THERMOCHEMISTRY STUDY OF THE EFFECT OF ALKALI CONTENT ON THE EARLY GEOPOLYMERISATION AT ROOM TEMPERATURE

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ABSTRACT:

The effects of alkali content on the leaching properties of kaolin and metakaolin and the early geopolymerisation have been systematically investigated by ICP-OES and isothermal calorimetry. Leaching test confirmed that increase of concentration of NaOH solution could improve the dissolution of Al and Si from kaolin and metakaolin but not necessarily in linear relation. Calorimetry of sodium silicate-metakaolin reaction systems indicated that the early geopolymerisation rate always increased with the increase of alkali content (Na/Al ratio from 0.63 to 1.00). Based on the hypothesis of full dehydrated analcime-like structure, i.e. supposing the final geopolymer is full polycondensed tridimention network of tetrahedral AlO_4 and SiO_4 (AlO_4 units play the role of network forming oxide while Na^+ balance the negative charge of AlO_4), a tentative geopolymerisation kinetics modeling analysis was proposed and it provided a quantitative understanding of the effects alkali content on geopolymerisation.

Keywords: geopolymer; Geopolymerisation; Isothermal Calorimetry; Alkali content; Kinetics

1. INTRODUCTION

Geopolymer, as a green alternative to cement, has attracted increasing attention from both academic and industrial community. To fully understand the formation of this new material, geopolymerisation mechanism has been investigated intensively [1]. The current theory of geopolymerisation involves two basic processes: (a) dissolution of source aluminosilicate; (b) polymerization between alumina, silicate and aluminosilicate species [2-5]. However, it is difficult to establish an exact mechanism for such a highly complicated reaction system, which is affected by properties of raw materials, type of activator and processing conditions.

Alkali cations are considered as a structure-forming element balancing the negative framework charge of tetrahedral aluminum [6], while OH⁻ ions (apparently valued by pH) are catalyst in the dissolution of source alunminosilicates [7]. Therefore, alkali content of

activator is one of the key factors in determining both the geopolymerisation process and the products. Previous studies confirmed that increasing of concentration of MOH solution (M=Na or K) was favorable for dissolving kaolin, which will release more heat, as a result, it will shorten the reaction time and possibly increase the reaction degree [8-12].

Isothermal calorimetry has been used to monitor the heat evolution of geopolymerisation in real time [10] but there is a lack of theoretical explanation for the distinguishable exothermic peaks and quantitative discrimination of geopolymerisation rate and degree. To obtain a better understanding of the effect of alkali content on the geopolymerisation, especially the early stage, isothermal calorimetry will be used as the main test method in present study. Based on a hypothesis that geopolymer can be considered with a fully dehydrated analcime-like structure, a tentative geopolymerisation kinetic will be attempted.

2. MATERIALS AND METHODS

(1) Materials

Soft kaolin was obtained from Fujian province. Kaolin was calciend at 900 °C for 1 h to transform into metakaolin. The compositions of metakaolin were determined by X-ray fluorescence as shown in Table 1. Specific surface area (SSA) was determined by laser particle analyser and metakaolinite phase proportion was calculated based on the element percentage of Al.

Chemical grade sodium hydroxide and distilled water were mixed within waterglass (modulus of 3.33, Na_2O=8.29%, SiO_2=29.91%) to prepare alkaline activators. Four activators were prepared with modulus n at 1.0, 1.2, 1.4 and 1.6 respectively. In experiment we kept the SiO_2 content in alkaline activator constant and varied the Na_2O content as shown in Table 2.

Table 1. Compositions and specific surface area of metakaolin as well as calculated metakaolinite proportion.

Oxide Weight/%	SiO_2	Al_2O_3	Fe_2O_3	K_2O
	55.57	41.55	0.56	0.433
Loss of ignition 0.91		SSA/ m^2/g 2.05		Metakaolinite 91.33%

Table 2. Nominal compositions of geopolymerisation systems, 10^{-3}mol.

