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Synthesis of volcanic ash-based geopolymer mortars by fusion method: Effects of adding metakaolin to fused volcanic ash

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Abstract

The present study aimed at improving the properties of geopolymer mortars obtained from volcanic ash as a source material. An alkali fusion process was used to promote the dissolution of Si and Al species from the volcanic ash and thus to enhance the reactivity of volcanic ash. Various amount of metakaolin (30%, 40%, 50% and 60% MK by weight) was used to consume the excess alkali needed for the fusion. The amount of amorphous phase was determined both in the volcanic ash and the fused volcanic ash and X-ray diffraction analysis was used to evaluate effect of the alkaline fusion method. Geopolymers were prepared by alkali activation of mixtures of powders of fused volcanic ash, various amount of metakaolin and river sand using a sodium silicate solution as activator. The geopolymer mortars were characterized by determination of setting time, linear shrinkage, scanning electron microscopy and compressive strength. The results of this study indicate that geopolymer mortars synthesized by the fusion method exhibit low setting time (7–15 min), low shrinkage (0–0.42%) and high compressive strength (41.5–68.8 MPa). This study showed that, by enhancing the reactivity of volcanic ash by alkali fusion and balancing the Na/Al ratio through the addition of metakaolin, all volcanic ashes can be recycled as an alternative source material for the production of geopolymers.

Keywords: Volcanic ash; Sodium hydroxide; Fusion process; Sodium silicate solution

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1. Introduction

The manufacture of Portland cement is a resource exhausting of raw materials and energy intensive process (3200–4200 KJ) owing to the high temperature in the making up of clinker (1400–1500 °C) and that releases large amounts of the green house gas (CO_2) into the atmosphere. Production of 1 t of Portland cement requires about 2.8 t of starting materials including fuel and other materials. As a result of de-carbonation of lime, manufacturing of 1 t of cement generates about 1 t of CO_2 [1]. Today, efforts are made by many researchers to promote the use of pozzolanic compounds such as metakaolin, fly ashes and others aluminosilicates to replace Portland cement. Another class of cementitious materials produced from an aluminosilicate precursor activated in a high alkali solution was developed. This cementitious material is termed geopolymer and was introduced by Davidovits in the early 1970 s. These geopolymers possess good mechanical properties i.e. high compressive strength and stability at temperature up to 1300–1400 °C [2]. The precursors for geopolymers are developed from different source materials such as kaolin [3], metakaolin, fly ashes, ground granulated blast furnace slag, natural zeolite [4] and lignite bottom ash [5]. Volcanic ashes contain a large amount of silica and alumina and could be used as aluminosilicate source material for making geopolymers [6]. They are vitreous or poorly crystallized materials that react with the portlandite generated during cement hydration to yield hydrated calcium silicates and aluminates with low solubility and good cementitious properties [7,8]. Recently,

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volcanic ashes from volcanic activities have been subject of attention by many researchers. Many cones of volcanic ashes exist along the «Cameroon line» oriented N30°E, specially at the side of mount Cameroon (the latest eruption took place in 1999), mount Manenguba, mount Bambouto, mountain of Galim, the Tombel plain around Djoungo, the Noun plain around Foumbot, the Kumba plain, the region of Lake Nyos and the Adamaoua plateau. These deposits are readily accessible and have the advantage of being naturally mined with enormous benefits at low cost mining. In Cameroon little amounts of these materials are used as additive for the production of Portland cement, improvement of the quality of untarred roads or as aggregate for concrete. Utilization of volcanic ashes as aluminosilicate for production of effective geopolymers could be of a great economic impact in countries with large deposits. The preparation of geopolymer cement using volcanic ashes could reduces the environmental impact of cement manufacture and if long term durability can be achieved materials similar to the ancient roman cemented structures can be prepared [9]. Any pozzolanic compound or source of silica and alumina that is readily dissolved in an alkaline solution will suffice as a geopolymer precursor and thus, volcanic ashes condensed with sodium silicate and geopolymerizes in a highly alkaline environment leading themselves to geopolymerization [10].

