PREPARATION AND MICROSTRUCTURE OF Na-PSDS GEOPOLYMERIC MATRIX

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In this paper, a total of 9 Na-PSDS Geopolymeric matrices with different molar ratio of SiO_2/Al_2O_3, Na_2O/Al_2O_3, H_2O/Na_2O is designated to investigate the influence of the three key ratios on mechanical properties and microstructure in accordance with orthogonal design principle. The experimental results show that Na_2O/Al_2O_3 and H_2O/Na_2O have the most significant effect on compressive strength amongst the three ratios. The highest compressive strength (34.9 MPa) can be achieved when $SiO_2/Al_2O_3 = 5.5$, $Na_2O/Al_2O_3 = 1.0$ and $H_2O/Na_2O = 7.0$. Comparing the IR spectra of 9 Na-PSDS Geopolymeric matrices also indicates that Geopolymeric matrix with the highest strength is the most fully reacted one and possesses the largest amount of Geopolymeric products. Subsequently XRD, ESEM-EDXA and MAS-NMR techniques are employed to further characterize the microstructure of the fully reacted Geopolymeric matrix. The microscopic analysis reveals that the fully reacted Na-PSDS Geopolymeric matrix possesses structural characteristics similar to gel substances in having a wide range of Si endowments, but predominantly the framework molecular chains of Si partially replaced by 4-coordinated Al tetrahedral. A 3D molecular structural model is also proposed based on the decomposition of MAS-NMR spectrum of the fully reacted Na-PSDS Geopolymeric matrix.

INTRODUCTION

Recent years have seen a great development in a new type of inorganic cementitious materials - Geopolymers around the world. Geopolymer is one type of three dimensional CaO-free aluminosilicate gel binders, which was introduced into the inorganic cementitious world by J.Davidovits in the later 1970s [1]. Geopolymer 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 reactive 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 three types of monolithic like geopolymeric products: $–SiO_4–AlO_4–$ (PS), or $–SiO_4–AlO_4–SiO_4–$ (PSS), or $–SiO_4–AlO_4–SiO_4––SiO_4–$ (PSDS) by sharing all oxygen atoms between two tetrahedral units, and thereby forming [2]. Compared to Portland cement, geopolymer possesses low energy consumption, less CO_2 emission, high early strength, less shrinkage, low permeability, good fire and acid resistance and excellent durability [1-10]. These merits make geopolymer exhibit promising potentials in the fields of civil, bridge, pavement, hydraulic, underground and militia engineering [11].

Compared to the PS and PSS types, PSDS Geopolymeric shows some advantages over the other two types such as easy operation, high strength, and strong bond to a concrete or steel substrate, excellent fire and high temperature resistance. The merits make Na-PSDS Geopolymeric have an excellent potentials for use in applications where exposure to high temperatures or fire is a concern, such as bridge, underground, tunnel and military engineering. However, a fully-reacted PSDS Geopolymeric matrix is not investigated systematically before. The microstructure of the fully-reacted PSDS Geopolymeric matrix is also quantitatively characterized. All these seriously influence the commercial application of PSDS geopolymeric cement.

In this study, a fully-reacted Na-PSDS Geopolymeric matrix is attempted to prepare at room temperature by optimizing the three key molar ratios: SiO_2/Al_2O_3, Na_2O/Al_2O_3, H_2O/Na_2O. The compressive strength and microstructure of the hardened Geopolymeric matrices are evaluated as a function of the three ratios. The influencing extent of each ratio on the compressive strength will be quantitatively determined on basis of the variance analysis. The microstructural changes as a function of ratios will also be investigated by using X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques. Based on the macroscopic and microscopic experiments, an almost fully reacted Na-PSDS Geopolymeric matrix with the highest strength and optimum microstructure can be obtained by properly adjusting the three molar ratios. Subsequently, the coordination status of two main construction elements (Al and Si), micrographics and chemical compositions of the fully reacted Na-PSDS Geopolymeric matrix are further characterized and examined by using Environment Scanning Electron Microscope equipped with Energy Dispersion X-ray Analysis (ESEM-EDXA), highly sensitive Magic Angle Spinning-Nuclear Magnetic Resonance Spectroscopy (MAS-NMR) techniques. Finally, a three-dimensional (3D) molecular model is proposed for the fully-reacted Na-PSDS Geopolymeric matrix based on the above microanalysis.

EXPERIMENTAL

Materials

Metakaolin used as the most mainly aluminosilicate reactive raw materials in this study is obtained by calcining pure kaolin from China Kaolin Clay Company, Su Zhou, P.R.China, at 700°C for 12 hours. The ^{27}MAS-NMR resonance spectrum of calcined kaolin i.e. metakaolin shows that 95 % or greater of 6-fold coordinated Al in the origin kaolin has been transformed into 4-fold coordinated one. The chemical compositions and physical properties of metakaolin are listed in Table 1. Analytical grade NaOH pellet and sodium silicate solution with the molar ratio of SiO_2/Na_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.

Methods

Specimens preparation for mechanical tests

In this study, NaOH, sodium 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 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 hours. The demoulded specimens are cured at 20°C and 95% R.H for 28 days. At least 6 specimens are made for each formula.

Herein it is important to point out that the pre-mix of NaOH, sodium silicate solution, rather than direct addition of NaOH pellet into Geopolymeric matrix is a key to ensure a enough long pot life to complete the above process. Otherwise, the setting and hardening process of Geopolymeric matrices become too rapid to complete the above specimen preparation.

