Quantitative kinetic and structural analysis of geopolymers. Part 2. Thermodynamics of sodium silicate activation of metakaolin

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Article history:
Received 11 July 2012
Received in revised form 25 January 2013
Accepted 26 January 2013
Available online 14 May 2013

Keywords:
Geopolymer
Isothermal conduction calorimetry
Kinetics
Sodium silicate

ABSTRACT

The paper describes the outcomes of a study using isothermal conduction calorimetry (ICC) to characterize the geopolymerization kinetics of metakaolin activated with sodium silicate. Two exothermic peaks are observed in the calorimetric curves for all systems reacting within the temperature range 20–40 °C. The peaks are assigned to the dissolution of metakaolin, and the formation of geopolymeric gels with disordered structure, respectively. Compared with the use of NaOH solution to activate metakaolin, the presence of soluble silicate in the activator hinders the reorganization of the local structure of geopolymeric gels and also suppresses the formation of zeolites or zeolite precursors. The ICC data are used via a thermochemical model to quantify the reaction kinetics of geopolymerization, by assuming that the geopolymeric gels have an analcime-like local structure and taking into account the speciation of the silicate monomers and dimers in the activator. Decreasing the modulus from 1.6 to 1.0 increases the fractional reaction extent from 0.12 to 0.26 after 72 h at 25 °C. When the modulus is 1.2, increasing the reaction temperature from 20 °C to 35 °C results in an improved reaction extent from 0.24 to 0.35. The rapid polymerization that occurs at 40 °C appears to hinder the further reaction of MK and consequently results in a lower reaction extent than at 35 °C. Combined with the findings from previous analysis of systems where NaOH was used to activate MK, the concentration of available Na⁺ appears to have a more pronounced influence on the extent of geopolymerization than temperature and the concentration of soluble Si. The higher reaction extent of the solid precursor particles with the soluble Si from the activator results in binders with more compact microstructure and higher mechanical strength. Considering the longer-term utilization of geopolymers, the addition of soluble silicate to the activator will delay the transformation of amorphous raw materials to locally ordered materials, potentially providing advantages in terms of microstructural stability in service.

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1. Introduction

The mechanism and kinetics of geopolymerization have been studied by using isothermal conduction calorimetry (ICC) in the first part of this study [1]. With the assumption that geopolymeric reaction products have an analcime-like local structure, the use of ICC enables reliable quantification of the thermochemical reaction extent for the relatively simple case of activation of metakaolin with sodium hydroxide solution. However, in most geopolymer preparation and production, activators including dissolved silicate are preferred, as their products tend to develop higher strength and denser microstructures [2,3]. Compared to the alkali hydroxide type activators, alkali silicate type activators are much more complex in terms of chemistry. The distribution of silicate species varies in aqueous sodium silicate solutions according to the silicate concentration, and the concentration and nature of the alkali metal(s) present [4].

The degree of polymerization of soluble silicates in highly alkaline solutions is usually low to moderate, mainly in the form of monomers, dimers and trimers, depending on the modulus Ms (the molar ratio of SiO₂ to Na₂O in the activator) [5]. The modulus Ms will thus play a very important role in determining the kinetics and products of geopolymerization, since the distribution of poly-silicate anions in solution can affect the precipitation of silicates to a significant extent [6]. Variation in Ms has been found to significantly affect the mechanical properties of geopolymers, with an optimum strength often observed at moderate values of Ms, between 1 and 2 in most cases, consistent with the development of a compact microstructure [2,7–10]. The setting behavior and rheological properties of geopolymer pastes are also largely determined by Ms [7,10–12], which is in part because the polymerization state of soluble silicate affects the viscosity remarkably,
particularly at the high concentrations (up to 35–45%) often used in geopolymer synthesis [13]. These experimental results have shown the need to develop a better understanding of the kinetics and mechanisms involved in the transformation from precursors to geopolymeric gels, so as to gain a better understanding of the relationship between the activator and the properties of the final products.