A previous study [11] has shown that geopolymer cements obtained from volcanic ashes at ambient temperature exhibit long setting time, higher shrinkage and low compressive strength. This is possibly due to the low geopolymeric reactivity of volcanic ashes which results from the low amorphous phase content in these materials. Nevertheless, volcanic ashes contain a substantial amount of silica and alumina. It is therefore reasonable to deduce that volcanic ashes can be used for the production of geopolymers with high mechanical strength via an alternative activation process. The alkali fusion is a conventional method for chemical analysis to decompose materials containing silicon and/or aluminum [12]. This method is generally used for the synthesis of zeolites [12,13]. The research work of Shigemoto et al. [13] showed that by fusion of fly ashes with sodium hydroxide pellets, most of fly ash particles were converted into sodium salts such as silicate and aluminate.

The present work aims to improve the properties of geopolymer mortars obtained from volcanic ash as a source material. Alkali fusion process [14–16] was introduced to enhance the reactivity of the volcanic ash. Various amount of high reactive metakaolin (30%, 40%, 50% and 60% MK by weight) was employed also as an additional aluminosilicate source to consume the excess alkali needed for the fusion. The amount of reactive phase and X-ray diffraction (XRD) patterns of the volcanic ash (Z_G) and the fused volcanic ash (f-Z_G) was determined to evaluate the effect of the fusion process in the reactivity of the volcanic ash. The geopolymer mortars were characterized by determination of setting time, linear shrinkage, scanning electron microscopy coupled with an Energy-dispersive X-ray spectroscopy (SEM-EDS) and compressive strength.

2. Experimental procedure

2.1. Materials

The volcanic ash (Z_G) and kaolin (MY_3) used in this study were extracted from Galim and Mayouom (West-Cameroon) respectively. Volcanic ash was previously studied by Tchakoute et al. [11] and Tchakoute et al. [16] and use to produce geopolymer cements. Kaolin was used by Njoya [17] in the production of ceramics and it was reported that kaolin consists of approximately 79% kaolinite and 8% quartz. Taking into account the density differences between quartz and kaolinite, MY_3 was enriched with kaolinite by wet sieving at 100 μm. The dried clay fraction (MY'_3) and volcanic ash (Z_G) were crushed in a mortar and ball mill respectively and then sieved to 80 μm. The clay fraction was calcined in a programmable electric furnace (Nabertherm, Mod_LH 60/14) for 4 h at a heating rate of 5 °C/min at 700 °C to get a highly reactive metakaolin (MK) [18].

Particle size distribution of the powders of volcanic ash (Z_G) and metakaolin (MK) were measured using a laser diffraction granulometer by Sympatec equipped with the HELOS optical system and the WINDOX software for data acquisition. The particle size distribution curves are shown in Fig. 1 and the average particle size (d_{50}) was 10.68 μm for Z_G and 9.95 μm for MK. The specific surface area of powders of Z_G and MK were determined using the Brunauer–Emmett–Teller (BET) method. It was performed

