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Geopolymerization process of alkali–metakaolinite characterized by isothermal calorimetry

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ABSTRACT

The geopolymerization process of metakaolinite activated by alkali and alkali silicate solutions was revealed. The effects of alkali concentration, modulus of alkali silicate solution and reaction temperature on geopolymerization were studied systematically by isothermal calorimetry, as well as X-ray diffraction and $^{27}Al/^{29}Si$ MAS NMR. Results show that the geopolymerization process of metakaolinite under alkali activation condition can be reasonably supposed into three stages: (I) destruction, (II) polymerization and (III) stabilization. The rate of geopolymerization in KOH solution is higher than in NaOH solution and reaches the maximum in 15 mol/L KOH solution during stage II. The extent of geopolymerization increases with increasing of alkali content regardless of the existence of silicate anions in activator.

1. Introduction

Geopolymers are a class of materials synthesized by alkaline activation of aluminosilicate source at ambient or higher temperature. Due to the properties of excellent heavy metal immobilization [1,2], high temperature stability [3], quick solidification with high strength [4] and biological compatibility [5], geopolymers are potentially used in the fields of waste treatment, fire proof, construction and military engineering and even as biomaterials. Geopolymerization is a complicated process responsible for the formation of geopolymer. The understanding of geopolymerization process and its influencing factors is useful for the application of geopolymeric materials. However, the exact process is not fully understood so far although the involved mechanism has been studied in the last 3 decades [6,7].

Several test methods have been employed to characterize the geopolymerization process. XRD is usually used to test the crystallization behavior of geopolymer products with little information during reaction. Energy-dispersive X-ray diffractometry (EDXRD) is a new method to measure the kinetics of geopolymerization but only effective at the initial setting period [8]. There is a similar shortcoming for environmental scanning electron microscopy (ESEM) [9]. $^{27}Al/^{29}Si$ NMR technology is available to show more information during geopolymerization [10,11]. Calorimetric characterization technique can provide real-time information during the whole process of geopolymerization that has irreplaceable advantages over other intermittently recording methods in studying the rate and the extent of geopolymerization [12–14]. A relatively small number of investigations on isothermal and non-isothermal DSC measurements for alkali–metakaolinite reaction systems have already been performed, for instance by Rahier et al. [15]. Those investigations showed that calorimetric analytical technique is a powerful characterization method to obtain the information for describing geopolymerization process.

Take both the complexity of geopolymerization and the faculty of isothermal calorimetric technology into consideration; TAM Air isothermal calorimeter will be chosen to study the real process and some effecting factors of alkali–metakaolinite reaction systems systematically. TAM Air isothermal calorimeter has 8 channels and it can observe the reaction heat changes taking place in different systems of metakaolinite reacting with various concentration of alkaline solutions synchronously. Furthermore, the solid metakaolinite and alkaline solutions can be mixed internally and it gives key information regarding initial reaction heat change that the DSC method cannot offer. Despite the isothermal calorimetric technology, XRD and MAS NMR analysis will be adopted. The aim of this study is to investigate the real process of geopolymerization and provide basic theoretical information for the application of geopolymers.

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Table 1
Main composition (mass fraction, %) and particle parameters of metakaolinite.

SiO_2	Al_2O_3	Fe_2O_3	K_2O	LOI/%	D_{10}/μm	D_{50}/μm	D_{90}/μm	Specific area/$m^2\,g^{-1}$
55.57	41.55	0.56	0.433	0.91	1.199	4.932	25.152	2.05

Table 2
Composition of geopolymerization systems.

No.	NaOH/g	KOH/g	Water/g	$Na_2O{\cdot}3.33SiO_2$/g	$K_2O{\cdot}2.68SiO_2$/g	MK/g	T/°C
S1	0	0	4	0	0	2	25
S2	1.44	0	4	0	0	2	25
S3	0.48	0	4	0	0	4	25
S4	0.98	0	4	0	0	4	25
S5	1.44	0	4	0	0	4	25
S6	1.92	0	4	0	0	4	25
S7	2.40	0	5	0	0	4	25
S8	1.44	0	6	0	0	4	25
S9	0	0.67	2	0	0	2	20
S10	0	1.01	2	0	0	2	20
S11	0	1.34	2	0	0	2	20
S12	0	2.02	2	0	0	2	20
S13	0	0.489	2.5	0	0.286	2	20
S14	0	0.359	2.3	0	0.286	2	20
S15	0	0.266	2.1	0	0.286	2	20
S16	0	0.196	2	0	0.286	2	20
S17	0.345	0	2	0.637	0	2	20
S18	0.345	0	2	0.637	0	2	35
S19	0.345	0	2	0.637	0	2	50