The primary aim of this paper is to extend the study of geopolymerization kinetics by the ICC method to sodium silicate–activated metakaolin systems. The influence of the effects of soluble silicate in activating solution and reaction temperature on the extent of reaction of metakaolin will be studied as a function of reaction time. The kinetic quantification results will be further linked with the mechanical and microstructural properties of resultant binders.

2. Experimental

2.1. Materials

The metakaolin (MK) used, and the process of its production, have been described elsewhere [1]. Briefly, the material possesses a specific surface area of 141.1 m²/g as determined by N₂ sorption and the Brunauer–Emmett–Teller (BET) method, 55.57 wt.% SiO₂, 41.55 wt.% Al₂O₃, and 0.91% loss on ignition at 1000 °C.

To study the effects of the addition of soluble silicate, the sodium silicate activating solutions with Ms of 1.0, 1.2, 1.4 and 1.6 were prepared by adding chemical grade NaOH pellets and distilled water into a commercial sodium water glass (supplied with Ms = 3.33, 9.28 wt.% Na₂O, 29.91 wt.% SiO₂). The mass concentration of the prepared activators, defined in terms of Na₂O + SiO₂, was kept constant at 35%, and correspondingly the molar concentration of Na₂O:nSiO₂ was in the range 4.27 mol/L (at Ms = 1.0) to 3.27 mol/L (at Ms = 1.6), where n is equivalent to Ms. The sodium silicate activating solutions were prepared at least 24 h before use to ensure that they had cooled to room temperature.

2.2. Calorimetry

The ICC measurements were performed in a 3114/3236 TAM 83 Air isothermal conduction calorimeter (Thermometric AB) using an internal mixing procedure [1]. It should be noted that the powder and liquid (loaded in an injector) were held separately in the reaction container in the calorimeter at the reaction temperature for 4–6 h to equilibrate prior to the experiment. Preliminary tests showed that when the liquid/solid ratio was higher than 0.6 mL/g, the mix could be mixed easily. Thus, to ensure successful mixing by the mini-blender in the instrument, the pastes studied were designed with a liquid/solid ratio of 0.8 mL/g. The molar compositions of the mixtures, and reaction temperatures, are provided in Table 1. The heat evolution rate data were calibrated by subtracting the heat evolution of MK mixed with water as a baseline [1].

2.3. Characterization and mechanical testing of geopolymers

To analyze the Si and Al environments before and after reaction, FTIR spectra were collected using a Nexus 670 FTIR spectrometer (Nicolet) in transmittance mode using the KBr pellet technique, with a resolution of 2 cm⁻¹. The spectra in the range 1300–800 cm⁻¹ were subjected to deconvolution analysis using the Peakfit software (Version 4.12) as described in [11]. XRD analysis of the hardened binders was conducted using an ARL 9900 Series X-ray workstation with Co Kα radiation, operated at 40 kV and 40 mA at a scanning speed of 2.4°/min. A JEOL scanning electron microscope (SEM) was used to analyze the morphology of fracture surfaces of selected specimens, which were sprayed with a thin Au coating to enhance conductivity, and imaged at an accelerating voltage of 15 kV.

To observe the effects of soluble silicate on the mechanical properties of geopolymers, cylindrical specimens with size of Ø 25 × 37.5 mm were prepared at a liquid/solid ratio of 0.65 mL/g and cured at 25 ± 2 °C for 24 and 72 h, for compressive strength testing. Six replicate specimens of each mix were tested by using a WHY-200 Auto Compressive Resistant tester (Shanghai Hualong, China) at a loading speed of 0.5 mm/min.