System	n	$Al_2O_3 \cdot 2SiO_2$	$Na_2O \cdot nSiO_2$
1	1.0	8.23	8.26
2	1.2	8.23	6.88
3	1.4	8.23	5.90
4	1.6	8.23	5.16

(2) Leaching test

Specified mass of (1.000±0.001 g) metakaolin or kaolin was mixed with 30 ml NaOH solution (concentration varies from 4 to 12 mol/L) for 5 min in a polypropylene tube at room temperature (25±2 °C). In the total 24 h continuous leaching, the tubes were manually vibrated for 2 min at each interval of 3 h to slow the sedimentation of solid particles. After centrifugation, 2.5 ml of the upper clear solution was acidified by HCl solution (2 mol/L) to pH<1 and then diluted to 25 ml. The silicon and aluminum in the diluted solution was then analyzed by Optima 2000 DV ICP optical emission spectrometer (OES, Perkin Elmer, USA).

(3) Isothermal calorimetry

Reaction heat of 3 batches of geopolymerisation systems (20 °C, 25 °C and 35 °C) were tested by using 3114/3236 TAM Air isothermal calorimeter (Thermometric AB, Sweden) with precision of ±20μW. Each batch had four different nominal compositions as shown in Table 2. All systems were prepared internally in order to observe the very early reaction heat change. Firstly, admix ampoules (loaded with solid metakaolin) and plastic injectors (filled with alkaline activator) were set in the reaction channels for an equilibration period of 6 h. Secondly, the alkaline activator was injected into ampoule and the mini-blender was started. The mixing time of each system was about 2 min and then began the record. To avoid the possible heat disturbance caused by the mini-blender as well as the water sorption by metakaolin particles, a special mixture was prepared and processed with the same procedure: distilled water + metakaolin at the same liquid/solid ratio. The heat evolution plot was obtained by subtracting heat value of water-metakaolin system from that of activator-metakaolin system.

3. RESULTS AND DISCUSSIONS

(1) Effect of concentration of NaOH solution on Al and Si dissolution

Fig.1 shows that the amount of Al and Si leached from the source materials increased as the concentration of NaOH solution increased, which is consistent with previous research [7, 8]. This trend was particularly prominent for kaolin-alkaline solution system by comparing Fig.1 (a) and (b).

There were at least three notable properties for current leaching results. Firstly, metakaolin dissolved more Al and Si than kaolin at a same concentration of NaOH solution. This implies that the change from 6-coordinated aluminum to 5- and 4-coordinated states [13] activated the solubility of aluminum source. Si in metakaolin seemed more soluble than that in kaolin, which was due to the destruction of kaolinite at c axis direction [14]. Secondly, the concentration of Al in leaching solution was higher than that of Si for kaolin, which was different from the finds by Xu and van Deventer [8]. Taking the quartz as another silicon source, the dissolved ratio of Si should be even lower. This difference was suspected to be caused by the source of kaolin: different mineral impurity in kaolin may change the dissolution property of Al and Si [15]. Thirdly, both of the total leached amounts of Al and Si from kaolin in 12 mol/L NaOH solution are both about 2.3 times of those in 4 mol/L NaOH solution. However, leached amounts of Al and Si from metakaolin in 12 mol/L NaOH solution are 1.72 and 1.65 times respectively of that in 4mol/L. This implies the increase of alkali content in activator can improve the dissolution quantity of Al and Si but not necessarily in linear relation. For metakaolin, increase of concentration from 6 mol/L to 12 mol/L can't significantly improve the leached Al and Si amount as expected. One explanation is the restraining effect of supersaturated Si and Al species in highly concentrated solution. Therefore it is necessary to choose an appropriate alkaline content in geopolymer synthesis because excessive alkali content can neither effectively improve the dissolution of Al and Si nor promote the followed condensation [16].
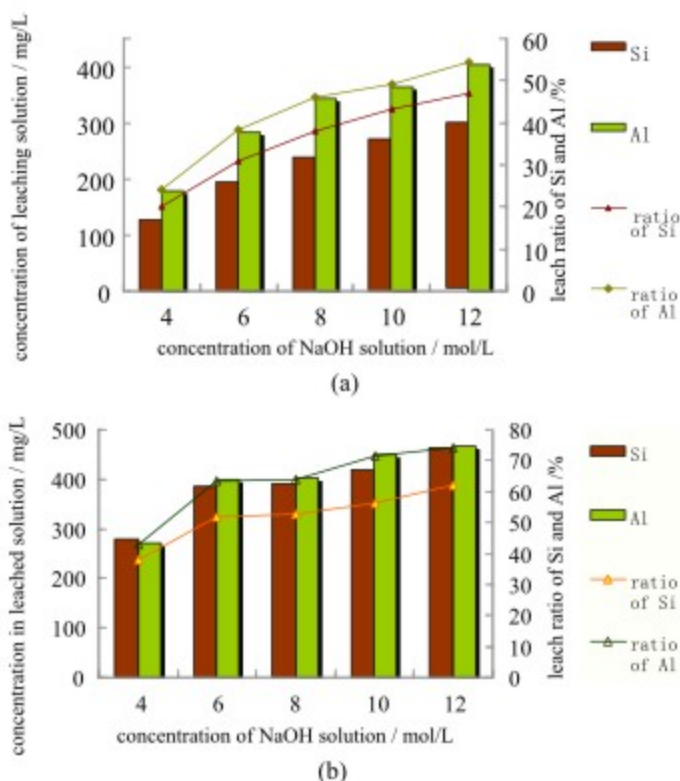
(a)

