutions with characteristic $Si/Al \geq 3$ is shown to be different from equivalent lower ratio systems based on solution chemistry data and predictions of the Partial Charge model (PCM). Evidence from solid-state NMR studies indicate that free $[Al(OH)_4]^-$ specie, present in low $Si/Al \leq 1$ systems, does not occur in the present systems, suggesting that the condensation reaction between $[Al(OH)_4]^-$ and silicate species is fairly quick. These experimental observations suggest that the condensation process in these systems occur in two stages: (a) quick condensation between aluminate and silicate species; followed by (b) a slow condensation stage solely involving silicate species.

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