Study of ion cluster reorientation process of geopolymerisation reaction using semi-empirical AM1 calculations

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ABSTRACT

In this paper all the possible reaction pathways involved in ion clusters reorientation process of metakaolin based Geopolymeric cement were systemically investigated according to thermodynamic theory. The reaction energy of every possible reorientation pathway was also calculated using computational chemistry method-semi-empirical AM1 calculation. The optimum reorientation pathway was analyzed based on the energy-minimized principle. The calculation results showed that Si–Al hybrid reorientation should be primary reorientation pathway of Geopolymeric cement made with NaOH or KOH activated metakaolin. This viewpoint was also verified by Nuclear Magnetic Resonance Spectroscopy equipped with Magic Angle Spinning technique (MAS-NMR). In addition, the semi-empirical AM1 calculations revealed that the reorientation reaction is easier and stronger in NaOH solution than in KOH solution.

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1. Introduction

In recent years a novel type of high performance inorganic cementitious materials—Geopolymeric cement is rapidly developed across the world. Geopolymeric cement is one type of CaO-free aluminosilicate gel binder, which was introduced into the inorganic cementitious world by J. Davidovits in the later 1970s [1]. Geopolymeric cement can be synthesized by mixing aluminosilicate reactive materials with less or no CaO component (such as metakaolin) and strongly alkaline solutions (such as NaOH or KOH), then curing at room temperature. Under a strongly alkaline solution, aluminosilicate materials are rapidly dissolved into solution to form free SiO_4 and AlO_4 tetrahedral units. With the development of reaction, mix water is gradually split out and these SiO_4 and AlO_4 tetrahedral units are linked alternatively to yield polymeric precursors (–SiO_4–AlO_4–,or –SiO_4–AlO_4–SiO_4–, or –SiO_4–AlO_4–SiO_4–SiO_4–) by sharing all oxygen atoms between two tetrahedral units, and thereby forming monolithic like geopolymer products [2]. Geopolymeric cement made with reasonable mixture design and formulation can exhibit superior properties to Portland cement; the production of geopolymeric cement requires much lower calcining temperature (600 to 800 °C) and emits 80 to 90% less CO_2 than Portland cement [3,4]. Reasonable strength can be gained in a short period at room temperature. In most cases, 70% of the final compressive strength is developed in the first 12 h. Low permeability, comparable with natural granite, is another property of geopolymeric cement [2,5,6]. It is also reported that resistance to fire and acid attacks for geopolymeric cement are substantially superior to those for Portland cement [7,8]. Apart from the high early strength, low permeability, and good fire and acid resistance, geopolymeric cement also can attain higher unconfined compressive strength and shrink much less than Portland cement [2,9,10]. Other documented properties include good resistance to freezing-and-thawing cycles as well as excellent solidification of heavy metal ions [2,5–14]. These properties make geopolymeric cement a strong candidate for substituting Portland cement applied in the fields of civil, bridge, pavement, hydraulic, underground, and military engineering [15,16].

At present research into the formation process of Geopolymeric cement has become a hot topic internationally. By far most of the researchers describe the formation process of Geopolymeric cement by means of traditional hydration mechanism of Portland cement or alkali slag cement. Only a 3-step process of dissolution–reorientation–polycondensation involved in geopolymerisation reaction was proposed [17]. However, the setting and hardening of Geopolymeric cement is so rapid that the 3-step process almost takes place at the same time. Therefore, it is impossible to isolate the three steps by experimental study, yielding no better understanding of the details of each step until now.

Semi-empirical quantum chemistry methods are based on the Hartree–Fock formalism, but make some approximations and obtain some parameters from empirical data. They are very important in computational chemistry for treating large molecules where the full Hartree–Fock method without the approximations is too expensive.