2. Experimental

2.1. Materials

Metakaolinite (MK) was the product by calcining kaolinite (Suzhou, China National Materials Group Corp.) at 900 °C for 6 h. The main chemical composition as determined by X-ray fluorescence and particle parameters as measured by laser particle size analyzer are given in Table 1. Different activators were prepared using NaOH, KOH, distilled water, sodium silicate solution ($Na_2O{\cdot}3.33SiO_2{\cdot}21.7H_2O$) and potassium silicate solution ($K_2O{\cdot}2.68SiO_2{\cdot}16.6H_2O$) at least 24 h prior to use.

2.2. Methods

2.2.1. Isothermal calorimetric characterizations

Reaction heat of 19 geopolymerization systems (see the composition details in Table 2) were tested by using 3114/3236 TAM Air isothermal calorimeter (Thermometric AB, Sweden) with sensitivity (precision) of ±20 μW. To minimize the environmental heat disturbance, the room temperature was set the same to the internal temperature of equipment for systems reacted at 20 °C and 25 °C. In order to obtain the whole heat change, all reaction systems were prepared internally. First, admix ampoules (loaded with solid metakaolinite) and plastic injectors (filled with alkaline solution) were set in the reaction channels for an equilibration period of 6 h. Second, the alkaline solution was injected into ampoule and the mini-blender was started (the heat disturbance caused by the mini-blender is so small that could be neglected). The mixing time of each system was about 2 min and then began the record.

2.2.2. XRD analysis

X-ray powder diffraction data were obtained using ARL X'TRA X-ray diffraction (Thermo Electron, USA) with Cu-Kα ray (12 kV, 30 mA) at a scan rate of 1°/min from 0° to 80° (2θ). Samples of air curing (AC, RH = 90 ± 5%, 20 °C) and steam curing (SC, 80 °C) for 3 d were broken into 2–3 mm fragments, ground in acetone and then dried at 65 °C for 6 h.

2.2.3. ^{27}Al, ^{29}Si MAS NMR tests

The high resolution solid state ^{27}Al, ^{29}Si NMR was acquired using AV400D Nuclear Magnetic Resonance spectrometer (Brucker, Swiss). The same powder as above prepared was disposed into zirconia rotor (5 mm diameter). The ^{27}Al spectra were acquired at a spinning rate of 9 kHz with 2048 scans and a relaxation delay of 0.5 s. ^{29}Si spectra were at a spinning rate of 5 kHz with 4010 scans and a relaxation delay of 1.5 s. The pulse frequency was 104.3 MHz and 79.5 MHz for aluminum and silicon nucleus with aqueous solution of $Al(NO_3)_3$ and tetramethylsilane as the references of chemical shift calculation, respectively.

3. Results and discussion

3.1. Process of NaOH solution activating MK

As shown in Fig. 1, an exothermic peak A appears immediately when either water or activator is mixed with MK, which

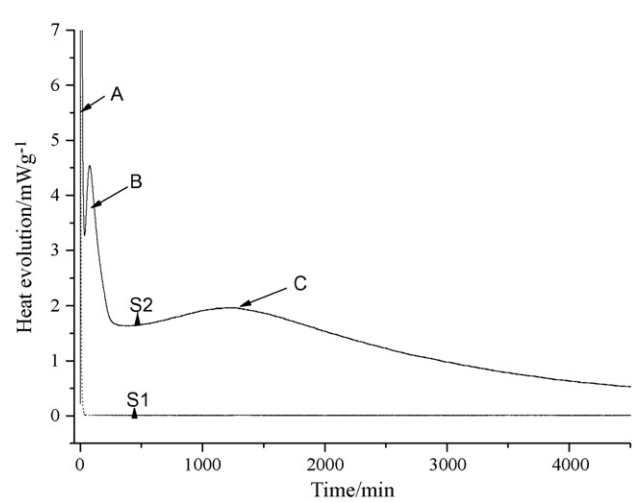

Fig. 1. Calorimetric curves of MK activated by 9 mol/L NaOH solution (S2) and mixed with distilled water (S1).