Compressive tests

The main factors influencing the mechanical strength and microstructure of the hardened Geopolymeric matrices include the molar ratio of Si to Al in the molecular chains, the type and amount of alkaline activator, the water content, curing regime (curing temperature, curing age), and the reactivity of aluminosilicate materials [12]. In this paper, we attempt to synthesis an almost fully reacted Na-PSDS type of Geopolymeric matrix with high mechanical strength and desirable microstructure at room temperature. Metakaolin produced by calcining pure kaolin is used as the main reactive alumniosilicate resource. Silica fume is used as the silicon supplementary materal. NaOH and sodium silicate solution are used as alkaline activator. Curing regime is fixed at room temperature and 28 day of curing period. As a result, the effects of the three key molar ratios of SiO_2/Al_2O_3 (to study the effect of Si-to-Al ratio), Na_2O/Al_2O_3 (to study the effect of amount of alkaline activator), H_2O/Na_2O (to study the effect of water content) on mechanical strength and microstructure are mainly systematically investigated in this study.

At the end of the curing period, the cubic specimens are taken from the curing room and are left to air dry for 24 hours. Compressive strength testing is performed according ASTM C39-96. At least 6 samples of each formula are tested. The average value is served as the ultimate compressive strength. A closed-loop servo-hydraulically controlled materials testing machine (Sintech 10/D MTS 810) is used to conduct compressive test. The loading is displacement controlled at a constant rate of 1.3mm/min for all the compression tests. The load is monitored by a computer controlled data acquisition system so that the maximum load could be determined.

Table 1. Chemical composition and physical properties of metakaolin.

SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	MnO	K_2O	P_2O_5	L.O.I.	∑	Fineness (%)	
										+45 µm	-2 µm
53.46	43.66	0.34	0.25	0.18	0.01	0.19	0.31	1.19	99.59	≤0.3	≥60

Sample preparation for microanalysis

The fragments from different formula are collected after compressive test. Some of them are used to conduct ESEM-EDXA analysis. The others are further finely crushed, and then immersed in an ethanol for 3 days to stop the further geopolymerization reaction and subsequently oven-dried at 60°C for 6 hours to remove the physically absorbed water. After that, these hardened Geopolymeric 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 are placed in desiccators for 24 hours.

FTIR analysis

Fourier transform infrared spectroscopy (FTIR) is performed on A Bio-Rad FTS 6000 FTIR by using KBr pellet techniques (3 mg of fine powders prepared previously are homogenously grinded with 300 mg of KBr powder together until the mixture has the consistency of fine flour, and then pressed into a disk).

XRD analysis

X-ray powder diffraction is recorded on a Philips PW1830 spectrometer with the following testing parameters: 40 KV, 30 mA, CuKα Radiation. The XRD patterns are obtained by a scanning rate of 1° per min from 10° to 80° (2θ) and steps of 0.05 (2θ)°. The wavelength is selected as 15.40562 nm (Cu).

ESEM-EDXA analysis

XL30-ESEM equipped with EDXA is used to characterize the microstructure and chemical compositions of the fully reacted Na-PSDS Geopolymeric matrix. The following test parameters are employed in this study: accelerating voltage of 20 keV, pressure and relative humidity in sample chamber of 4.2 Torr and R.H. 80 % respectively.

MAS-NMR analysis

A JEOL NM-ESH40MU Nuclear Magnetic Resonance Spectroscopy (NMR) is measured using the Magic Angle Spinning technique. Samples used for MAS-NMR range in a size of about 300 mg powder. These powder samples are first placed in a cylinder capsules made with Zr ceramic, and then inserted the capsule into sample hole. The compressed air is employed to drive the spinning of the capsule by blowing its bottom. In this study, the spinning speed of the capsule is 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 spectrometer is interfaced with a computer and equipped with a MAS broad-band probe for the solid state experiments. The peaks are fitted by Gaussian lines.

Chemical shifts 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 chemical shift values are calculated by taking the midpoint of the signal at half height. The accuracy is 0.5 ppm. Typically, ^{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 1.5 s. The 27Al 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.

Mercury intrusion porosimetry measurement (MIP)

An Autopore IV 9500 MIP is used for to investigate the porosity and pore size distribution of different geopolymers. The samples with the size of approximate 10 mm × 10 mm × 10 mm are obtained by cutting up the harden geopolymer pastes at the age of 28 days. These samples are first oven-dried for 24 hours at 50°C to remove the physically absorptive water in capillary, and then are placed into the glass penetrometer with the volume of 5 cc. After that, low pressure test is performed, followed by high pressure test (the maximum mercury press reaches 30 000 psi). The intrusion and evacuation of mercury is automatically controlled by computer with Autopore IV 9500 program. The cumulative intrusion and differential pore volume vs pore diameter are also measured and recorded with an increase of the pressure. The diameters of the pores intruded by the mercury are calculated using "Washburn equation", with a mercury contact angle of 130 degree.

Experimental program

The main objective of the study is to investigate the effects of the three factors: SiO_2/Al_2O_3 (Factor A), Na_2O/Al_2O_3 (Factor B) and H_2O/Na_2O (Factor C) on mechanical strength and microstructure. The three molar ratios are varied within the following ranges respectively: $5.5 \leq SiO_2/Al_2O_3 \leq 6.5$, $0.8 \leq Na_2O/Al_2O_3 \leq 1.2$, $7.0 \leq H_2O/Na_2O \leq 10.0$. The levels for each of the factors are set at three grades (low, intermediate, and high). Thus the experimental program here is three factors experiment with three levels for each factor, as shown in Table 2. Base on the factor-level table, a total of 9 experimental formulas is designed according to a L9(34) orthogonal design principle, as shown in Table 3. The interaction effect between different factors is not taken into account in the experimental arrangement.