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Semi-empirical AM1 calculation has shown to be successful in predicting the molecular structure and physical properties of silicates or alumino-silicate materials. By far the important conclusions from these studies are that the major structures and energetics of silicates or alumino-silicates can be accounted for by short-range directional forces or covalent bonding in a traditional sense. As a result, finite molecular clusters can be used to simulate the local environment and provide significant insight into the atomic forces and bonding pictures of silicates or alumino-silicates. With the development of computational power of personal computer, it is possible to calculate the bonding, breaking and formation processes, in particular, the reaction pathways and energetics involving silicates or alumino-silicates from the atomic point of view with AM1 calculation.
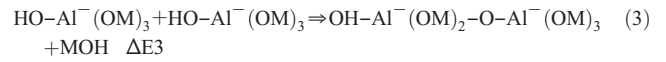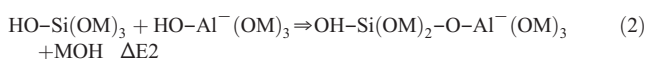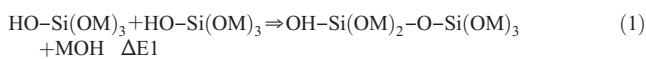
The starting and third steps, i.e. dissolution process and polycondensation process of metakaolin based Geopolymeric cement were previously studied using computational chemistry method by the authors [18,19]. However, the intermediate step-reorientation process between dissolution and polycondensation reactions is not investigated until now. What are the reorientation pathways? What type of molecular configuration is produced during the reorientation process: hybrid or homologue reorientation? These questions are not well answered at present. Hence, it is essential to investigate reorientation process in order to gain good insight into the whole formation process and the mechanisms of geopolymerisation reaction. In view of the difficulty in isolating the three steps in experiment, a computational chemistry method-semi-empirical AM1 calculation is conducted to study all the possible reorientation pathways involved in the formation process of metakaolin based Geopolymeric cement.

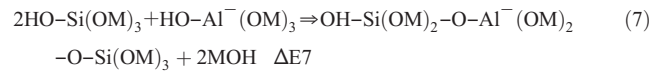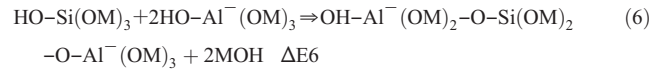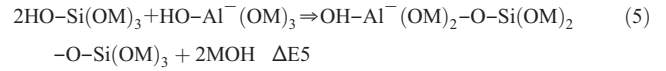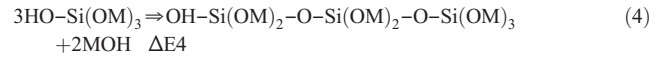## 2. Reorientation pathways of ion clusters

It is known that free $HOT(OM)_3$ (T represents Al^- or Si, M represents Na or K) ion clusters with great energy and high reactivity is formed after the dissolution process of metakaolin under highly alkaline solution attack [18]. As the dissolution process proceeds more and more $HOT(OM)_3$ ion clusters are released into solution, resulting in frequent collisions among them. When $HOT(OM)_3$ clusters collide with each other at a suitable angle and rate, a short-range directional force occurs and 2 or 3 ion clusters orientation are finally formed. As a result, the body energy of the alkaline solution system is greatly reduced and meta-stable intermediate geopolymeric products are produced. This process is called the orientation reaction.

In the present study the reorientation reaction among two or three ion clusters $HOT(OM)_3$ was taken as an example to investigate the possible reorientation pathways and the structural configuration of the reorientation products. From the thermodynamic point of view, three types of reorientation pathways can possibly take part in the reorientation process of two ion clusters as modeled in Eqs. (1) to (3). The Lowenstein aluminum avoidance principle sates that, whenever two tetrahedral are linked by one oxygen bridge, only one can be occupied by Al and there can hence be no Al–O–Al bridges [20]. Therefore, the reaction described in Eq. (3) impossibly proceeds, i.e., only Eqs. (1) and (2) pathways can possibly take place for two ion clusters reorientation. Similarly, four possible pathways for three ion clusters reorientation as shown in Eqs. (4–7). The corresponding energy-optimized geometries of the various reorientation clusters are also depicted in Fig. 1.

1) Two ion clusters reorientation:

$$HO-Si(OM)_3+HO-Si(OM)_3 \Rightarrow OH-Si(OM)_2-O-Si(OM)_3 \\ +MOH \quad \Delta E1 \tag{1}$$

$$HO-Si(OM)_3 + HO-Al^-(OM)_3 \Rightarrow OH-Si(OM)_2-O-Al^-(OM)_3 \\ +MOH \quad \Delta E2 \tag{2}$$

$$HO-Al^-(OM)_3+HO-Al^-(OM)_3 \Rightarrow OH-Al^-(OM)_2-O-Al^-(OM)_3 \\ +MOH \quad \Delta E3 \tag{3}$$