can be convincingly attributed to the instant absorption of solution on the surface of MK particles. The exothermic peak of S2 is significantly higher than that of S1 implying that alkali solution is more intensively adsorbed and OH^- anions begin attacking on Si–O and Al–O bonds. The dissolution of metakaolinite in alkaline solution is exothermic and in this process, the Si–O and Al–O bonds on particle surfaces are broken down. The rapid declining of peak A of S2 means the wetting process and initial reactions are slowing down but the reactions are still continuing to release heat. After peak A of S2 declining for 35 min, the second exothermic peak B appears suggesting the drastic breaking down of metakaolinite particles in combination with the formation of a few of alumina/silica-hydroxy species and oligomers, such as $OSi(OH)_3^-$, $Al(OH)_4^-$, $(OH)_3$–Si–O–Al–$(OH)_3$ and so on [15,16]. However, the high concentration of OH^- makes it not impossible that the fresh formed species are broken down again as intermediates.

The deconstruction products in alkali–MK system will polymerize into gels as their concentrations grows up. The polymerization is exothermic and becomes the main contribution of heat evolution (see peak C, mainly beginning from 420 min). After about 4500 min, the process goes into a thermally steady stage, during which the fresh formed small gels are probably transformed into larger networks by local reorganization. The total reaction time of S2 is about 7 d (not full scale shown in Fig. 1) and the released heat is 480 J/g. The reaction time of 7 d seems long; however, it remarkably depends on the raw materials, activators and reaction conditions. Metakaolinite used in this study has an average diameter of about 4.9 μm (Table 1). The relatively large specific surface area makes the dissolution of raw particles slow. Although the concentration of NaOH activating solution is as high as 9 mol/L, the solid/liquid ratio is 2.0 and the high solid/liquid ratio results in the low viscosity of the alkali–MK slurry and the continual structural reorganization and densification. The reaction temperature (25 °C) is low (the dividing lines between "low" and "high" temperature may be drawn at approximately 40–80 °C [13]) that also makes the geopolymerization slow. From the perspective of the changes in response to the reaction heat, the geopolymerization stages of alkali–MK can be supposed into three stages: (I) deconstruction, (II) polymerization and (III) stabilization as sketched in Fig. 2. However, these stages can hardly be separated clearly for they may occur simultaneously [7].

3.2. Effects of concentration of MOH solutions on geopolymerization

It is well known that the concentration of MOH (M = Na^+ or K^+) solutions has great effects on the mechanical properties of metakaolinite and/or fly ash based geopolymers [17–19]. Fig. 3 shows it also has great influence on geopolymerization process. The reaction heat evolution rate increases with the concentration of NaOH solution in stage I. The reaction rate of S5 is higher than that of S6 in stage II implying that there is an optimum alkalinity for activating MK and in this study the optimum concentration of NaOH solution is 9 mol/L. High concentration of Na^+ ions may be beneficial to dissolve aluminosilicate but undesirable to polymerization. According to the researches by Kolouŝek et al. [20], Wang et al. [21] and Subaer and van Riessen [22], there are still residual raw material particles in geopolymers formed from alkali–MK. By comparing the total heat evolution of each curve in Fig. 3, it is clear that the system tends to release more heat with the increasing concentration of NaOH solution. There is a similar trend for systems activated by KOH solutions as shown in Fig. 4. Thus the geopolymerization extent of raw materials can be characterized by the heat evolution: the more reaction heat the system releases, the higher extent of geopolymerization it obtains.