RESULTS AND DISCUSSION

Table 2. Factor-levels of Na-PSDS geopolymeric cement matrices.

Factors Levels	A (SiO_2/Al_2O_3)	B (Na_2O/Al_2O_3)	C (H_2O/Na_2O)
1	5.5	0.8	8.5
2	6.0	1.0	7.0
3	6.5	1.2	10

Preparation of the fully reacted Na-PSDS Geopolymeric matrix

The compressive strength of 9 different Na-PSDS geopomymeric cement matrices are given in Table 3. The effects of the three molar ratios (SiO_2/Al_2O_3, Na_2O/Al_2O_3, H_2O/Na_2O) are quantitatively determined by using the gradation analysis and variance analysis. Subsequently XRD and IR analysis of each Geopolymeric formula is also conducted. On basis of the macroscale and microscale results, an almost fully reacted Na-PSDS Geopolymeric matrix with the highest compressive strength and optimum microstructure can be obtained by properly selecting the three molar ratios.

Compressive tests

In order to determine the influencing extent of the three molar ratios (SiO_2/Al_2O_3, Na_2O/Al_2O_3, H_2O/Na_2O) and the optimum mixture proportion of Na-PSDS Geopolymeric matrix, the gradation analysis is first employed. The analysis is illustrated in tabular form in order that it can be clearly understood, as shown in Table 3. It can be seen from Table 3 that Na_2O/Al_2O_3 and H_2O/Na_2O show very important impact on the compressive strength of the harden Geopolymeric matrices among the three molar ratios. The corresponding gradation ranges are 16.7 and 16.2, respectively. Comparatively, SiO_2/Al_2O_3 has little influence on the compressive strength, whose gradation range is 9.5. Carefully comparing the difference among $\bar{I}_1$, $\overline{II}_2$, $\overline{III}_3$ shows that the hardened Geopolymeric matrix has the highest compressive strength at $SiO_2/Al_2O_3 = 5.5$, $Na_2O/Al_2O_3 = 1.0$, $H_2O/Na_2O = 7.0$.

The significance and influencing extent of the three molar ratios on compressive strength can be easily observed through the above simple gradation analysis. However, it is well known that the gradation analysis cannot quantitatively distinguish whether the compressive strength difference among different levels is caused by testing errors or by different level in the case of the same factor. In order to solve the problem, variance analysis is employed in the following studies. Table 4 gives the variances analysis of different factors involving in the synthesis of Na-PSDS Geopolymeric matrices.

Careful observation of Table 4 shows that the sum of square of S_{erro} is close to S_A. This means that the difference of experimental results among different levels of the factor C_A probably caused by the testing error, rather than by the factor's difference. Therefore, the sum of square of factor A can sum up to error term, i.e. $S_{collect} = (S_A + S_{erro})$. The observed mean squares (S_B and S_C) are to be tested against the error mean square ($S_{collect}/4 = 78.1$) with 4 degrees of freedom (df). The proper test statistic is the *F* statistic with 2 and 4 df. At the 25 %

Table 4. Variance analysis table of Na-PSDS geopolymeric cement matrices.

Source of variation	Sum of square	Degrees of freedom	Mean square	F ratio	Significance
S_A	143.0	2			
S_B	420.0	2	210.0	2.67	*(F0.25)
S_C	399.1	2	199.6	2.62	*(F0.25)
S_{ero}	169.3	2			
$S_{collect}$	312.3	4	78.1		
S_{tol}	976.4	8			

* *The asterisk indicates significance at the 25 percent level. This notation will be used throughout this paper.*

Table 3. The experimental program and the compressive strength of Na-PSDS geopolymeric cement matrices.

No.		SiO_2/Al_2O_3	Na_2O/Al_2O_3	H_2O/Na_2O	Compressive strength (MPa)
Na-PSDS1		1(5.5)	1(0.8)	1(8.5)	6.0
Na-PSDS2		1(5.5)	2(1.0)	2(7.0)	34.9
Na-PSDS3		1(5.5)	3(1.2)	3(10.0)	0.8
Na-PSDS4		2(6.0)	1(0.8)	2(7.0)	5.4
Na-PSDS5		2(6.0)	2(1.0)	3(10.0)	13.6
Na-PSDS6		2(6.0)	3(1.2)	1(8.5)	13.9
Na-PSDS7		3(6.5)	1(0.8)	3(10.0)	8.6
Na-PSDS8		3(6.5)	2(1.0)	1(8.5)	21.7
Na-PSDS9		3(6.5)	3(1.2)	2(7.0)	31.2
Gradation analysis	I_1	41.7	20.0	41.6	
	II_2	32.9	70.2	71.5	
	III_3	61.5	45.9	23	
	$\bar{I}_1$	13.9	6.7	13.9	
	$\overline{II}_2$	11.0	23.4	23.8	
	$\overline{III}_3$	20.5	15.3	7.7	
	Range	9.5	16.7	16.2	

significance level ($\alpha = 0.25$) the critical region of F is $F \geq 2.0$, which is usually taken as the upper tail of the F distribution, rejecting H_0 if $F \geq F_{1-\alpha}$ where α is the area above $F_{1-\alpha}$. A significant F will indicate that the difference between the factor and testing error has something in it besides the estimate of variance. It probably implies that there is a real difference in the means, and H_0 should be rejected.

