The role of active silica and alumina in geopolymerization

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Abstract:

In this study, the alkaline solutions (NaOH) with concentrations from 1M to 18M, red mud (RM) and silica fume (SF) were used as reactors in geopolymer reactions. RM contains 7.40% SiO_2 and 13.65% Al_2O_3 and SF has 94.50% SiO_2, but only the active oxides can participate in the geopolymer reactions. The activity of the oxides was investigated by determining the compressive strength of the samples under different curing conditions. The characteristics of the geopolymer samples were determined by using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermo-gravimetric analysis (TGA)/differential thermal analysis (DTA) and nuclear magnetic resonance analysis (NMR). The experimental results indicate that active silica mainly exists in SF. In the structure of geopolymers, the silicon can bond directly with each other (Si-Si) or be linked through 'bridging' oxygen (Si-O-Si) to form independent polymer chains, while aluminium atoms can only replace the silicon atoms in Si-O-Si polymer chains to form Si-O-Al instead.

Keywords: active silica, alumina, geopolymer, red mud, silica fume.

Classification number: 2.3

Introduction

Geopolymer is an inorganic polymer with structural units of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedrons [1]. The principle of the process is the formation of a polymer from the reaction of an alkaline solution (NaOH, KOH, Na_2SiO_3 and K_2SiO_3 solutions) with alumino-silicate resources [2, 3]. The structure of the geopolymer is a bonding of amorphous or semi-crystalline metal oxides with an alkaline element [4]. Therefore, raw materials for synthesising the geopolymer must contain major components of silicon dioxide, aluminium oxide and other oxides in amorphous and semi-crystalline forms. Crystal phases are inert, unreacted and not participated in geopolymer fabrication [5, 6]. The structures of the geopolymer are chains of -Si-O-Al-O- [7]. The mechanical properties of the geopolymer are influenced by the microstructure of the geopolymer.

The microstructure of the geopolymer is amorphous or semi-crystalline with three-dimensional structures based on tetrahedrons sharing oxygen atoms of the $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ molecular, which may exist in the poly-sialate form (Si:Al=2), the poly sialate disiloxo (-Si-O-Al-O) Al-O-Si-O-Si-O) (Si:Al=3) and other ratio sialate linkages (Si:Al>3). The sialate is an abbreviation for silicon-oxo-alumina [4].

The process of geopolymerization has 2 stages. The first stage is the synthesis of the geopolymer and the second stage is the polymeration of original materials with different alkaline activators. The alkali activation process of aluminosilicate is a complex process and has not been clearly explained yet [8, 9]. The major step of the geopolymer synthesis can be explained in the following stages [10, 11]:

- Extraction of active SiO_2 and Al_2O_3 in aluminosilicates by using the alkali hydroxide.

- Formation of tetrahedrons monomers.

- Formation of inorganic geopolymer structures by

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monomers condensation reaction.

Geopolymerization will begin with the breakdown of the bonding Si-O-Si and then, Al atom will replace silicon atom in Si-O-Si bonding to form aluminosilicate gel with extremely large molecules [12]. This geopolymer process occurs in alkali solution. The inorganic polymer network consists of 3-dimensional aluminosilicate. In particular, the negative charge of Al in tetrahedron monomerons $[AlO_4]^{5-}$ will bond with the positive alkali ions such as Na^+ and K^+.

Geopolymers comprise the following molecular units (or chemical groups) that are presently studied and implemented in several industrial developments [13].

- Si-O-Si- siloxo, poly(siloxo).

- Si-O-Al-O- sialate, poly (sialate).

- Si-O-Al-O-Si-O- sialate siloxo, poly (sialate siloxo).

- Si-O-Al-O-Si-O-Si-O- sialate disiloxo, poly (sialate disiloxo).

- (R)-Si-O-Si-O-(R) organo siloxo, poly silicone.

- Al-O-P-O- alumino phospho, poly (alumino phospho).

- Fe-O-Si-O-Al-O-Si-O- ferro sialate, poly (ferro sialate).

Hence, any material containing amorphous oxides of silicon and aluminum such as red mud, fly ash, slag, silica fume can be used as a geopolymer material source [14].