(b)

Fig.1. Al and Si leaching from kaolin (a) and metakaolin (b) in NaOH solution

(2) Effect of alkali content on the geopolymerisation process

It is clear from above analysis that moderate alkali content is beneficial to the dissolution of Al and Si from metakaolin. Fig.2 shows the effects of alkali content on the heat evolution of sodium silicate-metakaolin reaction systems. All three temperatures showed that the destruction process at the very early stage (the first one and half hour) made the major contribution to the heat evolution as indicated by the first distinct peak. The second peak can be attributed to the polycondensation. Taking the heat evolution as an indication of geopolymerisation rate, it was observed that increasing alkali content can improve the early geopolymerisation rate significantly, either destruction or polycondensation. This result agrees with previous findings in potassium based activation systems [12]. Besides the alkali content, temperature was another important factor affecting the geopolymerisation. The time for systems at 20 °C, 25 °C and 35 °C to complete early polycondensation was about 80 h, 52 h and 32 h. Mild elevating of temperature at low scale (division between low and high temperatures is referenced in [17]) can shorten the reaction time. Therefore during the engineering application of geopolymer, the out-side temperature should be taken into account.
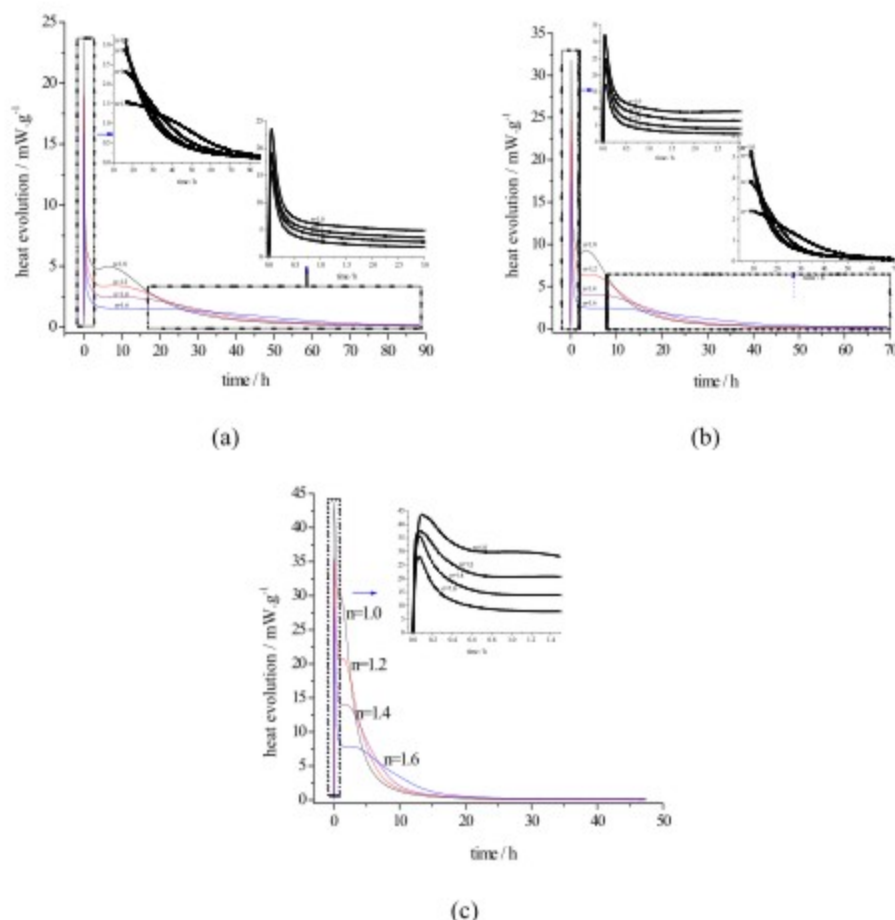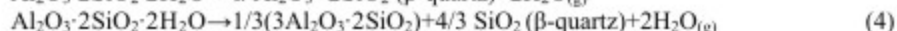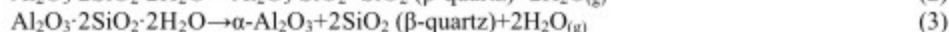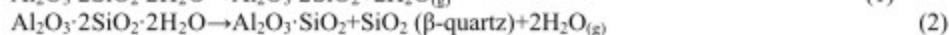
(a)