Comparing each mean square with the error mean square (S_{collect}) indicates that Factor B and Factor C, i.e. the molar ratio of Na_2O/Al_2O_3 and H_2O/Na_2O have considerable impacts on the compressive strength of the hardened Geopolymeric matrix at $\alpha = 0.25$, while the effects of other factors such as SiO_2/Al_2O_3 is negligible. A comparison of the values of $\bar{I}_1$, $\overline{II}_2$ and $\overline{III}_3$ for Factor B and Factor C shows that the compressive strength reaches the highest when selecting the intermediate level. The Geopolymeric matrix made with $Na_2O/Al_2O_3 = 1.0$, $H_2O/Na_2O = 7.0$ has the highest compressive strength. Considering that there is little effect of Factor A, $SiO_2/$ $/Al_2O_3 = 5.5$ are selected in order to reduce the amount of expensive silica fume in this study. The optimum mixture proportions determined according to the variance analysis is approximately consistent with that according to the gradation analysis. The conclusion induced by the variance analysis can be used as “feedback” to design a better experiment.

As a results, the optimum mixture of Na-PSDS Geopolymeric matrix is made on the basis of compressive strength with $SiO_2/Al_2O_3 = 5.5$, $Na_2O/Al_2O_3 = 1.0$ and $H_2O/Na_2O = 7.0$, i.e Formula Na-PSDS2.

FTIR analysis

The above mechanical test shows that the compressive strength of the hardened Geopolymeric matrices made with different mixture proportions has a considerable difference. In order to elucidate in a microscopic scale the difference of the compressive strength for different formula mentioned above (Na-PSDS1 to Na-PSDS9), FTIR technique is employed to characterize the microstructure of these hardened Geopolymeric pastes.

The IR spectra of various Geopolymeric matrices are presented in Figure 1. The chemical shifts of main IR bands and corresponding species are determined based on the references [13,14]. By carefully comparing these IR spectra, the following phenomena can be observed:

1) The strong band at 1086 cm^{-1} shifted towards the low wavenumber after geopolymerization reaction. The chemical shift is approximately 78 cm^{-1}. This demonstrates that an obvious change in the microstructure takes place during hydration reaction, resulting in a formation of new products with different microstructure from metakaolin. Similar results are also seen in the XRD spectra, as shown in Figure 2. According to the references [13,14], 1086 cm^{-1} peak is caused by symmetrical vibration of Si–O bond. The large shift toward the low wavenumber may be attributed to the partial replacement of SiO_4 tetrahedron by AlO_4 tetrahedron, resulting in a change in the local chemical environment of Si–O bond. In addition, This band at 1006 cm^{-1} is very strong but a lack of sharp feature is a indicative of the general disorder in the Si(Al)–O– network, reflecting the wide distribution of the SiQ^n (mAl) units in the polymeric molecular chains of Geopolymeric products. 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 second coordination sphere of silicon.

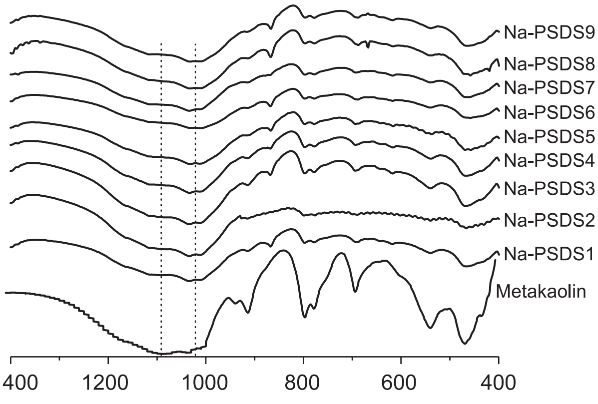


Figure 1. IR spectra of Na-PSDS geoopolymer with different mixture proportions.

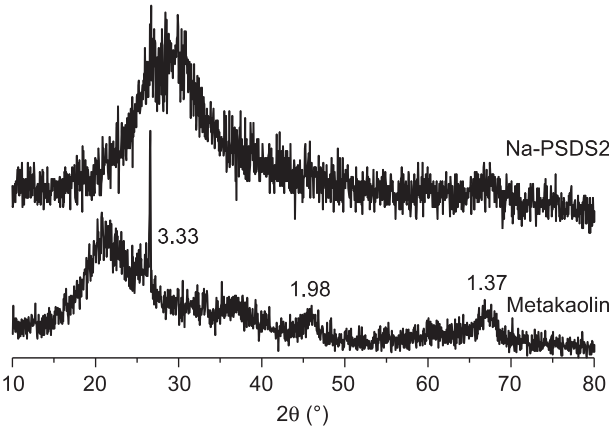


Figure 2. XRD spectra of Metakaolin and Na-PSDS2 geopolymeric cement products.

In general, if there is no aluminum atom in the second coordination sphere of silicon, the notation becomes SiQ^n (nSi). The stretching modes of the Si–O bonds of the SiQn units are IR active in the 850-1200 cm^{-1} region with the absorption bands of the SiQ^n unit with n = 4, 3, 2, 1, 0 centered at around 1200, 1100, 950, 900, and 850 cm^{-1}, respectively [15]. These values shifts to lower wave-numbers when the degree of silicon substitution by aluminum in the second coordination sphere increases, as a consequence of the weaker Al–O bond.

2) The intensities of the bands at 914 and 798 cm^{-1} in IR spectrum of metakaolin cause by 6 fold coordinated Al(VI)–OH stretching vibration and 6 coordinated Al(VI)–O stretching vibration, respectively, are considerably reduced or disappeared after geopolymerization reaction of Geopolymeric. In addition, a similar trend is also found for the Si–O symmetrically stretching band at about 697 cm^{-1}. This shows that 6-coordinated Al(VI) maybe changes into 4-coordinated one, and participate in the framework structure of Geopolymeric products during the process of hydration reaction.
3) A weak band at around 840 cm^{-1} can be observed in some geopolymeric mixtures. The band cannot be found in the IR spectrum of metakaolin. The new band is assigned to the bending vibration of Si–OH. This can be caused by some bond breakage sites in the network structure of Geopolymeric products for some Geopolymeric mixtures. The existence of Si–OH will cause a decrease in the degree of condensation, thus a reduction in mechanical strength.