RM is the solid waste in the manufacturing process of aluminum oxide by Bayer's technology. It contains excess sodium hydroxide (NaOH) and heavy metals that may cause many negative influences on human health and environment pollution. Thus, RM must be treated and disposed of in accordance with the regulations for hazardous waste management. The main components of RM are Fe_2O_3, SiO_2, Al_2O_3 and excess NaOH, which can be used as the material for the geopolymerization process. Furthermore, SF is also a solid waste in the metallurgical process. Silica fume has extremely fine particle size ranging from 0.1 μm to a few μm with a mean diameter of 1.5 μm. Fumed silica is mainly amorphous and hence, it is an auspicious material for geopolymerization. However, the geopolymer reactivity, physical and mechanical properties of the geopolymer products are influenced by the content of active SiO_2 and Al_2O_3 in RM and SF. The content of active SiO_2 and Al_2O_3 in RM and SF were evaluated by the amount of oxides dissolving in NaOH solutions of 1M to 15M at 80°C for 24 hours. The results showed that RM contains 4.76% active Al_2O_3 but does not contain active SiO_2 and SF contains 90.32% active SiO_2.

In this study, the geopolymer samples from RM were prepared by mixing the NaOH solution of 1M to 18M with RM in the NaOH/RM ratio of 0.4/1 (by weight). The samples were maintained at 60, 90, 120, 150, 180 and 210°C for 10 hours. Geopolymers' samples from SF were prepared by mixing the NaOH solution of 1M to 18M with SF in the NaOH/SF ratio of 0.2/1. The samples were pressed and maintained at room temperature.

The results of the microstructural analysis indicate that Si-Si and Si-O-Si bonds were formed to form independent polymer chains in the geopolymer samples. In the polymerization process, the Al atom can replace the Si atom in the polymer chain Si-O-Si to form Si-O-Al. For sufficient mechanical strength, active SiO_2 should be added to the geopolymer samples from RM; the samples from SF don't need added active oxides.

Experimental process

Materials

- RM from Tan Rai's Alumina Plant, Lam Dong Alumina Company in Vietnam.

- Silica fume (SF): Use 940U silica by Elkem Silicon Materials.

- Anhydrous NaOH: Bien Hoa Chemical Plant, Dong Nai Province in Vietnam.

Experimental process

Determination of active SiO_2 and Al_2O_3:

RM and SF were dried at 105 to 110°C to constant mass. About 2.5 g of the test sample (RM or SF) was put into a stainless-steel flask and then 25 ml of NaOH in varying concentrations (1 to 15M) were added. This was gently shaken several times, then cover with a lid and put in the oven at 80±2°C. After 24 hours, the kettle was stabilised at room temperature and the solution was filtered. The contents of silica and alumina dissolved in the solution were determined.

Experiment:

RM and SF were dried at 105 to 110°C to constant mass and sieved through a sieve of 0.08 mm.

The samples from RM were prepared by mixing RM with NaOH solution of 1M to 18M in the NaOH/RM ratio of 0.40/1 (by weight). The samples were formed in a stainless steel mold, pressed at 72 KN (10 N/mm²) and had sizes of 90x80x40 mm. Then, the samples were removed from the mold immediately. The size of the samples conforms to TCVN 6477:2016. The samples were heated at 60°C

to 210°C for 2h, 4h, 6h, 8h and 10h. They were cured at room temperature for 28 days and then, were subjected to compressive strength testing.

The samples from SF were prepared by mixing SF with NaOH solution of 1M to 10M in the NaOH/SF ratio of 0.20 (by weight) (Table 1). Samples were prepared by semi-dry pressing at 72 KN (10 N/mm²) in a mold with sizes of 90x80x40 mm. Then, they were removed from the mold immediately. The size of the samples conforms to TCVN 6477:2016. The samples were cured at room temperature for 28 days and then, were subjected to compressive strength and softening-coefficient. Some samples were selected to analyse the microstructure by using the methods of XRD, DTA-TG and NMR.

Table 1. Mixture proportion of geopolymer synthesis from SF and NaOH solution.