2) Three ion clusters reorientation:

$$3HO-Si(OM)_3 \Rightarrow OH-Si(OM)_2-O-Si(OM)_2-O-Si(OM)_3 \\ +2MOH \quad \Delta E4 \tag{4}$$

$$2HO-Si(OM)_3+HO-Al^-(OM)_3 \Rightarrow OH-Al^-(OM)_2-O-Si(OM)_2 \\ -O-Si(OM)_3 + 2MOH \quad \Delta E5 \tag{5}$$

$$HO-Si(OM)_3+2HO-Al^-(OM)_3 \Rightarrow OH-Al^-(OM)_2-O-Si(OM)_2 \\ -O-Al^-(OM)_3 + 2MOH \quad \Delta E6 \tag{6}$$

$$2HO-Si(OM)_3+HO-Al^-(OM)_3 \Rightarrow OH-Si(OM)_2-O-Al^-(OM)_2 \\ -O-Si(OM)_3 + 2MOH \quad \Delta E7 \tag{7}$$

3. Reaction energies of various orientation pathways

Semi-empirical AM1 restricted Hatree–Fock calculations were conducted on all the possible orientation pathways, as shown in Eqs. (1), (2), (4–7). The calculated reaction energies for various pathways are listed in Table 1.

As can be seen from Table 1, in NaOH solution the reaction energy of the hybrid reorientation reaction between $HOAl^-(OM)_3$ and $HOSi(OM)_3$ was lower than that of the homologue reorientation pathways between $HOSi(OM)_3$ and $HOSi(OM)_3$ apart from $\triangle E6_{(Na)}$ ($\triangle E2_{Na}< \triangle E1_{Na}$, $\triangle E5_{Na}<\triangle E4_{Na}$, $\triangle E7_{Na}<\triangle E4_{Na}$). This indicates that Si–Al hybrid reorientation process should theoretically be the easiest one among all the possible process and be the primary reorientation pathway. As a result, the Si–Al hybrid configuration should be the predominant molecular structure of the reorientation clusters. It is worth noting that Al–Si–Si reorientation reaction ($\triangle E5_{(Na)} = -47.499$ kJ/mol) exhibits the lowest reaction energy in all reorientation pathways of three ion clusters in NaOH solution, which implies that Al–Si–Si reorientation reaction should be primary reorientation pathways. In KOH solution, Si–Al hybrid reorientation also exhibits lower reaction energies than Si–Si homologue reorientation apart from $\triangle E2_K$ and $\triangle E6_K$ ($\triangle E2_K<\triangle E1_K$, $\triangle E7_K<\triangle E4_K$). This indicates that Si–Al hybrid reorientation process should theoretically be primary reorientation pathway in KOH solution. It is important to point out that Eq. (6) reaction energy ($\triangle E6$) was positive in various alkaline solutions ($\triangle E6_{Na} = 17.149$ kcal/mol, $\triangle E6_K = 23.742$ kcal/mol), which implies that the Al–Si–Al reorientation reaction should not occur spontaneously without an exterior heat resource. In addition, it was observed that the reorientation reaction energies in NaOH solution were lower than those in KOH solution ($E1_{Na}<\triangle E1_K$, $E2_{Na}<\triangle E2_K$, $E4_{Na}<\triangle E4_K$, $E5_{Na}<\triangle E5_K$, $E6_{Na}<\triangle E6_K$, $E7_{Na}<\triangle E7_K$), This suggests that the reorientation reaction is easier and stronger in NaOH solution than in KOH solution.