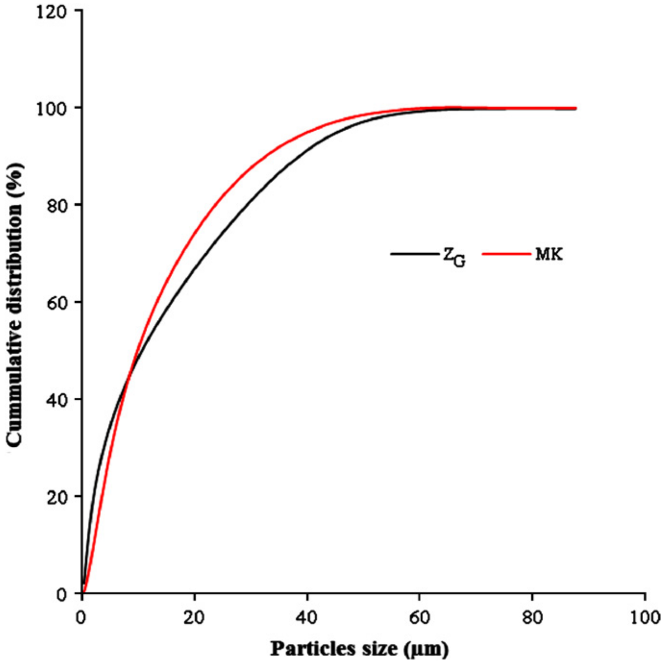

Fig. 1. Particle size distribution of the volcanic ash (Z_G) and metakaolin (MK).

via nitrogen adsorption using an automatic homemade apparatus by the *Laboratoire Environnement et Mineralurgie* (LEM, Nancy-France), were 15.7 m^2/g for Z_G and 20.5 m^2/g for MK. Chemical analyses of Z_G and MK were carried out by ICP-AES (Inductive Coupled Plasma-Atomic Emission Spectrometry) and the major element contents are listed in Table 1. The mineralogical composition of MY'$_3$, MK and Z_G were obtained using a Bruker D8 advance diffractometer, operating on the Co kα radiation and 2θ scanning ranging from 3° to 64° with a scanning step of 0.035 °. The XRD patterns are shown in Figs. 2 and 3 respectively for MY'$_3$ and Z_G. The MY'$_3$ contains kaolinite, illite, quartz and hematite (Fig. 2). Most of the diffraction peaks of kaolinite disappeared after heating owing to the formation of amorphous silica [19]. The XRD pattern of kaolin (MY'$_3$) and metakaolin (MK) clearly showed the amorphization of kaolin during the thermal activation. The metakaolin (MK) is mainly constituted of an amorphous silicate or aluminosilicate phase indicated by the broad band registered between $2\theta=5$–13° and $2\theta=18$–40°. The only crystalline phases detected in the metakaolin (MK) (Fig. 2) are quartz, hematite and illite while volcanic ash (Z_G) contains muscovite, anorthoclase, diopside, hematite, maghemite, nepheline and minor amount of amorphous phase indicating by a few broad band registered between $2\theta=20$–43° (Fig. 3).

The aggregate used was a collected river sand with major particles passing through a 500 mm mesh sieve. The chemical composition of sodium silicate used in this study was: 28.7% of silicon oxide (SiO_2), 8.9% of sodium oxide (Na_2O) and the modulus $Ms=3.22$. The sodium hydroxide used in this study was NaOH pellets of 99% purity.

2.2. Geopolymer synthesis

Alkali fusion of volcanic ash (Z_G) was performed by thoroughly mixing the volcanic ash with sodium hydroxide pellets at a low alkali/volcanic ash mass ratio of 0.7 in a Hobart mixer (*M & O*, *modèle N50- G*) for 5 min, followed by fusing the resulting mixture in a *Carbolites furnace*

Table 1
Chemical composition of volcanic ash (Z_G) and metakaolin (MK). LOI: Loss on ignition.

Element as oxide	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	MgO	CaO	K_2O	Na_2O	P_2O_5	Cr_2O_3	LOI	SiO_2/Al_2O_3	Total
Z_G	41.36	15.41	12.88	3.04	0.2	6.45	7.88	0.90	2.22	0.48	0.03	9.31	4.55	100.10
MK	48.31	40.48	2.62	4.45	0.03	0.36	0.04	1.30	0.15	0.02	0.02	2.43	1.42	100