Sample	Ratio NaOH/SF	NaOH (M)
SF-Na1M	0.2	1
SF-Na2M	0.2	2
SF-Na3M	0.2	3
SF-Na4M	0.2	4
SF-Na5M	0.2	5
SF-Na6M	0.2	6
SF-Na7M	0.2	7
SF-Na8M	0.2	8
SF-Na9M	0.2	9
SF-Na10M	0.2	10

Results and discussion

Characteristics of the raw materials

The chemical compositions of RM and SF were determined by the XRF method, and the results are shown in Table 2. We can see that the silica content of SF is high, about 94.50% SiO_2. Additionally, the results in Table 2 shows that RM has a high L.O.I (loss on ignition) of about 12.50%, while SF has 2.74%.

The mineral composition of RM and SF were determined by using XRD and XRD patterns, which are shown in Fig. 1. The average particle size of RM was 9.5 μm by using the laser diffraction method.

Table 2. Composition of the materials.

Name	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	L.O.I
RM (%)	7.40	13.65	56.05	3.63	12.50
SF (%)	94.5	0	0	0	2.74

C - Cristobalite SiO_2
Go - Goethite: FeOOH
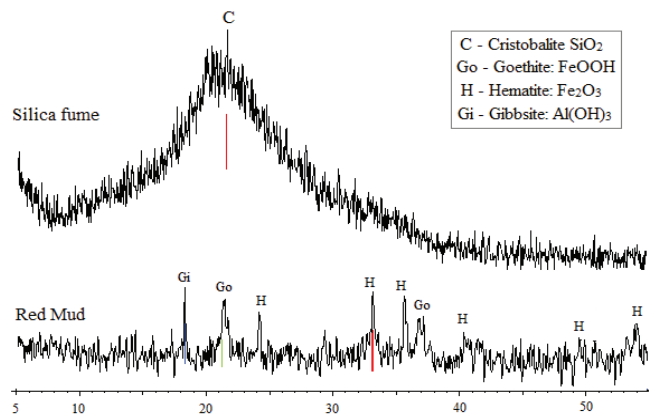H - Hematite: Fe_2O_3
Gi - Gibbsite: $Al(OH)_3$

Fig. 1. XRD spectrum of the material.

Mineral compositions of RM are Goethite (FeOOH) 21%, Hematite (Fe_2O_3) 14% and Gibbsite ($Al(OH)_3$) 5%. The amorphous phase is 60%. The amorphous phase of SF is extremely high, about 99% SiO_2. The main crystal phase is cristobalite (SiO_2), and its content is extremely low.

The results of DTA of RM and SF are shown in Fig. 2 and Fig. 3. That was performed from room temperature up to 1,000°C (heating rate 5°C/min) (Fig. 3).
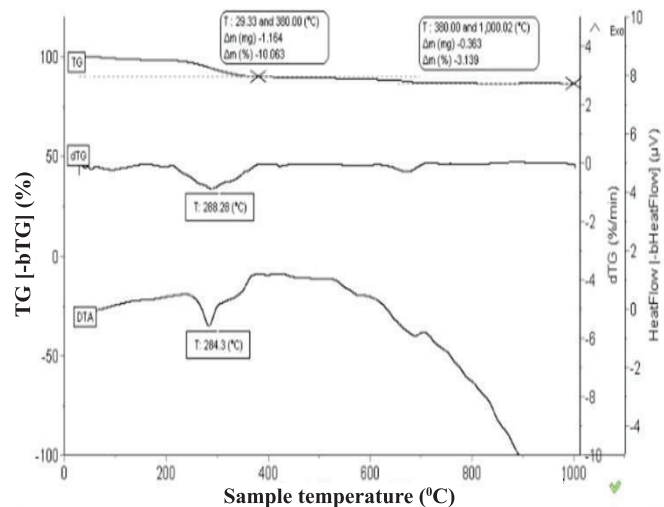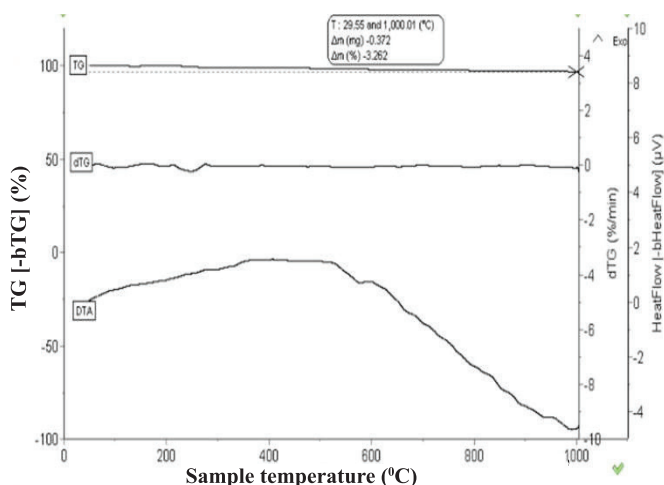

Fig. 2. The DTA curve of RM.