Based on the above analysis of IR spectra, we can conclude that during geopolymerizaiton reaction of Geopolymeric, SiO_4 and AlO_4 tetrahedaron will be released from the surface of metakaolin particles under the attack of strongly alkaline solution. The VI coordination of Al is changed to IV coordination. As the dissolution proceeds, more and more SiO_4 and AlO_4 tetrahedarons go into the alkaline solution. After undergoing structural reorientation to a certain extent, the SiO_4 and AlO_4 tetrahedarons will produce polycondensation reaction, thus a formation of Geopolymeric products with a framework structure. It is the bonding of AlO_4 (IV) with SiO_4 that causes the great changes in the original Si–O chemical environment, resulting in different chemical shifts, reduction or disappearance of some characteristic bands in IR spectra. When the mixture proportion of Geopolymeric matrix is not designed properly, incomplete poycondensation reaction will occur, thus some bond breakage in the framework structure. The breakage bonds will be saturated by OH. As a result, the Si–OH bending band at 840 cm^{-1} will appear in some Geopolymeric formulas such as Na-PSDS1, Na-PSDS3, Na-PSDS4, Na-PSDS5, Na-PSDS6, Na-PSDS8 and Na-PSDS9. From Figure 1, it is clear that Na-PSDS2 has a prominent band at 1006 cm^{-1}, which is the characteristic band of Na-PSDS Geopolymeric products. The Si–OH bending band at 840 cm^{-1} can not be seen. Thus, it is reasonable to assume that Na-PSDS2 is the optimum one among the 9 formulas. The hydration degree of Na-PSDS2 is the largest and the compressive strength is also the highest.

The above macroscopic and microscopic experimental results reveal that an almost fully reacted Na-PSDS Geopolymeric matrix can obtain when the molar ratio $SiO_2/Al_2O_3 = 5.5$, $Na_2O/Al_2O_3 = 1.0$ and $H_2O/Na_2O = 7.0$, i.e formula Na-PSDS2. Na_2O/Al_2O_3 and H_2O/Na_2O have very important influences on strength gain and desirable microstructure of Na-PSDS Geopolymeric matrix. Comparatively SiO_2/Al_2O_3 exhibits little impact. However, the sodium content is used to satisfy the charge-balance requirements within the structure, without proving an excess which can form sodium carbonate and may destroy the polycondensation process. The water content for a critical polycondensation reaction is less obvious. Whereas it is clearly necessary to provide sufficient water to facilitate initial mixing and act as a carrier for ionic transport. The excess water maybe dilutes the polycondensation reaction or leaches more soluble components and transports them away from the reaction zone.

Microstructural characteristics of the fully reacted Na-PSDS Geopolymeric matrix

XRD analysis

It is seen from Figure 2 that there is a large diffuse halo peak at about 20-40°($2\theta_{max}CuK_{\alpha}$) in X-ray diffractogram of the fully reacted Na-PSDS Geopolymeric matrix, i.e. formula Na-PSDS2. This indicates that Na-PSDS Geopolymeric products are mainly X-ray amorphous materials consisting of randomly developed Si–Al polytetrahedra with a lack of periodically repeating Si–Al atomic ordering. In addition, several sharp peaks (3.33 Å, 1.98 Å, 1.37 Å) are also seen from Figure 2. According to the XRD-pattern, these sharp peaks are identified as quartz. With respect to X-ray diffractogram of metakaolin, quartz is an impurity in the metakaolin.

ESEM-EDXA

Figure 3 shows ESEM micrograph of the hardened

Table 5. Main resonance models and their relative proportions in ^{29}Si MAS-NMR spectrum of Na-PSDS geopolymeric cement matrix.

Resonance models	$SiQ^4(3Al)$	$SiQ^4(2Al)$	$SiQ^4(4Si)$
Resonance shifts (ppm)	-84.5	-90.8	-102.6
Areas of resonance	88.3	968.5	125.8
Relative Proportions (%)	7.47	81.9	10.64

Na-PSDS2 Geopolymeric matrix. It can be clearly seen that the microstructure of Geopolymeric products is sponge-like. No crystal with regular shape is observed in the bulk Geopolymeric matrix.

EDXA is also performed on the whole region shown in the above ESEM micrograph to determine its chemical composition after polycondensation reaction. Great cautions should be taken due to the large volume of the electronic interacting sphere at 20 kV accelerating voltage. The oxide molar ratios of SiO_2/Al_2O_3, $Na_2O/$ $/Al_2O_3$ are 6.28, 1.07, respectively, which are close to the theoretical values of Na-PSDS geopolymeric matrix ($SiO_2/Al_2O_3 = 6.0$, $Na_2O/Al_2O_3 = 1.0$).

In addition, x-ray mappings of three types of main elements (Na, Si and Al) of Na-PSDS Geopolymeric matrix are also collected and displayed in Figure 4. It can be seen from Figure 4 that Na, Si and Al are uniformly distributed across the bulk paste. This means that the sponge-like Geopolymeric products are generated evenly homogeneously during the whole process of hydration.