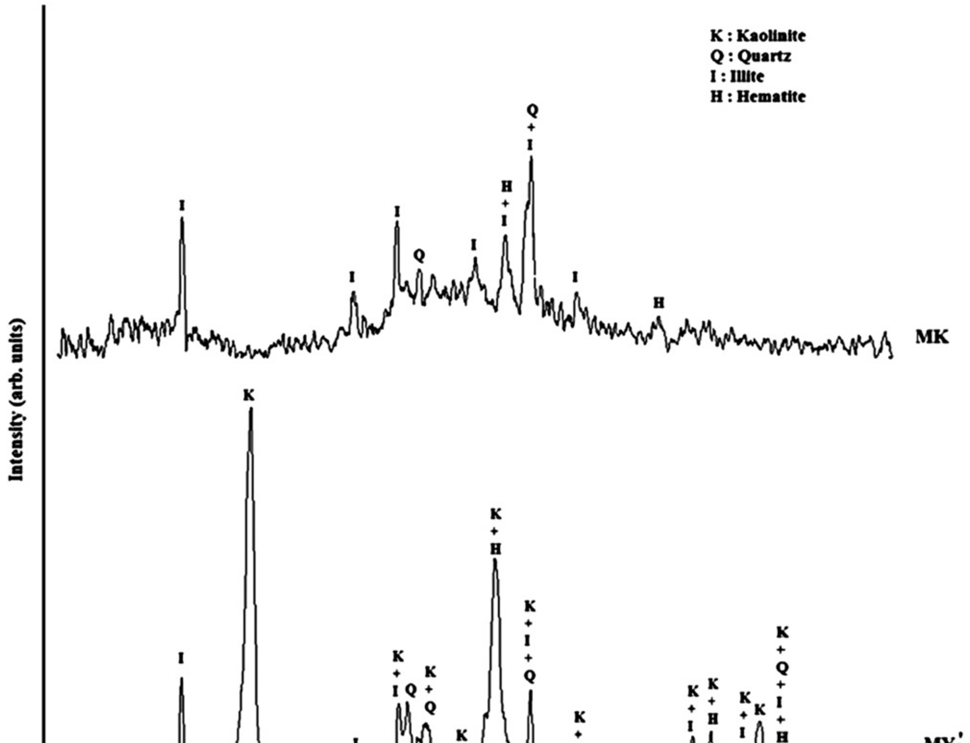

Fig. 2. XRD patterns of kaolin (MY'$_3$) and metakaolin (MK).

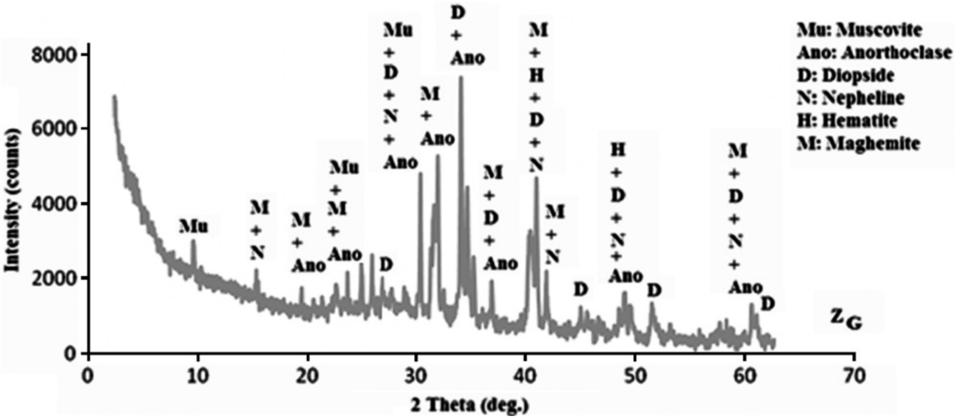

Fig. 3. XRD pattern of volcanic ash (Z_G).

(Serial No. 11/92/1736. Type BOF 11/13) at 550 °C for 1 h at a heating rate of 5 °C/min. NaOH pellets to volcanic ash mass ratio of 0.7 is chosen according to the conclusion of a previous work [16]. The fused volcanic ash (f-Z_G) were cooled naturally in air at ambient temperature and then ground in a mortar to obtain a homogenous sodium silicate-rich mixture. The volcanic ash and fused volcanic ash powders were submitted to XRD analysis to provide an estimate of the effect of the fusion process. In order to determine the amount of amorphous phase contained both in the volcanic ash and the fused volcanic ash, the method performed by Chindaprasirt and Rattanasak [20] was used. Thus, 3 g of powder was treated with 30 mL of sodium hydroxide (8 M) at 60 °C for 1 h. The sample was cooled to room temperature and filtered through pre-weighed membrane-filter. The insoluble residue was washed to neutral pH, dried at 105 °C for 24 h and weighed. The amount of amorphous phase was determined as the weight of powder material minus the residue.