Fig. 3. Thermal analysis of fumed silica.

On the DTA curve of RM, there is an endothermic peak at 284°C, corresponding to the decomposition of $Al(OH)_3$ to Al_2O_3 and FeOOH to Fe_2O_3 [15]. The loss of ignition of RM is 10.06% after heating up to 380°C, and it continuously decreased to 3.14% from heating 380°C to 1,000°C. There is no significant heat effect on the DTA curve of SF; the loss on ignition of SF is only 3.26% during the heating.

The NMR spectrum of ^{29}Si of SF is shown in Fig. 4. The symbols Qn(mAl) are used to describe the structural monomers in aluminosilicates, where n represents the valence of the central silicon and m is the Al number around the SiO_4 monomer.

The MNR spectrum ^{29}Si of SF exhibits a narrow peak of 50.3% at 108.77 ppm. This peak is related to the number of wavelengths that may be present. The bond Q4(0Al) has a large component in the material, which is characterised by silica-rich SF.
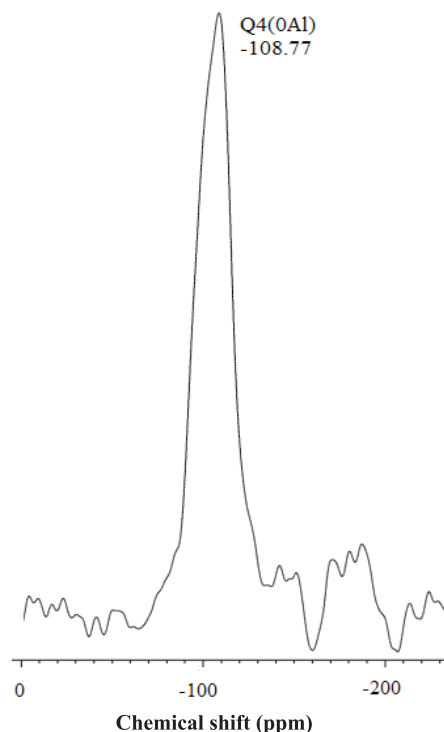

Fig. 4. NMR spectrum of ^{29}Si of SF.

The ratio of active SiO_2 and Al_2O_3 in the material

The content of active SiO_2 and Al_2O_3 in the raw materials are indicated in Table 3.

The results in Table 3 indicate that RM did not contain active SiO_2. The highest content of active alumina extracted from RM is 4.76% at the sodium hydroxide solution concentration of 5M, and the highest active silica content extracted from silica fume is 90.32% at the solution concentrations of at least 5M.

Effects of active SiO_2 and Al_2O_3 on properties of the geopolymer

The samples from RM had not hardened. That is

Table 3. The rates of active SiO_2 and Al_2O_3 in the raw material.

Samples		NaOH concentration (M)							
		1	*3*	*5*	*7*	*9*	*11*	*13*	*15*
RM	SiO_2 (%)	0	0	0	0	0	0	0	0
	Al_2O_3 (%)	4.13	4.74	4.76	4.76	4.76	4.76	4.76	4.76
SF	SiO_2 (%)	90.06	90.07	90.32	90.32	90.32	90.32	90.32	90.32

explained by the absence of active SiO_2 in RM. Although the content of SiO_2 in RM is 7.4% (Table 2), but they are not active SiO_2 and hence, they cannot participate in the geopolymer reaction. The content of active Al_2O_3 in the RM is 4.76% (Table 3) but they cannot polymerize because Al^{3+} is a modifier ion, and thus, they cannot form independent polymer chains.

In the presence of active SiO_2, a part of Al^{3+} having 4 oxygen coordination can replace Si^{4+} in the $[SiO_4]^{4-}$ tetrahedron to create a geopolymer network.