MAS-NMR analysis

Magic-angle spinning MAS-NMR spectroscopy can provide useful structural data for aluminosilicates (zeolites, clays, ceramics, Portland cements, Geopolymeric et.al). In particular ^{29}Si and ^{27}Al MAS-NMR studies represent a very powerful tool [16].

27Al MAS-NMR

Earlier investigations [17-19] 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 $[Al(H_2O)_6]^{3+}$.

The ^{27}Al MAS-NMR spectroscopy of the fully reacted Na-PSDS Geopolymeric matrix is shown in Figure 5. 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 the reference [2]. In addition to the resonance at 40 ppm, a small resonance at -15.6 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 Na-PSDS 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 can-

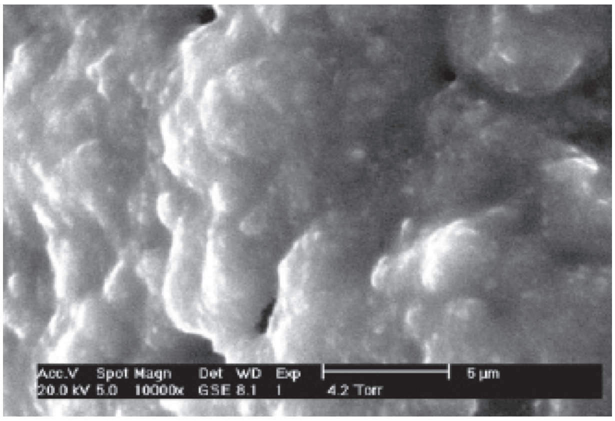
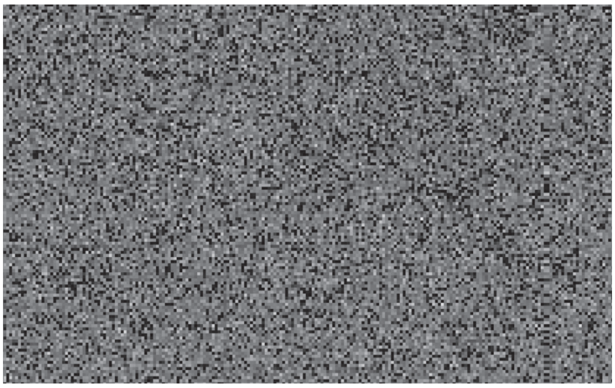


Figure 3. ESEM micrograph of Na-PSDS geopolymeric cement matrix.


Na


Si

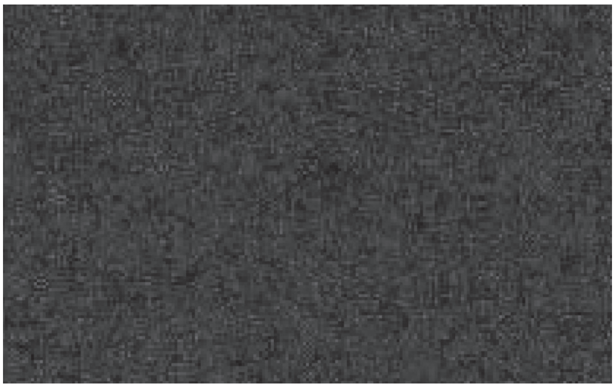

Al

Figure 4. Mapping of three types of elements (Na, Si, Al) of Na-PSDS geopolymeric cement matrix.

not differentiate the various molecular configurations proposed for Geopolymeric: 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. Therefore the combination of the ^{27}Al MAS-NMR and ^{29}Si MAS-NMR spectra make it possible to better understand the structure nature of Na-PSDS.

^{29}Si MAS-NMR

^{29}Si MAS-NMR spectrum of Na-PSDS Geopolymeric matrix is illustrated in Figure 6. It can be seen that Na-PSDS gives a broad resonance in the range of -70ppm to -110ppm associated with a strong resonances at -84.5 ppm, a very strong resonance at -90.8 ppm and two small resonances at -76.8 ppm and -102.6 ppm. Broad resonances are generally found in zeolitic gels before crystallization of the zeolites. The ^{29}Si broad resonances indicate that the Si and Al tetrahedras in Na-PSDS Geopolymeric matrix are not regularly ordered along the polymeric chains.

A previous study has shown that the chemical shift of ^{29}Si in an amorphous or highly disordered state as geopolymer would be increase by approximately 5 ppm when comparing with the zeolite with the same chemical compositions [1,20]. The three main resonances in ^{29}Si MAS-NMR spectrum of Na-PSDS Geopolymeric matrix, namely -84.5 ppm, -90.8 ppm and -102.6 ppm, corresponding to the ordered ^{29}Si chemical shifts of -89.5 ppm, -95.8 ppm, -107.6 ppm in zeolite, can be assigned to SiQ^4(3Al), SiQ^4(2Al) and SiQ^4(4Si) units, respectively [20].

MIP measurement

Figure 7 gives the cumulative intrusion of hardened Na-PSDS geopolymeric matrix. As can be see that the cumulative pore volume with pore diameter smaller than 1000 nm accounts for 75 % of the total porosity. The total porosity is also very low, only 5.0 %. This indicates that the microstructure of Na-PSDS geopolymeric matrix is very dense. The result is good agreement with above ESEM observations.

MOLECULAR STRUCTURAL MODEL OF Na-PSDS GEOPOLYMERIC MATRIX

On basis of the previous XRD, FTIR, ESEM-EDXA, and MAS-NMR spectra, it can be observed that the fully reacted Na-PSDS Geopolymeric paste shows structural characteristics similar to glassy or gel substances in having a wide range of Si endowments, but predominantly the network molecular chains of Si partially replaced by 4-coordinated Al tetrahedral, i.e. SiQ^4(3Al), SiQ^4(2Al) and SiQ^4(4Si).