3. Results

3.1. ICC testing

Fig. 1 shows the heat evolution rates of MK activated with sodium silicate solutions at 20–40 °C, in the first 72 h of reaction. Two distinguishable peaks are observed in all of the calorimetry curves during the recording period. A first sharp peak (denoted I) appears immediately after mixing, followed by a second broad exothermic peak (denoted II). Increasing the liquid/solid ratio seems not to change the number of exothermic peaks [14,15], which indicates that the basic geopolymerization paths are constant as liquid/solid ratio varies.

The maximum heat evolution rate in peak I increases significantly as the reaction temperature increases. At 20 °C, all the curves show a maximum rate of around 24 mW/g MK, and no significant difference in heat evolution rate is found between the four systems. As the temperature increases, the differences between the systems with different Ms become more notable; at 40 °C, the heat evolution rates are 45 and 70 mW/g MK for Ms = 1.2 and 1.6 respectively. As Ms increases (i.e., as alkali concentration decreases in the sample formulations used here), the heat evolution rates in both peaks I and II decrease consistently, at each temperature above 20 °C. This indicates that more rapid reactions occur in these two stages when the activator alkali concentration is higher. Peak II (sometimes overlapping with peak I) also indicates the reaction duration. At a given temperature, the heat evolution duration is prolonged as Ms increases, particularly for the system with Ms = 1.6 at 20, 25 and 30 °C. This means that introducing more soluble silicate in the activator, or decreasing the amount of alkali cations available, will make the reaction slower in the later stages.

The cumulative heat released by all systems in these two stages is summarized in Table 2. The total heat release in each case is in the range 230–490 J/g MK for the first 72 h, which is consistent with the results obtained by Rahier et al. for comparable systems using differential scanning calorimetry (DSC) [16]. As temperature increases, the total heat release generally increases, except...
when $\text{Ms} = 1.0$, where the slow initial dissolution at $20^\circ\text{C}$ results in a higher total heat release than at $30^\circ\text{C}$ and $40^\circ\text{C}$. A similar phenomenon, where slow reaction at low temperature results in higher heat release, was also noted in sodium hydroxide activation of metakaolin [1].

The variation in total heat release is mainly due to the differences in the dissolution extent of metakaolin, and the different polymerization reactions which take place as a function of Si/Al ratio. The reaction process involved in the dissolution of metakaolin is complicated, involving several basic steps, including absorption.

**Fig. 1.** Effects of sodium silicate modulus and reaction temperature on heat evolution rate of MK geopolymerization: (a) $20^\circ\text{C}$, (b) $25^\circ\text{C}$, (c) $30^\circ\text{C}$, (d) $35^\circ\text{C}$ and (e) $40^\circ\text{C}$. 
of aqueous components on and in MK particles, breaking of bonds (Al=O, Si=O), and formation and exchange of Si=OH and Al=OH species. The heat release due to water absorption has been corrected in the ICC data presented here by use of an MK-water paste as baseline comparison, as noted in Section 2.2. Thus, the first exothermic peak indicates the enthalpy of the initial chemical reactions, i.e., the dissolution of MK, as shown in Eq. (1):

$$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 5\text{H}_2\text{O} + 4\text{OH}^- \rightarrow 2\text{Al}((\text{OH})_2)_2 + 2\text{SiO}((\text{OH})_2)$$

(1)

Using the standard enthalpies of formation of MK (−3213.4 kJ/mol [17]), $\text{H}_2\text{O}$ (−285.8 kJ/mol [18]), $\text{OH}^−$ (−230.0 kJ/mol [18]), $\text{Al}((\text{OH})_2)_2$ (−1500.8 kJ/mol [18]) and $\text{SiO}((\text{OH})_2)$ (−1436.1 kJ/mol [18]), the dissolution enthalpy $\Delta H_{\text{d}}$ is calculated to be −208.3 kJ/mol. This explains the first strong exothermic peak in the ICC data. At lower Ms, the concentration of the NaOH component of the sodium silicate solutions is higher, giving an increased alkalinity. This leads to a higher dissolution extent, as indicated by a more intense first exothermic peak.