4. Experimental verification

4.1. Raw materials

Metakaolin used as the most mainly aluminosilicate materials in this study is obtained by calcining pure kaolin from China Kaolin Clay Company, Su Zhou, P.R. China. The optimum calcination temperature of kaolin is obtained through a series of calcination experimental. After each cacination test, ^{27}Al MAS-NMR resonance spectrum is measured to know the amount of 4-fold coordinated Al. The more the amount of
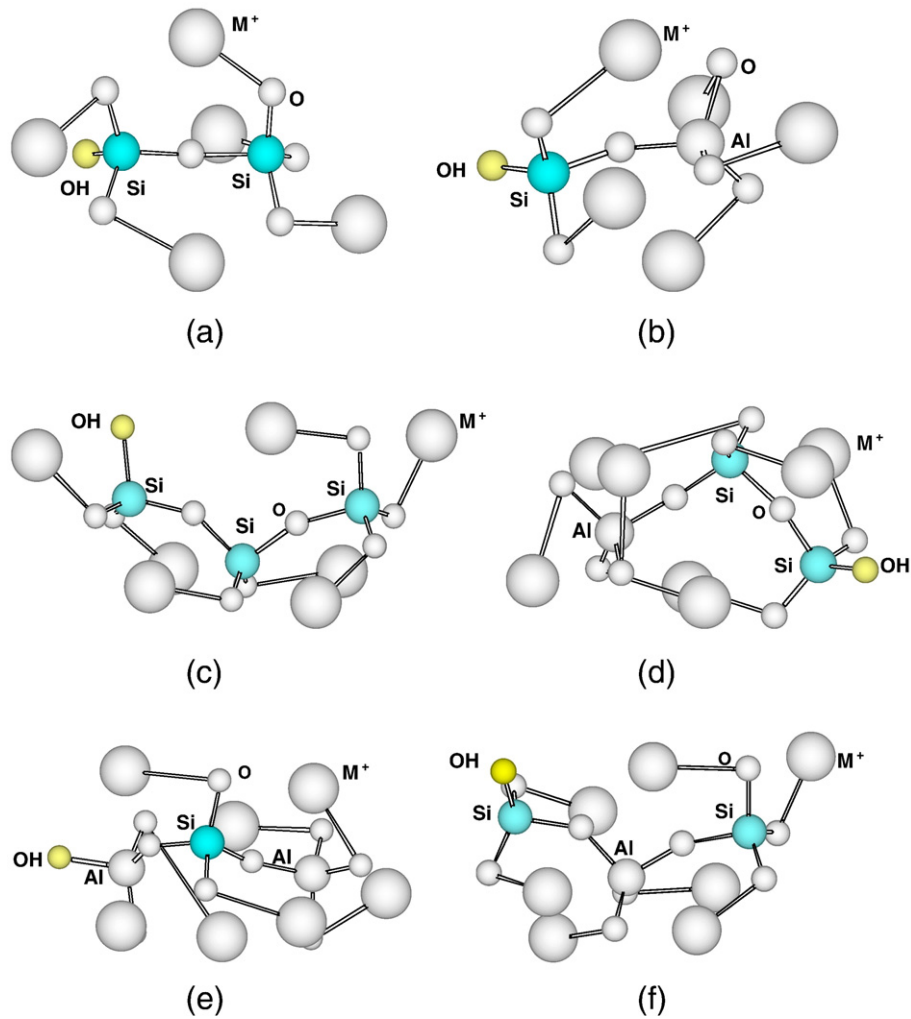
Fig. 1. Energy-optimized geometries of various reorientation clusters: (a) Si–Si reorientation; (b) Si–Al reorientation; (c) Si–Si–Si reorientation; (d) Al–Si–Si reorientation; (e) Al–Si–Al reorientation; (f) Si–Al–Si reorientation.

4-fold coordinated Al, the higher the reactivity of metakaolin. When the kaolin is calcined at 700 °C for 12 h, the ^{27}MAS-NMR resonance spectrum shows that 95% or greater of 6-fold coordinated Al in the origin kaolin has been transformed into 4-fold coordinated one. Analytical grade MOH (M denotes Na or K) pellet and alkaline silicate solution with the molar ratio of SiO_2/M_2O of 3.2 and the solid content of 37% are used as alkaline reagents. Silica fume with 95% or greater of SiO_2 content is used as silicon additive to compensate the shortage of silicon in metakaolin. Distilled water is used throughout the experiment.

4.2. Methods

4.2.1. Specimen preparation

In this study, MOH, alkaline silicate solution and water are firstly mixed in a beaker and cooled down to room temperature, and then metakaolin and silica fume powders are slowly added into the above pre-mix alkaline solution and mixed for 3 min. After that, the fresh geopolymeric cement matrix is rapidly poured into cubic steel mould of 40 mm by 40 mm by 40 mm. All samples are vibrated for 2 min on the vibration table and set at room temperature. In order to prevent the evaporation of mixing water, the specimens are covered by plastic film during the setting and hardening process. The mould is removed after 24 h. The demoulded specimens are cured at 20 °C

and 95% R.H for 28 days. At least six specimens are made for each formula.