(b)

(c)

Fig.2. Effects of modulus n of sodium silicate solution on the geopolymerisation process at 20 °C (a), 25 °C (b) and 35 °C (c).

(3) Theoretical reaction enthalpy of metakaolin based geopolymerisation

As a calcined product of kaolin, metakaolin mainly contains five silicates: metakaolinite, sillimanite, mullite, $\alpha-Al_2O_3$ and $\beta-$quartz. Eq.1 to Eq.4 describes the transformation from kaolinite to these silicates. Table 3 lists the reaction enthalpy of destruction of silicates in strong alkaline solution.

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O_{(g)} \tag{1}$$

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot SiO_2 + SiO_2 (\beta\text{-quartz}) + 2H_2O_{(g)} \tag{2}$$

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow \alpha\text{-}Al_2O_3 + 2SiO_2 (\beta\text{-quartz}) + 2H_2O_{(g)} \tag{3}$$

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow 1/3(3Al_2O_3 \cdot 2SiO_2) + 4/3\ SiO_2 (\beta\text{-quartz}) + 2H_2O_{(g)} \tag{4}$$

The calculation result listed in Table 3 can explain the first abrupt exothermic peak in Fig.2. Most calcined products in metakaolin process an exothermic destruction except for β-SiO_2, which has a small positive enthalpy value of 1.4 kJ/mol. Under the isothermal and pressure-constant condition, the destruction enthalpy is the theoretical energy change

absorbed from surroundings or released to surroundings. With calcination at 700 °C, it is thermodynamically difficult for the calcined system to form mullite, $\alpha-Al_2O_3$ and $\beta-$quartz. Thus calcined kaolin can be treated as metakaolinite and the calcination can be regarded an energy storage process. Rahier et al. [4] attributed the significant decline of geopolymerization thermal when temperature of kaolin calcination was higher than 900°C to some new formed phases. From this calculation, the phases may be mullite and some other minerals.