The nature of the second exothermic peak is explained by the continuous polymerization between the dissolved species and silica oligomers present in activation solution. The polymerization products are too complex to enable us to perform exact thermodynamic calculations, however, as a whole system, this will be further discussed in the following sections.

Therefore, with reference to Part 1 of this study, it is reasonable to ascribe the nature of the reaction processes responsible for these two peaks to two basic stages: (I) dissolution of MK under alkaline conditions, and (II) polymerization between the dissolved Al and Si and the silicate monomers present in the activator. In Stage I, MK particles dissolve to release Al and Si once in contact with activator solutions, as indicated by the first exothermic peak. When the concentrations of Al and Si monomers and other small dissolved species reach a critical level exceeding saturation conditions in the alkaline environment prevailing here, polymerization becomes the dominant reaction and the second exothermic peak appears. The aluminosilicate oligomers will further polymerize into amorphous polymers or ‘proto-zeolitic nuclei’, which are thermodynamically metastable, and will transform into aluminosilicate gels or semicrystallized phases [19,20]. Unlike the NaOH-activated systems studied in [1], there is no third exothermic peak appearing in the systems reacting at higher temperatures here, meaning that the fast nucleation of aluminosilicate gels promotes the setting the paste and hinders their further reorganization, which is the process that leading to the third exotherm in NaOH activated binders. This implies that the products in sodium silicate activation systems require higher energy to reorganize the local structure than in sodium hydroxide activation systems, as proposed in the literature for other aluminosilicate geopolymer systems [7].

### 3.2. XRD study of the geopolymerization products

Fig. 2 shows XRD data for MK and the geopolymer samples obtained after 72 h of reaction at 20 °C and 30 °C. After reaction with sodium silicate activators, the center of the broad feature observed, often described as an ‘amorphous hump’, has shifted from 25° 2θ in MK to 32° 2θ. This shift to higher 2θ angle upon reaction is also found in NaOH-activated systems [1], and is usually attributed to the formation of geopolymeric gels [21,22].

The XRD patterns of geopolymers formed at 30 °C (Fig. 2b) are similar to the patterns of products activated with NaOH at the same temperature [1], and there are no detectable crystallized zeolite phases in the systems studied here after 72 h of reaction. One notable feature in the patterns is the increased diffraction intensity at ~32° 2θ with lower Ms, i.e., with higher alkali concentration as the samples are formulated here. This trend was also noted in the XRD patterns of products activated with NaOH [1]. Combined with the results related to total heat release, it indicates that the amount of geopolymeric gel formed increases with the alkali concentration, which is consistent with the current understanding of the alkali activation mechanism. According to this mechanism, at a given silica concentration, a higher available OH− concentration results in more extensive dissolution of MK and consequently more Al and Si monomers become available to participate in polymerization.
4. Quantification of geopolymerization kinetics

4.1. Thermochemical properties

The definition of precursor and reaction product species, and thus the calculation of their thermochemical parameters, is critical in quantifying the extent of geopolymerization from ICC data. Comparing these geopolymer materials with the products in Part I of this study [1] when NaOH solution was used as the activator, the geopolymers produced in the current study are less ordered and without detectable crystalline zeolitic phases. This suggests that the soluble silicate in the activator hinders the formation of zeolite precursors and their later crystallization. This trend has also been observed in fly ash-based geopolymer synthesis [8], and the reason for this behavior is related to the Si/Al ratio in the initial gels and liquids. Zeolite nuclei are more favored, relative to the amorphous gel product, at Si/Al ratios close to 1 in alkali activated metaakolins systems [23]. Introducing soluble silicate into the activator increases the Si/Al ratio above 1, particularly in the early stages of reaction when the MK particles are only partially converted, meaning that only a fraction of the Al has been released from the particle into the initially Si-rich activating solution, and so the effective Si/Al ratio of the gel is high. This does not preclude the possibility of formation of zeolites with high Si/Al ratio, such as zeolites NaY and NaP, however, the observation of these crystalline structures in geopolymers similar to those studied here has only been noted for systems cured and/or aged at high temperature, and the development of a higher degree of crystallinity requires months or longer at temperatures exceeding 85 °C [24].