It can be seen from Figure 6 that the broad resonance in range of -70 ppm to -110 ppm of ^{29}Si MAS-NMR spectrum is mainly composed of three SiQ^4(mAl) units: SiQ^4(3Al), SiQ^4(2Al) and SiQ^4(4Si). However, the three resonances assigned to the three different SiQ^4(mAl) units are so close that the interaction between resonances occurs, resulting in a lack of spectral resolution. In order to address it, Gaussian peak deconveolution is adopted in this study to separate and quantify SiQ^4(mAl) units, as shown in Figure 6. Quantification of network ordering may allowed to establish the molecular model for describing speciation of silicon according to the types and relative proportions of SiQ^4(mAl) units.

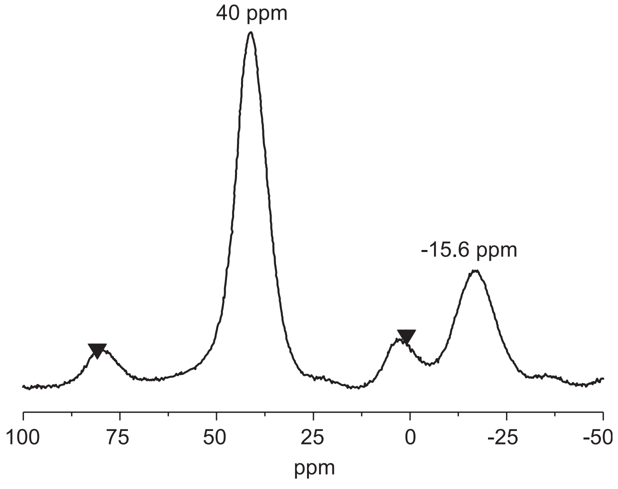


Figure 5. ^{27}Al MAS-NMR spectra of Na-PSDS geopolymeric cement paste (Resonance corresponding ▼ is caused by spinning sidebands effect).

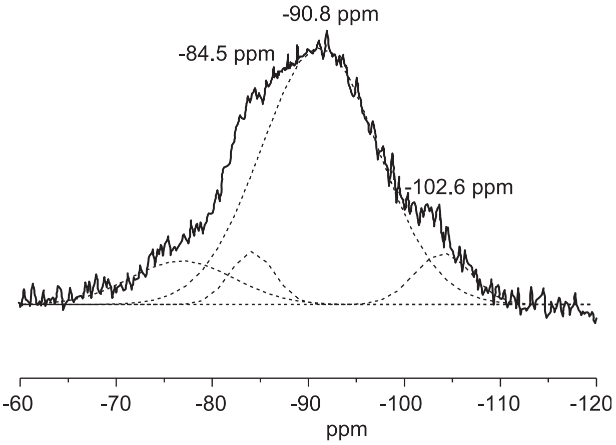


Figure 6. ^{29}Si MAS-NMR spectrum and the corresponding deconvelution spectra of Na-PSDS geopolymeric cement paste (Heavy line is the experimental spectrum, and dotted lines is the deconvelution spectra).

According to the types of SiQ^4(mAl) units and their relative proportions, we can calculate the molar ratio of Si: Al using Equation (1) proposed in literature [21]. The ratio of Si: Al equal to 2.85 for Na-PSDS synthesized in this study, which is approximate to the theoretical value of Na-PSDS Geopolymeric matrix (Si: Al = 3.0: 1).

$$Si/Al = \sum_{m=0}^{4} I_{Si(mAl)} / \sum_{m=0}^{4} \frac{m}{4} I_{Si(mAl)} \qquad (1)$$

where, $I_{\mathrm{Si(mAl)}}$ is the intensity of each peak in the deconveluted ^{29}Si MAS-NMR spectra.

Some studies [12] proposed that structural configuration of Na-PSDS Geopolymeric matrix was similar to that of orthose. One novel molecular structural model of Na-PSDS Geopolymeric matrix is proposed based on the structural configuration of orthose, as shown in Figure 8. The model is different from the structural models of Na-PSDS Geopolymeric matrix established by J. Davidovits and Valeria F. F. respectively [12,13]. In the proposed model, SiO_4 and AlO_4 tetrahedras are so arranged that the types and relative proportions of the main SiQ^4(mAl) units are statistically consistent with the decomposed results of ^{29}Si MAS-NMR spectrum and the molar ratio of Si: Al (2.85). And all Al atoms are 4-coordination and have Si nearest neighbors.

CONCLUSIONS

In this paper, three key parameters SiO_2/Al_2O_3, Na_2O/Al_2O_3, H_2O/Na_2O influencing the synthesization of Na-PSDS Geopolymeric matrix at room temperature are systematically investigated. A total of 9 Na-PSDS Geopolymeric matrices with different SiO_2/Al_2O_3, Na_2O/Al_2O_3, H_2O/Na_2O is designated to investigate the effects of the three parameters on mechanical strength and microstructure in accordance with orthogonal design principle. The gradation and variance analysis on experimental results shows that SiO_2/Al_2O_3 has a significant impact on compressive strength. The highest compressive strength (34.9MPa) can be achieved when $SiO_2/Al_2O_3 = 5.5$, $Na_2O/Al_2O_3 = 1.0$ and $H_2O/Na_2O = 7.0$. The corresponding microstructure is also proved to be the optimum one amongst the 9 Geopolymeric mixtures according to IR spectra. As a result, the above mixture is regarded as a fully reacted Na-PSDS Geopolymeric matrix.