Table 3 Theoretical destruction enthalpy of aluminosilicates possibly existed in metakaolin in strong alkali solution, kJ/mol

Mineral	Potential reaction formula	$\triangle H$
Metakaolinite	$Al_2O_3 \cdot 2SiO_2 + 5 H_2O + 4 OH^- \rightarrow 2 Al(OH)_4^- + 2 OSi(OH)_3^-$	
H_{f298}^0	-3316.8 -285.8 -230.0 -1502.5 -1426.1	-191.4
Sillimanite	$Al_2O_3 \cdot SiO_2 + 4 H_2O + 3 OH^- \rightarrow 2 Al(OH)_4^- + OSi(OH)_3^-$	
H_{f298}^0	-2585.8 -285.8 -230.0 -1502.5 -1426.1	-12.1
Mullite	$3Al_2O_3 \cdot 2SiO_2 + 11 H_2O + 8 OH^- \rightarrow 6 Al(OH)_4^- + 2OSi(OH)_3^-$	
H_{f298}^0	-6810.4 -285.8 -230.0 -1502.5 -1426.1	-73.0
$\alpha-Al_2O_3$	$\alpha-Al_2O_3 + 3 H_2O + 2 OH^- \rightarrow 2 Al(OH)_4^-$	
H_{f298}^0	-1671.0 -285.8 -230.0 -1502.5	-16.6
$\beta-SiO_2$	$\beta-SiO_2 + H_2O + OH^- \rightarrow OSi(OH)_3^-$	
H_{f298}^0	-911.7 -285.8 -230.0 -1426.1	1.4

To obtain an approximate thermodynamic basis for calculation, three assumptions are proposed. Firstly, assume the final product has fully polycondensed tridimensional network, i.e. tetrahedral AlO_4 and SiO_4 all convert into dehydrated analcime-like amorphous aluminosilicate $[AlO_2^- \cdot nSiO_2]$, abbreviated as PG (perfect geopolymer), in which the AlO_4 units play the role of network forming oxide while Na^+ balance the negative charge of AlO_4. PG has similar thermodynamic properties as dehydrated analcime. Secondly, if the activator is waterglass solution modified by NaOH at low modulus (≤ 1.6) and high pH (≥ 14), assume all the silicon will take pate in polymerization and also form SiO_2 glass. Additionally simplify silicon in different forms as SiO_3^{2-}, which is stale at high pH. Thirdly, when $1<n<3$, suppose the standard molar formation enthalpy $\triangle H_{298}^0$(PG) of PG can be mechanically calculated by Eq.5. Thus the geopolymerisation of current studied systems can be simplified into Eq.6 (only from the point of reaction enthalpy change):

$$\triangle H_{298}^0{}_{(PG)} = \triangle H_{298}^0{}_{(dehydrated\ analcime)} + (n-2) \cdot \triangle H_{f298}^0{}_{(SiO2\ glass)} \qquad (5)$$

$$Al_2O_3 \cdot 2SiO_2 + SiO_3^{2-} \xrightarrow{OH^- + Na^+} 2 [AlO_2^- \cdot 1.5SiO_2] \qquad (6)$$

It should note that $[AlO_2^- \cdot 1.5SiO_2]$ is just a schematic structure formula of perfect geopolymer and $\triangle H_{298}^0$ is a result of mechanically combining the $\triangle H_{298}^0$ of dehydrated analcime (-2974.8 kJ/mol) and the $\triangle H_{298}^0$ of $SiO_{2(g)}$ (-902.2 kJ/mol), referenced from [23]. Taking the $\triangle H_{298}^0$ of SiO_3^{2-} (-1101.1 kJ/mol) into calculation, the total geopolymerisation enthalpy will be -628.1 kJ/mol.