The lowest compressive strength of the samples (SF-Na1M) is 13.43 MPa. The highest compressive strength of the samples (SF-Na8M) is 54.79 MPa. The concentration of NaOH increased from 1M to 3M to increase the compressive strength of the samples from 13.43 MPa to 18.50 MPa. Notably, when using NaOH 4M, the compressive strength of the samples increased significantly - an increase of 67.5% compared to NaOH 3M (Fig. 5). This may explain that the concentration NaOH from 1M to 3M was insufficient to trigger the reaction. The higher the alkaline solution, the better the polymerization reaction.
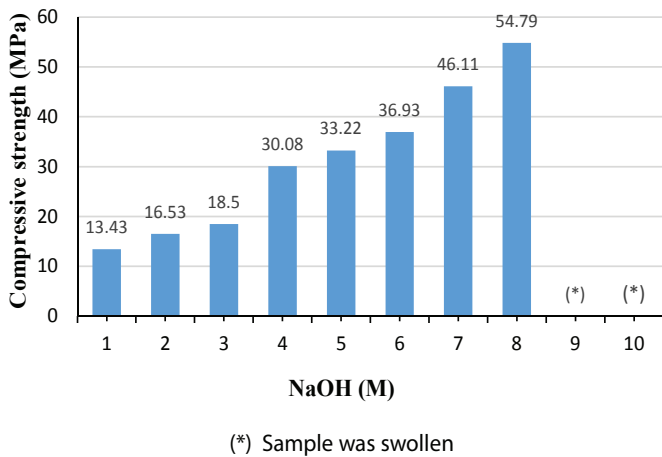

(*) Sample was swollen

Fig. 5. Effect of NaOH concentration on geopolymer Compressive Strength.

Softening-coefficient is defined as the ratio of the compressive strength of a material saturated with water to that in the dry state. The lowest and the highest softening coefficient of the samples SF-Na1M and SF-Na8M were 75.28% and 99.87%, respectively. The softening-coefficient was rapidly increased from 75÷80% (of the samples SF-Na1M to SF-Na3M) to 99.19÷99.87% (of the samples SF-Na5M and SF-Na8M) (Fig. 6).
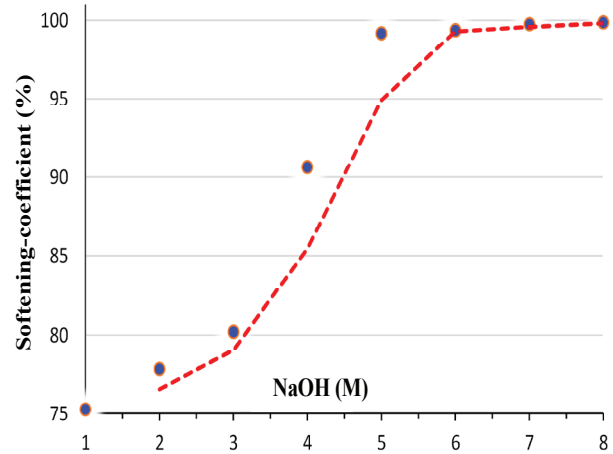

Fig. 6. Effect of NaOH concentration on the softening-coefficient.

The low softening-coefficient of the samples SF-Na1M to SF-Na4M can be explained by the low amount of alkaline solution, which is not enough to dissolve silicon and aluminum for geopolymerization. Thus, when the sample is saturated by water, many unreacted raw materials will be easily degraded to wash off, reducing the compressive strength of the sample. When the concentration of NaOH solution was increased above 5M, the geopolymer reaction increased, which led to the increase of softening-coefficient. However, when using the alkaline solution with a concentration higher than 8M, the geopolymer samples were swollen, which leads to crack and deformation. These samples did not have compressive strength.

The sample SF-Na4M was selected for structural analysis by XRD (Fig. 7), DTA-TG (Fig. 8) and NMR (Fig. 9).