Although no well-crystallized zeolite phases are found in the sodium silicate-activated systems here, the local structure of the geopolymer gels is proposed to be analcime-like as discussed in Part 1 of this study [1], and consistent with local structural analysis of silicate-activated metakaolin geopolymers [25–27]. The standard enthalpies of geopolymer gels of composition NaAlSi₅O₁₀·nH₂O as a function of Si/Al ratio can thus be calculated from the standard enthalpies of formation of analcime ([NaAlSi₂O₆·H₂O] and amorphous silica glass (SiO₂), according to Eq. (2):

\[
\Delta H_f^0(\text{geopolymer}) = \Delta H_f^0(\text{analcime}) + (m-2) \cdot \Delta H_f^0(\text{fam-SiO}_2)
\]

(2)

where \( \Delta H_f^0(\text{analcime}) = -3303.2 \text{kJ/mol} \) [28] and \( \Delta H_f^0(\text{fam-SiO}_2) = -904.2 \text{kJ/mol} \) [18].

It can be seen in Table 2 that the Na/Al molar ratio is < 1, which means that the Na⁺ present is stoichiometrically not enough to balance the negative charges if all Al atoms from the MK are converted to geopolymer gel and a tetrahedral environment. So, the reactions are based on the available Na⁺ in the activator as a limiting reagent. With these assumptions and the proposed parameters, the geopolymers derived from the current four systems are NaAlO₂·1.55SiO₂·H₂O, NaAlO₂·1.6SiO₂·H₂O, NaAlO₂·1.75SiO₂·H₂O and NaAlO₂·1.8SiO₂·H₂O according to the stoichiometric compositions of the four reaction systems from Ms = 1.0 to 1.6. Their standard enthalpies of formation are thus calculated to be -2851.1, -2941.52, -3033.94 and -3122.36 kJ/mol respectively.

The other required thermochemical parameters relate to the silicates supplied by the activator. Although the geopolymeric gels are assumed to be similar in local structure regardless of the activator type, the detailed reaction paths leading to gel formation will be different on a chemical level. The soluble silicate species present in the activator make the reaction much more complicated than that in NaOH activated systems, because the silicate monomers have a wide distribution of Qⁿ environments. The exact distribution of these species in each specific solution can be determined from NMR spectra or by other chemical methods, but for the purposes of the calculations presented in this study, to simplify the calculation, it is assumed that the silicates are present mainly in Q⁰ (SiO(OH)₃)⁻ and SiO₂(OH)₂⁻ and Q¹ (SiO₂(OH)₂⁻) environments. This is a reasonable assumption to make in this context because Q⁰ and Q¹ are the two most abundant environments when 1.0 < Ms < 1.5 [29], and when the pH is 13–14 the silicate ions in sodium silicate solution are mainly deprotonated either once or twice [16]. Using the standard enthalpies of formation of MK (Al₂O₃·2SiO₂) (~3213.4 kJ/mol) [17], OH⁻ (~230.0 kJ/mol) [18], Na⁺ (~240.3 kJ/mol) [18], H₂O (~285.8 kJ/mol) [18], SiO₂(OH)₃⁻ (~1436.1 kJ/mol) [18] and SiO₂(OH)₂⁻ (~1386.7 kJ/mol) [18], the theoretical reaction enthalpy of each systems can then be estimated.