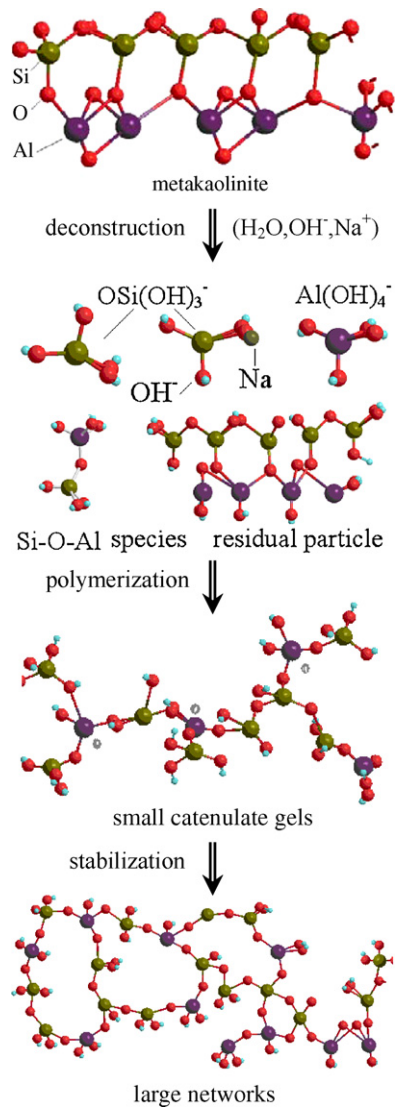

Fig. 2. Sketch of the geopolymerization process, including the deconstruction of MK by the activation of alkaline solution, the polymerization of generated alumina/silica-hydroxy species and the stabilization of fresh formed structures.

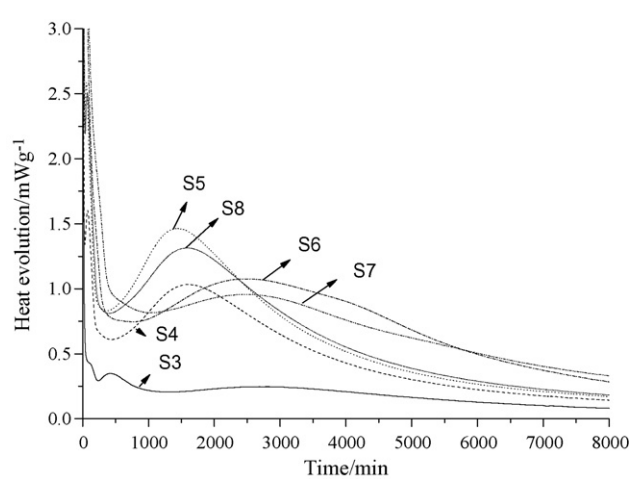

Fig. 3. Effects of concentration of NaOH solution on MK-based geopolymerization: from low (S3) to high (S6) concentration; S7-12 mol/L at higher liquid/solid ratio (1.25) than S6 (1.0); S8-6 mol/L at higher liquid/solid ratio (1.5) than S4 (1.0).

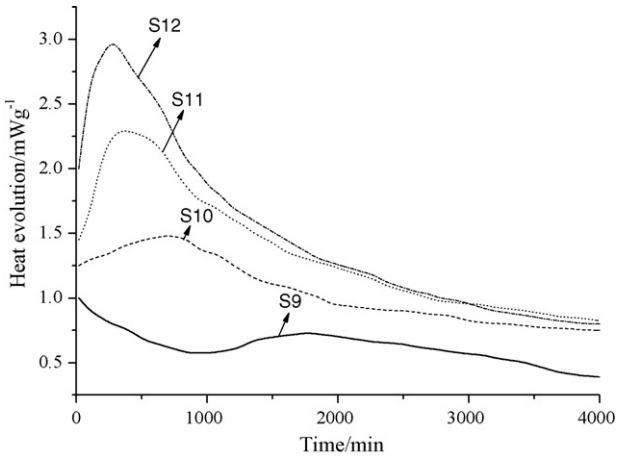

Fig. 4. Effects of concentration of KOH solution on MK-based geopolymerization, from low (S9) to high (S12) concentration.

S5 has a similar adsorption–deconstruction stage with S8, like S6 with S7. S5 has higher reaction rate than S8 (the same as S6 comparing to S7) in the early polymerization stage, but the reaction slows down after 2500 min. The difference in composition between S5 and S8 is the water content and from this point of view it is concluded that too much water diluted the concentration of OH^- resulting in lower destruction ability of activator. The polymerization is a water releasing process, therefore kinetically it is unfavorable for $Al(OH)_4^-$, $OSi(OH)_3^-$ and some other oligomers to polymerize when surrounded by too much water. S7 has the same concentration of activating solutions with S6 but the liquid/solid ratio is higher. Comparison between S6 and S7 shows that higher liquid/solid ratio makes the geopolymerization period longer, which confirms the above discussion of S2. As a result, not only the concentration of alkali solution is dominant to geopolymerization rate, the liquid/solid ratio has also great influences.