On the XRD spectra of the samples SF and SF-Na4M, there is no new mineral peak. On the XRD spectrum of SF, there is only one peak corresponding to Cristobalite, which indicates that most of the silica content in SF was activated and they participated in the geopolymer reaction. Additionally, this proves that the formed phases during geopolymerization were amorphous.
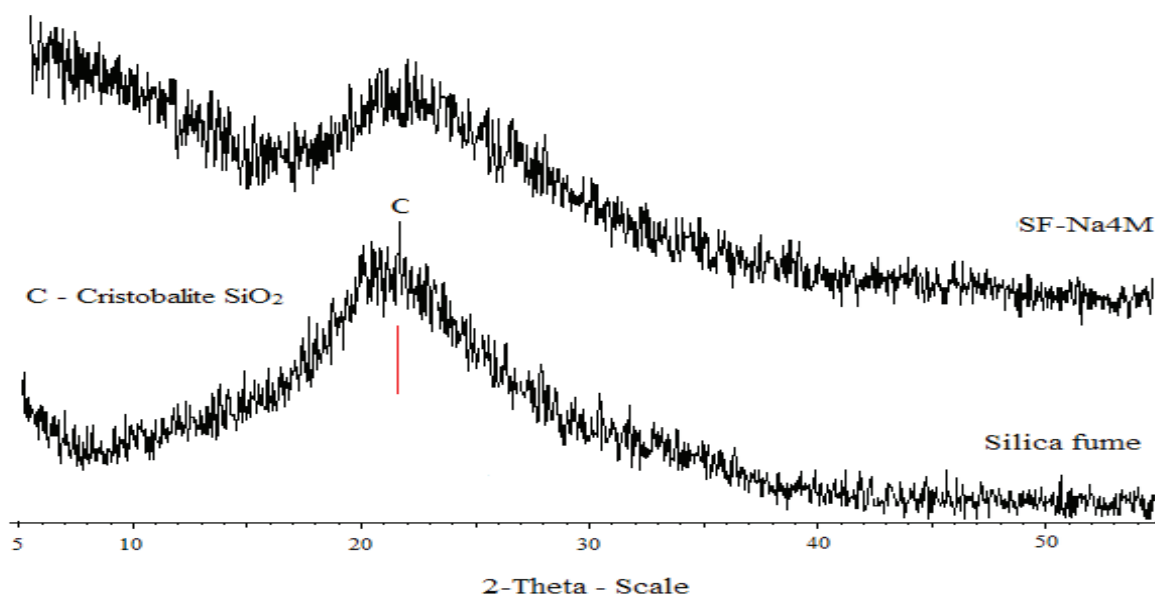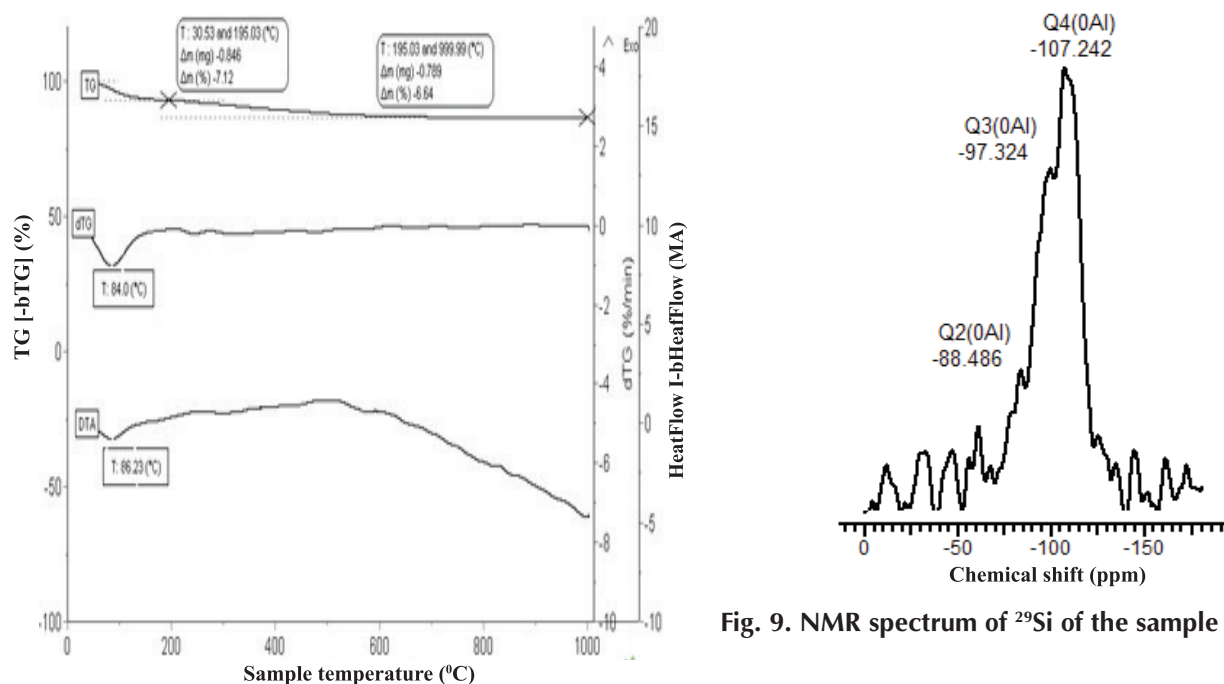
Fig. 7. XRD spectra of SF and SF-Na4M.