Table 3 describes the reactions that are used here to represent the process of geopolymerization in each of the systems. With Ms decreasing from 1.6 to 1.0, the amount of Si₄O₉(OH)⁴²⁻ is assumed to decrease linearly. This is because when NaOH was added into the sodium water glass to decrease its modulus, depolymerization reactions occurred among the polymeric silicate tetrahedral species as sketched in Eqs. (3) and (4), which show examples of this process for trimeric and dimeric species respectively:

\[
\text{SiO}_2\text{O}_3\text{(OH)}_3^{-3} + \text{OH}^- = \text{SiO}_2\text{O}_3\text{(OH)}_4^{2-} + \text{SiO}_2\text{O}_2\text{(OH)}_2^{2-} \quad (\Delta H_f^0 = -134.6 \text{kJ/mol})
\]

(3)

Fig. 3. The geopolymerization extent (in terms of the conversion of metakaolin) as a function of the modulus of sodium silicate activator at 25 °C. The calculated amount refers to the amount in the theoretical calculation based on the quantity of available sodium silicate.

![Graph showing the relationship between geopolymerization extent and Ms](image-url)
\[
\text{Si}_2\text{O}_3(\text{OH})_4^{2-} + 2\text{OH}^- \\
= 2\text{SiO}_2(\text{OH})_2^{2-} + \text{H}_2\text{O} \quad (\Delta H^o = -329.4 \text{ kJ/mol})
\]

where the standard formation enthalpies \(\Delta H^o\) of the species are obtained from [18]: \(\text{Si}_3\text{O}_5(\text{OH})_3^{2-} = -3292.0 \text{ kJ/mol}\), \(\text{Si}_2\text{O}_3(\text{OH})_4^{2-} = -2269.9 \text{ kJ/mol}\), \(\text{SiO}_2(\text{OH})_2^{2-} = -1386.7 \text{ kJ/mol}\), \(\text{OH}^- = -230.0 \text{ kJ/mol}\), and \(\text{H}_2\text{O} = -285.8 \text{ kJ/mol}\).

These depolymerization reactions result in a reduction in the degree of polymerization of silicate tetrahedra. A strong heat release during preparation of the sodium silicate solutions with low modulus was noted, consistent with the exothermic nature of reactions (3) and (4), and also the exothermic dissolution of solid NaOH into an aqueous environment. However, all solutions were cooled to room temperature before use in ICC experiments, so this did not influence the observed heat flow data.
The actual balance between \( \text{SiO}^{2-} \) and \( \text{SiO}_2^{4-} \) depends on pH, and will also vary according to Ms. However, here their concentration ratio is further assumed to be 1 to simplify the calculation, as a higher or lower ratio does not change the reaction enthalpy \( \Delta H^{0} \) significantly due to the small enthalpy difference associated with deprotonation. For example, for Ms = 1.0, the calculated overall enthalpy of reaction is \(-343.1 \text{kJ/mol}\) or \(-336.7 \text{kJ/mol}\) if the silicate present in \( Q^{0} \) sites is assumed to be either all \( \text{SiO}^{2-} \) or all \( \text{SiO}_2^{4-} \), respectively. With the calculated reaction enthalpies, an overall reaction extent can be evaluated. This overall “reaction extent” is an index showing how far the geopolymerization proceeds, at a basic chemical level.

4.2. Effects of polymerization state of soluble silicate on the extent of geopolymerization

As a first approximation, the overall extent of geopolymerization is defined as the ratio of the measured cumulative reaction heat to the calculated reaction enthalpy. Fig. 3 plots two types of reaction extents defined in terms of MK: one is based on the overall (superficial) reaction extent at 25 °C, and the other is adjusted to account for the excess MK in the mixture by considering that only enough MK to correspond to a 1:1 Na/Al ratio will react. The reaction extent of MK activated with sodium silicate solution is much lower than in systems activated with NaOH solutions [1], but appears to be reasonable based on additional experimental evidence as discussed below.