The alkali cation types have different effects on the geopolymerization process as shown by comparing Fig. 3 with Fig. 4. It is observed that KOH solution has better activating efficiency (includes reaction rate and extent) than NaOH solution. Although with the effect by 5 °C lower reaction temperature, S10 has an equal maximum heat evolution rate (about 1.5 mW g^{-1}) to S5 both at the concentration of 9 mol/L, which is likely caused by the higher alkalinity of K^+ cation. It seems that aluminosilicate is more dissolvable in KOH solution; this is consistent with that carried out by van Jaarsveld and van Deventer [17] which has shown K^+ is positive to the strength of geopolymeric materials.

3.3. Effects of modulus of alkali silicate solution on geopolymerization

As shown in Fig. 5, the reaction rate increases with the declining of modulus of potassium silicate solution during stage I and stage II. When the modulus is 1.6 (S16), the polymerization stage will extend remarkably, which is consistent with the result by Provis and van Deventer [8]. The systems of S13–S16 have equal soluble SiO_2 content and the declining of modulus is resulting from the increasing of KOH content. This indicates that the increase of alkali content is propitious to improve the reaction rate and extent when potassium silicate solution is used as activator. Comparing Figs. 4 and 5, it is noted that potassium silicate solutions have better activating efficiency than KOH solutions, in which even with more alkali content. It confirms again the different activation mechanisms of hydroxide and silicate containing activators [23] and soluble SiO_2 can accelerate geopolymerization by inducing the polymerization of the destructed products.

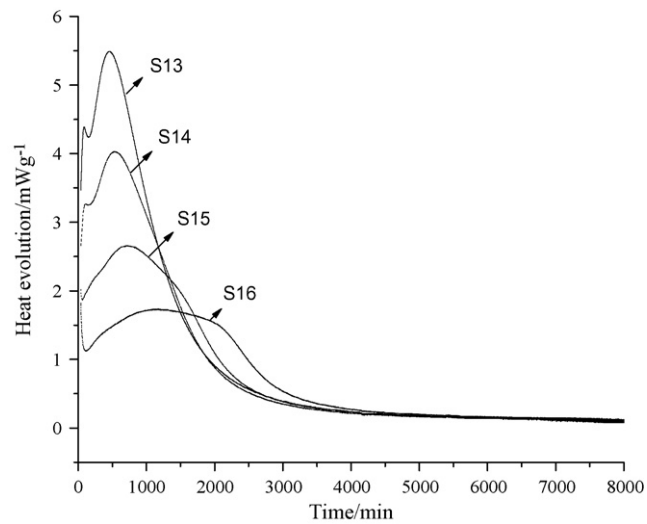

Fig. 5. Effects of modulus of K-water glass on MK-based geopolymerization, from low (S13) to high (S16) modulus.

The variation of total heat evolution of S13–S16 implies that the reaction extent of raw material increases with increasing of Na_2O content of alkali silicate solution at constant soluble silicon content. On the other hand, investigation by Duxson et al. [24] showed that the reaction extent of raw material increased with decreasing soluble silicon content at constant Na_2O/H_2O ratio. The modulus of alkali silicate solution is expected to play a defining role in determining the reaction extent of raw material. In particular, the reaction extent of raw material will increase with the decrease of modulus whichever geopolymerization systems are at constant soluble silicon content or at constant Na_2O/H_2O ratio.

3.4. Effects of reaction temperature on geopolymerization

Compressive strength increased with the moderate elevation of reaction temperature [12,25] but the mechanical performance could not reflect directly the improvement of the reactivity of raw materials. Along with the temperature increasing from 20 °C to 50 °C as shown by S17–S19 in Fig. 6, the reaction rate increases in stage I and the period of stage II is shortened. The total heat evolution in 5500 min of systems at 20 °C and 50 °C is similar