Fig. 8. The DTA curve of SF-Na4M.

Fig. 9. NMR spectrum of ^{29}Si of the sample SF-Na4M.

Nuclear Magnetic Resonance Analysis (NMR) of ^{29}Si

The DTA-TG curves of the samples SF-Na4M are shown in Fig. 8.

Beyond only a peak of evaporation at 86°C, there is no significant heat effect on the DTA curve of the sample SF-Na4M (Fig. 8). On the TG curve, the loss on ignition is 13.76% (loss of 7.12% from room temperature to 195°C and 6.64% from 195°C to 1,000°C).

The NMR spectrum (Fig. 4) clearly shows that the 3-dimensional structure of SF was changed. The NMR spectra of SF appeared at a peak of -108.77 ppm such as Q4 (0Al) linkage (Fig. 4). After the polymerization process, two new vertices were found at -97.324 ppm and -88.486 ppm corresponding to Q3 (0Al) and Q2 (0Al) (Fig. 9). Alkaline dissolution starts with the attachment of the base OH⁻ to

the silicon atom, which is, thus, able to extend its valence sphere to the penta-covalent state and the new linkages are formed. Furthermore, it was found that the geopolymer reaction of the SF-Na4M sample did not occur completely. The amorphous content of SiO_2 is extremely high. This explains that the geopolymer samples still exists in Q4(0Al). SiO_2 with structure Q4(0Al) was not completely soluble and concentration of Q4(0Al) was lower than the original. In addition, the NMR intensity proportional to the number of [29]Si nuclei should allow the quantification of the phase. The characteristics of NMR pickups for the geopolymer samples are shown in Table 4.

Table 4. Characteristics of the ^{29}Si NMR spectrum of the SF-Na4M sample.

	Qn(mAl)	ppm	Width (ppm)	Intensity (%)
SF	Q4(0Al)	-108.707	23	50.3
	Q4(0Al)'	-107.242	17	37.2
GP	Q3(0Al)	-97.324	6	27.6
	Q2(0Al)	-88.486	5	9.3

From the data in Table 4, we have:

$$\sum (Q4(0Al)' + Q3(0Al) + Q2(0Al))$$
$$= \sum Q4(0Al) = 100\%$$

We also have the magnitude of the sum of the components in the geopolymer sample:

$$I_{(Q4(0Al)' + Q3(0Al) + Q2(0Al)} = I_{Q4(0Al)'} + I_{Q3(0Al)} + I_{Q2(0Al)}$$
$$= 37.2 + 27.6 + 9.3 = 74.1\%$$

The percentage (%) of links in the geopolymer sample is calculated as follows:

Amount of phase A on phase B

$$\frac{W_A}{W_B} = \frac{I_A}{I_B} \times \frac{I_{oB}}{I_{oA}}$$

where: I_{oA}, I_{oB} are the intensity of standard diffraction beam.

The results of the linked units Qm(nAl) were shown in Table 5.

Table 5. Proportion of Qm(nAl) in the SF-Na4M.

	Qn(mAl)	ppm	Amount of phase (%)
SF	Q4(0Al)	-108.707	100
	Q4(0Al)'	-107.242	50.20
GP	Q3(0Al)	-97.324	37.25
	Q2(0Al)	-88.486	12.55

The samples from RM were not solidified although the active Al_2O_3 content was 4.76% compared to the total of 13.65%. The geopolymer samples from SF have high compressive strength, with the highest one being around 54.72 MPa of the sample SF-Na8M. This proves that active SiO_2 is indispensable and plays the most important role in the geopolymerization process. Al_2O_3 only plays a role in modifying the silicon polymer network.