Figs. 4 and 5 provide supporting evidence for this calculation, obtained by deconvolution analysis of the FTIR spectra of geopolymerization products obtained at 20 and 30 °C. The bands at 867–876 cm\(^{-1}\) are due to OH bending in Si–OH groups [30], probably associated with \( Q^{2} \) sites and/or unreacted activating solution [31], while the new bands at 1005–1017 cm\(^{-1}\) are assigned to T–O–Si (T: tetrahedral Si or Al) asymmetric stretching in the geopolymer networks, and change substantially both in shape and in intensity as a function of Ms. The band at 952–967 cm\(^{-1}\) corresponds to Si–O stretching in Si–O–Na structures [30] which form in these systems by association of the alkanol from the activating solution with the deprotonated under-coordinated \( Q^{2} \) or lower) sites in the relatively immature aluminosilicate framework. The bands at 1082–1225 cm\(^{-1}\) are consistent with the T–O–Si asymmetric stretching in the unreacted MK. If it is assumed that the relative areas of the resolved bands of unreacted MK are proportional to their concentrations, a general trend is that the quantities of newly formed products increases with a decreasing in Ms.

Evidence from consideration of the mechanism whereby Na\(^+\) balances the charge on Al tetrahedra also supports this conclusion. In Part 1 of this study [1], when the MK was activated with 6 mol/L NaOH solution at an overall Na/Al ratio of 0.74, the fractional reaction extent after 72 h was 0.20. The system with Ms = 1.2 here has an Na/Al ratio of 0.76, which is similar to the 6 M NaOH activation system. At the same reaction temperature, 25 °C, the adjusted extent of reaction value is also around 0.20. This finding further suggests that the Na/Al ratio could be the most important factor in determining the reaction extent of raw materials. The soluble silica present in the activator can change the overall Si/Al ratio of the system, and also affects the microstructural properties of hardened products, as shown in Fig. 6 and consistent with the literature [2]; however, soluble silica seems overall to be less important than the available Na\(^+\) in controlling the final extent of reaction reached.
4.3. Effect of reaction temperature on geopolymerization extent

Fig. 7 presents the effects of reaction temperature on the extent of geopolymerization for the system with Ms = 1.2, calculated from the ICC data based on the assumption that the reaction enthalpy given in Table 3 is constant within the 20–40 °C temperature range of interest. As indicated by the slopes of the curves, the reaction accelerates significantly with increasing temperature. The rate of reaction at 40 °C is highest in the first 5 h, and the ICC data show that the second peak in system at 40 °C appears after only 30 min (see Fig. 1e), meaning that the polymerization in this system occurs at very early time. However, the continuous reaction after 5 h in the system at 35 °C releases more heat overall, and results in a higher reaction extent than is observed at 40 °C. This indicates that the fast formation of geopolymeric gels hinders the further reaction of MK and consequently decreases the reaction extent; similar observations have been developed from synthetic geopolymer systems with tailored rates of Al release, where a rapid early reaction led to a reduced overall extent of reaction due to hindered mass transport effects [32]. This result suggests that there could be an optimum reaction temperature for a given MK, reacted with a given activator, to obtain the highest reaction extent. The use of ICC to determine this optimum temperature appears to be a good alternative to other mechanical and chemical methods.

4.4. Relationship between reaction extent and mechanical properties of hardened binders

Fig. 8 plots the compressive strengths evolution of hardened binders at 25 °C. The fast setting and hardening behavior of the MK geopolymer pastes results in rapid strength development. After 24 h of reaction, the compressive strength of the binder with Ms = 1.2 reaches 22 MPa, which increases to 40 MPa when the curing time is prolonged to 72 h. With increasing Ms (and thus decreasing alkali content), the compressive strength decreases. The compressive strength depends on many factors, including the gel/residual MK ratio, the nature of gels and their interaction with residual particles, as well as the hardness of the gel and the residual precursor [33]. Regardless of the effects of the hardness of the residual phase for the systems studied here (as metakaolin particles are weak and unlikely to contribute much to the total strength), the quantity and nature of the amorphous phase could be expected to be major contributors to the strength of the material as a whole, as the cross-linking and compaction provided by this phase will give strength to the material. Comparing Figs. 3 and 8, the trend in compressive strength of samples fits well with the trend in reaction extents, although the liquid/solid ratio in the compressive strength samples is different from the systems studied by calorimetry. Considering that the quantity of amorphous phase that could potentially be generated through solidification of the activator is equivalent for the four systems, as the total dissolved solids concentration of the activators is constant, the mechanical strength appears to be approximately proportional to the reaction extent of MK and the resultant quantity of gel phases.