(4) Tentative modeling on geopolymerisation kinetics

Researches by van Deventer research group have attempted to establish kinetics models for quantificational description of geopolymerisation [18-21]. By using Energy Dispersive X-ray Diffractometry (EDXRD), Provis et al. built up a reaction kinetic model for determining the setting behavior and the effect of silica content in geopolymer-forming systems. However,

only the relative extent of reaction is measurable by EDXRD technique. Based on current isothermal calorimetry results, it was reasonably concluded the early geopolymerisation roughly includes two processes: destruction and polycondensation, both of which are exothermic. From the point of the metakaolin particle change, the geopolymerisation is somewhat similar to the alkali activation of slag [22] and the corresponding equation is selected as Eq.7.

$$[1-(1-\alpha)^{1/3}]^N = K \cdot t \tag{7}$$

The differential equation is:

$$\frac{d\alpha}{dt} = \frac{3K}{N}(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{1-N} \tag{8}$$

In which,

α – reaction extent;

K – reaction rate constant;

N – reaction dominating factor: N<1, dominated by surface reaction; N=1, dominated by interface kinetics; N>1, dominated by diffusion;

$\frac{d\alpha}{dt}$ – reaction rate, obtained by normalization of heat evolution [e].

The definition of geopolymerisation extent α is difficult but inevitable. With increasing concentrations of destructed species and their interaction, $Al(OH)_4^-$, $SiO(OH)_3^-$ and some oligomers will polycondense and release water step by step [12]. It seems an alternative to model geopolymerisation from the aspect of heat change to avoid the problem of uncertainty of formed species at specific step. Above four reaction systems all contain 8.23×10^{-3} mol metakaolin and the theoretical heat evolution should be 2586.4 J/g. Take integration of the heat evolution in Fig.2 (b) and define reaction extent α is the ratio of integrated heat/theoretical heat evolution, the geopolymerisation extent vs. reaction time is shown in Fig.3.
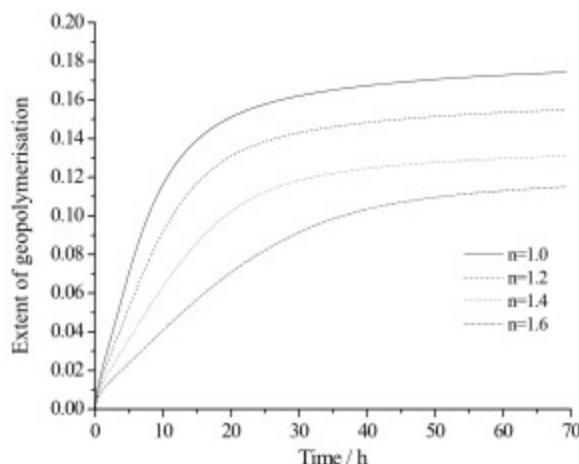

Fig.3. Effects of modulus of sodium silicate solution on the geopolymerisation extent at 25°C.

It is clear that when the modulus n increases from 1.0 to 1.6, the final geopolymerisation extent (72 h) decreases from 0.76 to 0.50. Taking Na/Al ratio into consideration, the geopolymerisation extent increases with the improve alkali content in a lineal relation.

However, for sodium silicate solution activation systems at constant Si/Al ratio=2.0, it can't obtain a complete geopolymerisation, even the Na/Al nears 1.0.

Normalized and predicted rate dα/dt vs. the extent of geopolymerisation is plotted in Fig.4 and Fig.5 with the corresponding fitting parameters (carried out by Statistics 6.0 with nonlinear least squares model estimation) given in Table 4. With the alkali content decreasing, the reaction rate constant decreased remarkably while the reaction dominating factor also rose a little, implying that the diffusion of destructed species became slower. This result is consistent with the change of character of activator: the less NaOH added in waterglass, the less $[SiO_4]$ Q^0 formed, resulting in higher viscosity of solution and in return making the diffusion more difficult. The reaction dominating factor decreased inexpertly when n=1.6, which may be caused by the self-polycondensation of SiO_4 in activator. This phenomenon suggests that the activator plays a very important role in determine the reaction mechanism.