Herein it is important to point out that the pre-mix of MOH, alkaline silicate solution, rather than direct addition of MOH pellet into geopolymeric cement matrix is a key to ensure an enough long workability time to complete the above process. Otherwise, the setting and hardening process of geopolymer become too rapid to complete the above specimen preparation.

4.2.2. MAS-NMR analysis

Six specimens of each formulation are firstly crushed. Some fragments are collected from each specimen, and then immersed in an ethanol for 3 days to stop the further geopolymerization reaction, subsequently oven-dried at 60 °C for 6 h to remove the physically absorbed water. After that, these hardened geopolymeric cement paste fractions are further ground into very fine particles with agate mortar, and remove the coarse particles with the sieve of 80 μm in diameter. The fine powders from 6 specimens are homogeneously mixed and placed in desiccators for 24 h.

A JEOL NM-ESH40MU Nuclear Magnetic Resonance Spectroscopy equipped with Magic Angle Spinning technique (MAS-NMR) is used to analyze the molecular configuration types of polycondensation clusters of hardened geopolymeric pastes made with MOH activated metakaolin. In this study, the spinning speed of the sample capsule is

Table 1
Reaction energies of various reorientation pathways.

Molecular structure cluster	Formation heat (a.u)	Reaction energies (kcal/mol)											
		$\Delta E1_{Na}$	$\Delta E1_{K}$	$\Delta E2_{Na}$	$\Delta E2_{K}$	$\Delta E4_{Na}$	$\Delta E4_{K}$	$\Delta E5_{Na}$	$\Delta E5_{K}$	$\Delta E6_{Na}$	$\Delta E6_{K}$	$\Delta E7_{Na}$	$\Delta E7_{K}$
$OH-Si(ONa)_2-O-Si(ONa)_3$	−943.114												
$OH-Si(OK)_2-O-Si(OK)_3$	−791.193												
$OH-Si(ONa)_2-O-Al-(ONa)_3$	−884.189												
$OH-Si(OK)_2-O-Al-(OK)_3$	−689.315												
$OH-Si(ONa)_2-O-Si(ONa)_2-O-Si(ONa)_3$	−1294.427												
$OH-Si(OK)_2-O-Si(OK)_2-O-Si(OK)_3$	−1131.905												
$OH-Al-(ONa)_2-O-Si(ONa)_2-O-Si(ONa)_3$	−1252.430												
$OH-Al-(OK)_2-O-Si(OK)_2-O-Si(OK)_3$	−1041.579	−60.541	−19.634	−60.895	−13.435	−30.217	−26.630	−47.499	−31.988	17.149	23.742	−36.217	−27.220
$OH-Al-(ONa)_2-O-Si(ONa)_2-O-Al-(ONa)_3$	−1128.503												
$OH-Al-(OK)_2-O-Si(OK)_2-O-Al-(OK)_3$	−890.170												
$OH-Si(ONa)_2-O-Al-(ONa)_2-O-Si(ONa)_3$	−1241.148												
$OH-Si(OK)_2-O-Al-(OK)_2-O-Si(OK)_3$	−1036.810												
$HO-Si\equiv(ONa)_3$	−500.935												
$HO-Si\equiv(OK)_3$	−437.849												
$HO-Al-(ONa)_3$	−441.657												
$HO-Al-(OK)_3$	−342.170												
$NaOH$	−119.298												
KOH	−104.139												