4.5. Limitations of using ICC in studying geopolymerization kinetics

It has been demonstrated in this study that ICC is a useful technique for analysis of the kinetics of MK-based geopolymerization. However, there are also limitations associated with this technique. First, to determine the general reaction extent, the thermochromical parameters of the reactants and products must be obtained or estimated. For metakaolin and some other relatively pure precursors, the thermodynamic parameters are available; however, for fly ash which is composed of various glasses and crystalline phases, the thermodynamic parameters are not available and not easy to estimate. Second, this technique can only provide a general geopolymerization rate and extent, which is defined in thermochemical (as opposed to microstructural or geometric) terms. The extent of reaction can only realistically be measured by this technique at relatively early age, but is difficult to compare directly with data obtained from SEM image analysis or other microstructure-based techniques, because these are insensitive to the degree of local (chemical/nanostructural) evolution taking place within the binder gel itself. The reaction extent as quantified from ICC data here seems useful as a general index describing how far the system evolves toward a final ideal structure, although this does differ from the extent of transformation of metakaolin on a microstructural level.

Thus, for tasks including comparing the reactivity of raw materials derived from different sources, after different types of thermal or mechanical pretreatment, or to find the temperature dependence or activating solution dependence of the rate and extent of geopolymerization of a particular precursor, ICC is certainly a valuable technique. The study of geopolymerization of fly ash and slag is useful for the large-scale industrial application of geopolymer products, since these seem to be the most promising precursors at
present, and further research into the application of ICC techniques in this area will be undertaken and reported in the future.

5. Conclusions

The geopolymerization process and early-age reaction products of sodium silicate-activated metakaolin, reacted at 20–40 °C, have been studied using isothermal calorimetry in combination with structural and microscopic analysis. The calorimetric curve shows two distinguishable exothermic peaks in the first 3 days after metakaolin is brought into contact with sodium silicate solution. The first peak corresponds to the dissolution of metakaolin, followed by a broad exothermic peak which indicates the multistep polymerization process of Al and Si monomers in the solution phase. Unlike in NaOH-activated systems, no third exothermic peak (which was attributed to gel reorganization in NaOH activation of metakaolin) is observed in sodium silicate-activated systems, and no crystalline phases are found in any of the systems studied here.

By the application of a simplified description of silicate speciation in the activator, and by using an aluminate as a model structure to predict the thermochromy of sodium aluminosilicate geopolymers, the reaction extent of geopolymerization has been quantified from the ICC data. Increasing the activator modulus from 1.0 to 1.6 decreases the fractional reaction extent from 0.26 to 0.12 after 72 h at 25 °C. The most important conclusion of this research (combining the outcomes of Parts 1 and 2) is that the Na/Al in the geopolymerization process has a more pronounced influence on the geopolymization extent of metakaolin than do temperature and Si/Al ratio. Since the early-age reaction extent is limited (less than 40% at 72 h) at temperatures <40 °C, in either NaOH-activated or sodium silicate-activated metakaolin, it seems that benefits are obtained from the use of silicate-containing activators, in which the soluble silicate will polymerize and help to make the binder compact, and thus provide better mechanical and transport properties.

Acknowledgements

ZZ thanks Halok Pty Ltd. for the geopolymer research project support for part of the work conducted in this study.

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