However, by comparing the predicted data cures with that from experiment, it should admit that the kinetic formula is only well fitted in the very early stage (α < 0.02) although the relativity R is acceptable. This is just a tentative analysis of alkali influence on geopolymerisation kinetics rather than a full-blown theory. Maybe using two kinetic formulas will be more effective in describing the geopolymerisation process: one is destruction kinetic and the other is polycondensation kinetic. The Eq.3 seems suitable for the former but some other formula should be carefully built up for polycondensation. Further work will be carried out for better describing the geopolymerisation kinetics as well as some other factors, such as accelerating or retarding ions, water/clay ratio, etc.

Table 4. Fitting parameters of kinetic formula

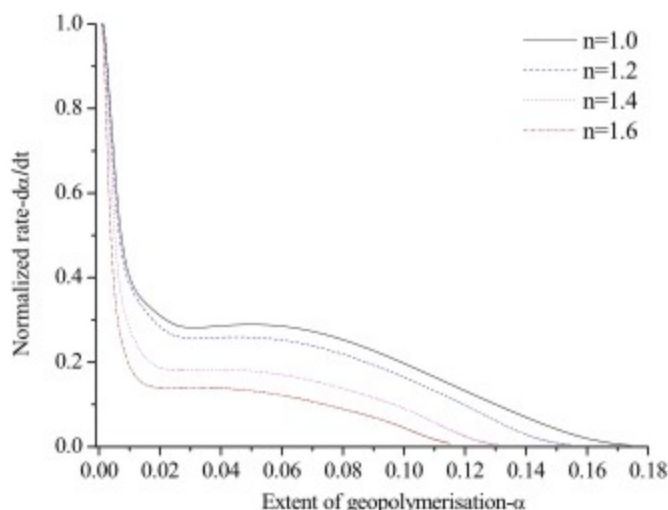| n	$K \times 10^{-3}$	N	relativity R
1.0	4.76	1.69	0.76
1.2	4.58	1.69	0.78
1.4	3.19	1.91	0.83
1.6	3.19	1.66	0.87

Fig.4. Normalized geopolymerisation rate dα/dt vs. extent of α at 25 °C.
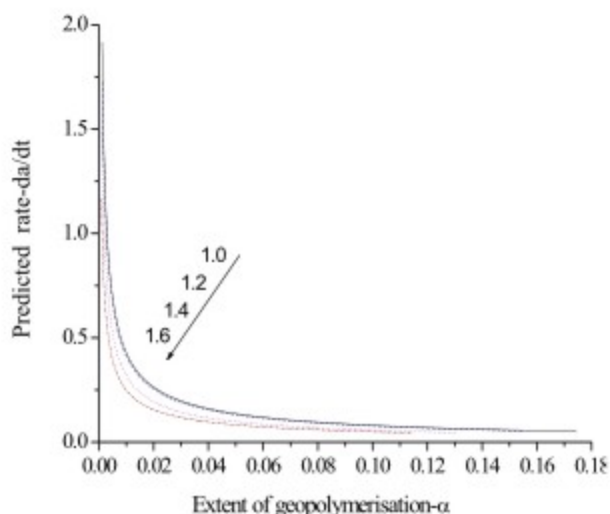
Fig.5 Predicted geopolymerisation rate $d\alpha/dt$ vs. extent of α at 25 $^{\circ}$C.

4. CONCLUSIONS

ICP-OES and isothermal calorimetry results showed that the increase of alkali content in activator can improve the dissolution quantity of Al and Si from kaolin and metakaolin but not necessarily in linear relation. The early geopolymerisation rate always increased with increasing of alkali content (Na/Al from 0.63 to 1.00) at a constant Si/Al ratio=2. Elevating temperature was an effective way to accelerate the geopolymerisation. Based on the hypothesis that the final geopolymer product has fully polycondensed tridimensional network, tentative analysis on geopolymerisation kinetics was carried out and it provided the quantitative relationship between alkali content and the very early geopolymerisation stage at acceptable relativities. Further work leaves on the respective modeling on the destruction kinetic and polycondensation kinetic as well as their affecting factors.

ACKNOWLEDGEMENTS

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