Note: ΔE_{Na} denotes reaction energies in NaOH solution, ΔE_{K} denotes reaction energies in KOH solution.
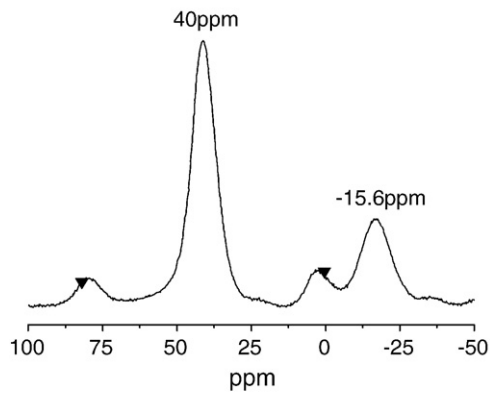
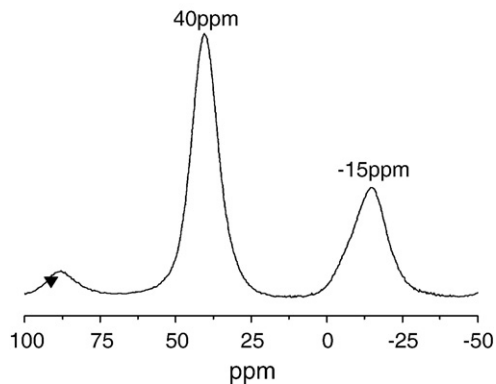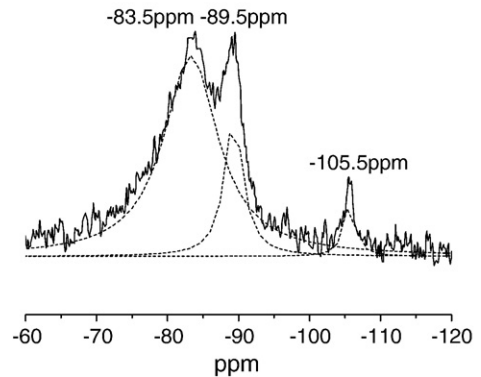**Fig. 2.** ^{27}Al MAS-NMR spectral of geopolymeric pastes made with NaOH and KOH (Resonance corresponding ▼ is caused by spinning sidebands effect). (a) Geopolymer made with NaOH. (b) Geopolymer made with KOH.
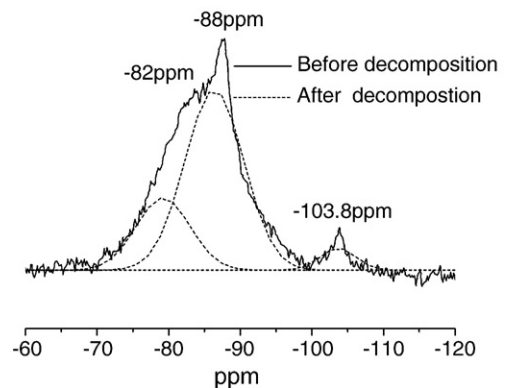

Fig. 3. ^{29}Si MAS-NMR spectral and its decomposition of geopolymeric pastes made with NaOH and KOH. (a) Geopolymer made with NaOH. (b) Geopolymer made with KOH.

Table 2
Main resonance models and their relative proportions in ^{29}Si MAS-NMR spectrum.

Types of geopolymer	Geopolymer made with NaOH			Geopolymer made with KOH		
Resonance models	SiQ^4(4Al)	SiQ^4(2Al)	SiQ^4(4Si)	SiQ^4(4Al)	SiQ^4(2Al)	SiQ^4(4Si)
Reorientation pathways	Hybrid	Hybrid	Homologue	Hybrid	Hybrid	Homologue
Resonance shifts (ppm)	−83.5	−89.5	−105.5	−82	−88	−103.8
Areas of resonance	239.53	60.48	17.34	237.21	644.94	47.21
Relative proportions (%)	75.48	19.06	5.46	25.52	69.40	5.08

4.8 kHz. ^{29}Si and ^{27}Al spectra are measured and recorded at ^{29}Si NMR frequency of 79.3 MHz and ^{27}Al frequency of 72.18 MHz. The ^{27}Al spectra are acquired over a spectra width of 41.67 kHz (acquisition time = 0.04 s), with 2048 scans and a relaxation delay of 0.5 s. The ^{29}Si spectra are obtained over a spectra width of 50.0 kHz (acquisition time = 0.04 s), with 8192 scans and a relaxation delay of 15 s. Chemical shifts of NMR spectra are referenced to external TMS in CDCl$_3$ for the ^{29}Si nuclei and to external aqueous AlCl$_3$ for the ^{27}Al nuclei. The spectrometer is interfaced with a computer and equipped with a MAS broad-band probe for the solid state experiments. Due to broad features of ^{29}Si NMR spectrum, it is very difficult to deconvolute the broad unresolved peak of geopolymeric gels. In order to address it, Gaussian peak deconvolution, similar to the reports of literature [21], is employed to separate and quantify SiQ^n(mAl) units with peak positions adopted from extensive studies of geopolymers [2]. Herein, SiQ^n(mAl) units is the conventional notation used to described the structural units in aluminosilicates, where n represents the degree of condensation of SiO$_4$ tetrahedra. In this way, if $n = 0, 1, 2, 3$ and 4, then silicon is respectively in isolated mono-group (SiQ^0), in dislicates and chain end groups (SiQ^1), in middle groups in chains (SiQ^2), in sheet sites (SiQ^3), and in three-dimensional cross-linked sites (SiQ^4). The letter m represents the number of aluminum atoms in the first coordination sphere of silicon. In general, if there is no aluminum atom in the second coordination sphere of silicon, the notation becomes SiQ^n(nSi).