Subsequently XRD, ESEM-EDXA, DSC-TG, and MAS-NMR techniques are employed to further characterize the microstructure of the fully reacted Geopolymeric matrix. The microscopic analysis shows that the fully reacted Na-PSDS Geopolymeric matrix possesses structural characteristics similar to gel substances in having a wide range of Si endowments, but predominantly the framework molecular chains of Si partially replaced by 4-coordinated Al tetrahedral. A 3D molecular structural model is also proposed based on the decomposition of ^{29}Si MAS-NMR spectrum of the fully reacted Na-PSDS Geopolymeric matrix synthesized from the optimum mixture proportion.

Acknowledgement

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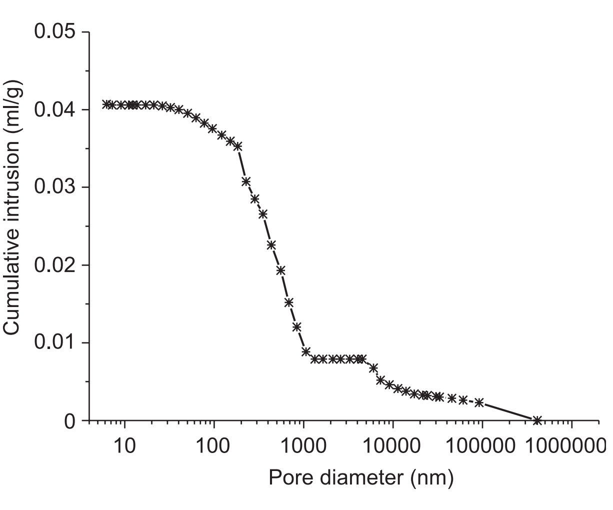

Figure 7. Mercury intrusion curves of Na-PSDS geopolymeric matrix.

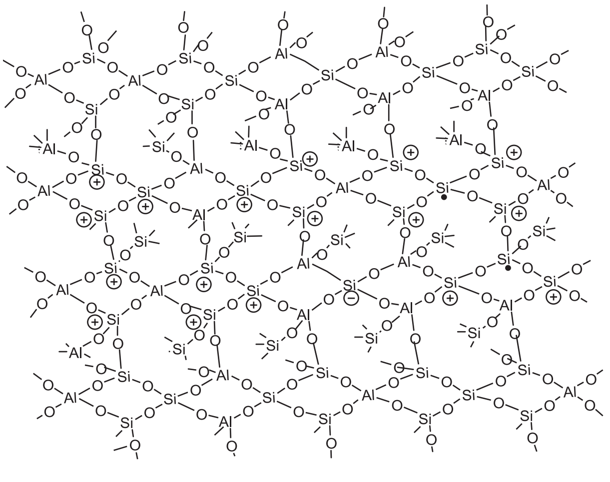

Figure 8. Molecular structure model of fully reacted Na-PSDS geopolymeric cement matrix.

References

1. Davidovits J.: J.Therm.Anal. *35*, 429 (1989).
2. Davidovits J. in: Proceedings of the First European Conference on Soft Mineralogy, p.25-48, Ed. Davidovits J., Orlinsl J., The Geopolymer Institute, France 1988.
3. Davidovits J., Comrie D. C., Paterson J. H., Ritcey D. J.: Concr. Int.: Design & Constr. *12*, 30 (1990).
4. Duxson P., Provis J. L., Lukey G. C.: Cem.Concr.Res. *37*, 1590 (2007).
5. Hongling W., Haihong L. and Fengyuan Y.: Colloid. Surf. A *268*, 1 (2005).
6. Nowak R: The New Sci. *197*, 28 (2008).
7. Sofi M., van Deventer J. S. J., Mendis P. A.: Cem.Concr. Res. *37*, 251 (2007).
8. Van Jaarsveld J. G. S., Van Deventer J. S. J.: Miner.Eng. *10*, 659 (1997).
9. Bakharev T.: Cem.Concr.Res. *35*, 658 (2005).
10. Lyon R. E., Foden A., Balaguru P. N., Davidovits M., Davidovits J.: J. Fire and Mater. *21*, 67 (1997).
11. Davidovits J. in: *Concrete technology, past, present, and future*, p. 383-397, Ed. Mehta P. K., American Concrete Institute, U.S.A. 1994.
12. Davidovits J. in: *Proceedings of Geopolymere '99*, p.9-40, Ed. Davidovits J., Davidovits R., James C., Institute Geopolymer, France 1999.
13. Barbosa V. F. F., MacKenzie K. J. D., Thaumaturgo C.: Int. J. Inorg. Mater. *2*, 309 (2000).
14. Akolekar D., Chaffee A., Russell F. H.: Zeolites *19*, 356 (1997).
15. Van Jaarsveld J. G. S., Van Deventer J. S. J., Schwartzman A.: Miner. Eng. *12*, 75 (1999).
16. Engelhardt G., Fahlke B., Mngi M., Lippmaa E.: Zeolites *3*, 239 (1983).
17. Pu W., Zhaolu P., Lingbao W.: *Mineralogy*, p. 260-265, China Geological Press, Beijing 1984.
18. Juxson P., Provis J. L., Lukey G. C., Separovic F., Van Deventer J. S. J.: Langmuir *21*, 3028 (2005).
19. Davidovits J.: J. Mater. Educ. *16*, 91 (1994).
20. Engelhardt G., Michel D.: *High-resolution solid-state NMR of silicates and zeolites*, p.182, Wiley, New York 1987.
21. Duxson P., Provis J. L., Lukey G. C., Separovic F., van Deventer J. S. J.: Langmuir *21*, 3028 (2005).