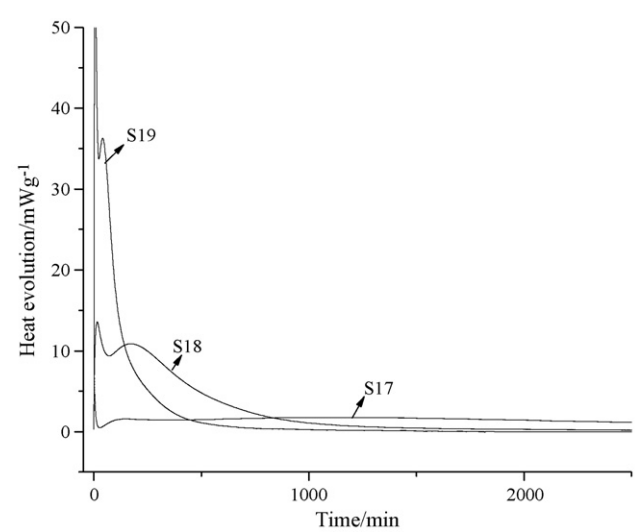

Fig. 6. Effects of temperature on geopolymerization, from low (S17) to high (S19) temperature.

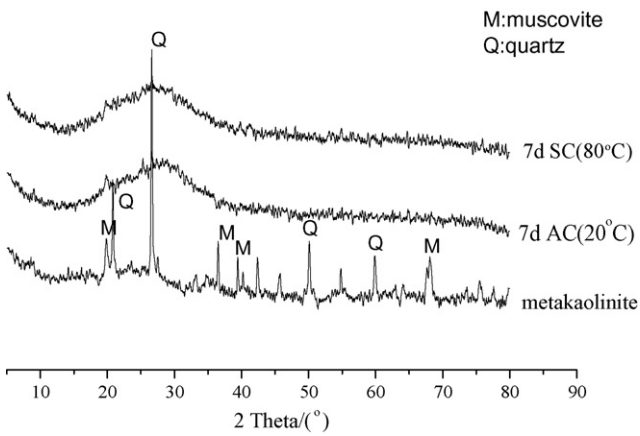

Fig. 7. X-ray diffractograms of geopolymers synthesized by activating metakaolinite with sodium silicate solution ($Na_2O{\cdot}1.2SiO_2{\cdot}13.8H_2O$).

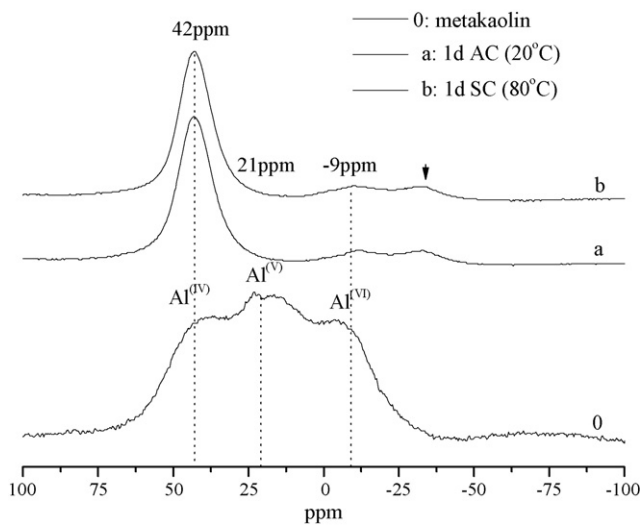

Fig. 8. ^{27}Al MAS NMR spectra of metakaolinite and geopolymers of different curing temperature (peak marked with ↓ is due to the spinning sidebands effect).

(337 J/g and 338 J/g, respectively) while that of system at 35 °C is more (405 J/g). The deconstruction of raw materials is slow at 20 °C and in the process the polymerization is consequently slow. When the temperature is 35 °C, it is believed that the polymerization of the deconstructed species speeds up resulting in the decline of the concentration of free Si^{4+} and Al^{3+} species that promotes the deconstruction of the raw materials as well as its reaction degree. The destruction rate is suited to the polymerization rate at 35 °C at this activation condition. But if the temperature rises to 50 °C, a large amount of Si^{4+} and Al^{3+} species will form at the moment of metakaolinite particles contacting with liquid activator and polymerize into gels quickly, covering on the particle surface and hindering its further deconstruction.