Conclusions

Active silica plays the most important role in the geopolymerlyzation process because it makes the bonding and structure of the geopolymer. Silicon has the ability to bind directly to one another (Si-Si) or cross-link through silanes (Si-O-Si). When bonded via oxygen, the polymer chain can be expressed through coordinated multilane bonds, creating a three-dimensional network. The ions of the alkali oxides such as Na_2O, K_2O, CaO, MgO do not create a chain and are located in the hole coordinates.

When selecting raw materials for geopolymer materials, besides requiring materials containing the SiO_2 and Al_2O_3 components, the activity of SiO_2 must be present. In the geopolymerization process, active silica will form the bonds of monomer to achieve a geopolymer. Aluminium atom acts as a modifying ion. Al atom can only replace the Si atom in the polymer chain Si-O-Si.

It is necessary to add active SiO_2 when using RM of Tan Rai, Lam Dong to synthesize geopolymer. The active SiO_2 can be obtained from industrial waste such as fly ash, SF or glass water solution. The bonding and structure of geopolymer materials will be determined by the ratio of NaOH solution/SF and active silica. Silicon has the ability to bind directly to one another (Si-Si) or cross-link through

silanes (Si-O-Si). When bonded via oxygen, the polymer chain can be expressed through coordinated multilane bonds, creating a three-dimensional network. The ions of the alkali oxides such as Na_2O, K_2O, CaO, MgO do not create a chain and are located in the hole of structure network.

REFERENCES

[1] J. Davidovits (1989), "Geopolymers and geopolymeric materials", *Journal of Thermal Analysis and Calorimetry*, **35(2)**, pp.429-441.

[2] J. Giancaspro, P.N. Balaguru, and R.E. Lyon (2006), "Use of inorganic polymer to improve the fire response of balsa sandwich structures", *Journal of Materials in Civil Engineering,* **18**, pp.390-397.

[3] K. Goretta, J. Fuller, and E. Crawley (2006), "Geopolymers", *Air Force Office of Scientific Research Report,* Document # OSR-H-05-05.

[4] J. Davidovits (1994), "Geopolymers: man-made rocks geosynthesis and the resulting development of very early high strength cement", *Journal of Material Education,* **16,** pp.911-939.

[5] J. Davidovits (2002), "30 years of successes and failures in geopolymer applications, market trends and potential breakthroughs", *Geopolymer Conference,* Melbourne, Australia.

[6] J. Davidovits (1994), "Properties of geopolymer cements", *Proceedings 1st International Conference on Alkaline Cements and Concretes,* Scientific Research Institute on Binders and Materials (Kiev State Technical University, Ukraine), **199,** pp.131-149.

[7] J. Davidovits (2011), *Geopolymer chemistry and applications 3rd edition,* Institute Geopolymer - France.

[8] František škvára (2007), "Alkali activated materials or geopolymers?", *Ceramics - Silikáty,* **51**, pp.173-177.

[9] Joseph Davidovits (1999), "Chemistry of geopolymeric system terminology", *Géopolymère '99: Second International Conference*, pp.9-39.

[10] Van Chanh Nguyen, Dang Trung Bui, Van Tuan Dang (2008), "Recent research geopolymer concrete", *The 3rd ACF International Conference,* pp.235-241.

[11] Muhd Fadhil Nuruddi (2010), "Construction of infrastructures for sustainable futures"*, Seminar Nasional Aplikasi Teknologi Prasarana Wilayah*.

[12] R.E. Lyon, P.N. Balaguru, A. Foden, U. Sorathia, J. Davidovits, and M. Davidovics (1997), "Fire resistant aluminosilicate composites", *Fire and Materials*, **21**, pp.67-73.

[13] J. Davidovits (2015*), Geopolymer Chemistry and Applications 4th Edition,* Geopolymer Institute.

[14] H. Xu and J.S.J. Van Deventer (2000), "The geopolymerisation of alumino-silicate minerals", *International Journal of Mineral Processing*, **59**, pp.247-266.

[15] V.M. Sglavo, S. Maurina, A. Conci, A. Salviati, G. Carturan, G. Cocco (2000), "Bauxite "red mud" in the caramic industry. Part 2: Production of clay - based ceramic", *Journal of the European Society,* **20,** pp.245-252.