4.3. Mix proportions and compressive strength

The mix proportions of geopolymer made with NaOH and KOH is given as follows:

$$\frac{molar SiO_2}{molar Al_2O_3} = 4.5, \quad \frac{molar Na_2O}{molar Al_2O_3} = 0.8, \quad \frac{molar H_2O}{molar Na_2O} = 5.0$$

The mix proportions have been optimized in reference [22]. The average compressive strengths are 34.8 and 24.7 MPa, respectively, for geopolymer pastes made with NaOH and KOH.

4.4. Results and discussion

4.4.1. ^{27}Al MAS-NMR

Earlier investigations [23] showed that in aluminate anions, 4-coordinated Al (with respect to oxygen) resonates at 60–80 ppm, and that in aluminosilicates, 4-coordinated Al resonates at 50–20 ppm, while 6-coordinated Al resonates at 0–10 ppm from [Al(H$_2$O)$_6$]$^{3+}$.

The ^{27}Al MAS-NMR spectra of the geopolymeric pastes made with NaOH and KOH activated metakaolin respectively are shown in Fig. 2. It can be seen that there is a predominant resonance at 40 ppm that assigned to the 4-coordinated Al and its belongs of AlQ^4(4Si) type with respect to reference [2]. In addition to the resonance at 40 ppm, a very small resonance approximately at −15 ppm that assigned to the 6-coordinated Al can also be observed. These 6-coordinated Al is caused by traces of kaolin in metakaolin due to the uncompleted calcinations. The absence of any other resonance excludes any residual singular building units of low molecular weight such as AlQ^4(0Si), AlQ^4(1Si) and AlQ^4

(2Si). Thus, geopolymeric products are mainly three-dimensional framework aluminosilicates with polymeric building units.

Although ^{27}Al MAS-NMR is a powerful tool in determining the coordination environment of Al, it cannot differentiate the various molecular configurations proposed for geopolymer: poly(sialate) (Si–O–Al–O–)$_n$, poly(sialate-siloxo) (Si–O–Al–O–Si–O–)$_n$ or poly(sialate-disiloxo) (Si–O–Al–O–Si–O–Si–O–)$_n$ polymeric building units. This differentiation can be achieved by using ^{29}Si MAS-NMR spectroscopy.

4.4.2. ^{29}Si MAS-NMR

^{29}Si MAS-NMR spectra and their decomposition using Gaussian peak deconvolution for two hardened geopolymeric pastes made with NaOH and KOH respectively are displayed in Fig. 3. The corresponding types of functional species and their relative proportions are also calculated and listed in Table 2.

It can be seen that there are three main resonances in ^{29}Si MAS-NMR spectrum of Geopolymer made with NaOH or KOH, at approximately −82 to −83.5 ppm, −88 to −89.5 ppm and −103.8 to −105.5 ppm, assigning to SiQ^4(4Al), SiQ^4(2Al) and SiQ^4(4Si) units respectively [26]. SiQ^4(4Al), SiQ^4(2Al) units are, we know, both of hybrid orientation clusters, accounting for approximately 95%. While SiQ^4(4Si) unit is homogenous orientation clusters, only accounting for 5%. This implies that Si–Al hybrid reaction is the prominent orientation pathways, which are in good agreement with the calculated results.

5. Conclusion

In this paper, all of the possible reaction pathways involved in the reorientation process of metakaolin-based geopolymeric cement were systemically investigated according to thermodynamic theory. The reaction energy of every possible reorientation pathway was also calculated using the semi-empirical AM1 method. The optimum reorientation pathway was analyzed on the basis of the energy-minimized principle. The calculation results showed that Si–Al hybrid reorientation should be primary reorientation pathway of Geopolymeric cement made with NaOH or KOH activated metakaolin, which was also verified by MAS-NMR spectra. In addition, the semi-empirical AM1 calculations revealed that NaOH solution had stronger capability in reorientation reaction than KOH solution.

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