Fig. 7 presents the XRD patterns of raw MK and geopolymers cured at 20 °C and 80 °C for 7 d after they were set for 1 d at room condition. Under the strong alkali activation conditions, the muscovite phase contained in raw kaolinite as impurity suffered the geopolymerization process. The quartz phase has been found to be largely unreactive [26]; however, the main peak of quartz in present work is indistinguishable, which can be caused by the overlapping of the broad hump focused at approximately 27–39° (2θ). The geopolymer structural transition from amorphous to crystalline has already demonstrated that even small increases in synthesis temperature (from 70 °C and 90 °C to 120 °C) result in a readily observable increase in crystallinity [7]. But in this study, the formed products are X-ray amorphous. The similarity of two geopolymer curves indicates that temperature during polymerization–stabilization stage slightly affects the crystallization behavior of geopolymers. This implies that the crystallization behavior of geopolymers depends not only on temperature; it also depends on the other conditions, especially as the style of activator and the curing time. First, sodium silicate solution ($Na_2O{\cdot}1.2SiO_2{\cdot}13.8H_2O$) is used as activator and the high concentration of silicon in the solution makes the products more stable in amorphous phase even after 7 d curing [27]. Second, the following curing at 80 °C is only 7 d and this period could be too short for the products to complete the transition from amorphous to crystalline.

Figs. 8 and 9 show the chemical shifts of ^{27}Al and ^{29}Si of geopolymers after 1 d curing at different temperature. ^{27}Al MAS NMR spectra indicate that the six-coordinated Al(VI) (−9 ppm) and five-coordinated Al(V) (21 ppm) in metakaolinite are almost completely converted into tetrahedral structure Al(IV) (42 ppm) both in 20 °C and 80 °C cured systems. It means that temperature has little effect on the geopolymerization of active Al in raw materials during stage III. Curve a of ^{29}Si MAS NMR spectra shows a small peak at −103 ppm, which is probably the characteristic of $SiQ^4(1Al)$ of

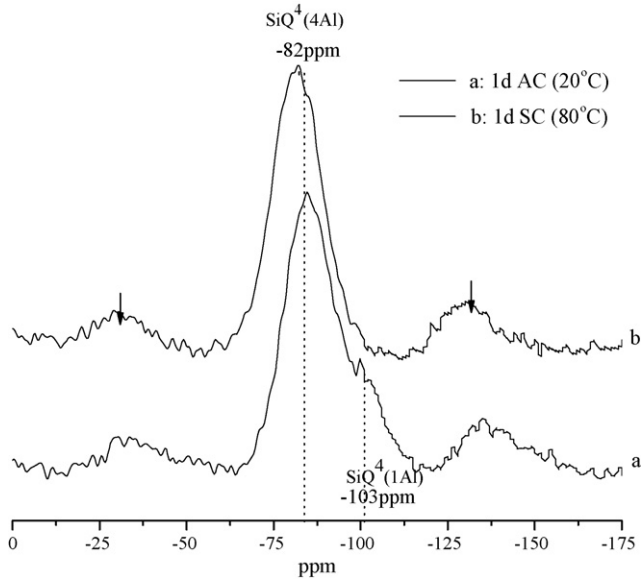

Fig. 9. ^{29}Si MAS NMR spectra of geopolymers of different curing temperature (peaks marked with ↓ are due to the spinning sidebands effect).

residual MK. At the corresponding position of curve b, this peak disappears. Combining the above discussion, it implies that the appropriate elevation of reaction temperature is not only favorable for accelerating of geopolymerization, but also positive to increase the reaction extent of raw materials.

4. Conclusions

By using isothermal calorimetric technology, the geopolymerization process of alkali–metakaolinite system was supposed into three stages: (I) destruction, (II) polymerization and (III) stabilization. The alkali concentration of liquid activators, modulus of alkali silicate solutions and reaction temperature had different effects at different stages. The appropriate elevation in concentration of alkali solution could speed up the reaction during stage II and improve the geopolymerization extent of raw materials. The period of geopolymerization could be shortened by increasing the alkali content, namely decreasing the modulus when alkali silicate solution was used. It suggested that an optimum reaction temperature could

increase the reaction rate and the extent of the reaction of raw materials. From the standpoint of understanding the geopolymerization process, the information gained currently is helpful. However, to get a generally applicable knowledge for the engineering application of geopolymeric materials, further studies of the quantitative relationship between geopolymerization rate/extent and reaction parameters (includes temperature, particle size, style and concentration of activator) remain to be performed.

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