Geopolymer mortars were prepared by activating blends of fused volcanic ash (f-Z_G), metakaolin (MK) and river sand at f-Z_G/MK mass ratios of 70/30, 60/40, 50/50 and 40/60 by a sodium silicate solution. The ratio of a binder material to river sand was set at 1/2 by weight. Source materials of four ratios were respectively mixed in a Hobart mixer with sodium silicate solution for 10 min to form four homogenous slurries. For each slurry mortar, a liquid/solid mass ratio 0.60 was used. Each slurry mortar obtained was used to determine the setting time and cast in cylindrical PVC moulds (diameter 31 mm; height 62 mm and diameter 10 mm, height 20 mm). Once molded, the samples were vibrated for 5 min on an electrical vibrating table (*M & O, type* 202, *No* 106) to remove entrapped air bubbles. During the hardening of the geopolymer mortar samples, the cylinders were covered with a thin film of polyethylene to avoid water evaporation and then kept for 24 h at ambient atmosphere in the laboratory before demolding. The geopolymer mortars obtained with 30%, 40%, 50% and 60% metakaolin were labeled as Z_1, Z_2, Z_3 and Z_4 respectively. The calculated Si/Al and Na/Al ratios for all geopolymer mortar samples are summarized in Table 2.

Table 2
The calculated Si/Al and Na/Al ratios for all geopolymer mortar samples.

Geopolymers	Z_1	Z_2	Z_3	Z_4
Si/Al	2.38	2.17	1.99	1.85
Na/Al	1.12	1.00	0.91	0.84

Depending on the number of days (1, 7, 14, 21 or 28 days) the hardened geopolymer cylinder mortars stayed in the ambient atmosphere in the laboratory, linear shrinkage and compressive strength measurements were carried out. The geopolymers mortars which were molded in cylindrical PVC mould having diameter 10 mm and height 20 mm, were used for SEM-EDS analysis.

The setting time was measured with a fresh geopolymer mortars using the Vicat apparatus according to the EN 196-3 standard [21]. The needle used was 1.00 ± 0.05 mm in diameter. Blends of fused volcanic ash (f-Z_G), metakaolin (MK) and river sand at f-Z_G/MK mass ratios of 70/30, 60/40, 50/50 and 40/60 were placed in the mixer bowl respectively. Then, the Hobart mixer was operated at gear 1 for 10 min. Within the 10 min, the prepared amount of activator was poured into the mix on two separate times. Geopolymer mortars were cast into the 40 mm height, 80 mm diameter conical mould in two layers. Each layer was tamped with a rod for 25 times. For every 5 min interval, the specimen was placed on the Vicat apparatus to measure the initial setting time.

Measurement of linear shrinkage was carried out with a Vernier Calliper on the hardened geopolymer mortars aged of 1, 7, 14, 21 or 28 days respectively. Linear shrinkage was calculated using the following equation:

$$R_L = \frac{L_0 - L}{L_0} \times 100$$

Where L_0 is the initial length of specimens at first days and L is the length of specimens after a given number of days.

Compressive strength was determined on all hardened geopolymer cylinder mortar samples aged of 28 days using an electro-hydraulic press with capacity of 60 KN (*M & O, type* 11.50, *No* 21). The specimens were subjected to a compressive force at average rate of 3 mm/min until the specimen failed (refer to ASTM C 109 standard test methods). Compressive strength was calculated from the failure force, F, using the following equation:

$$\delta = \frac{F}{A}$$

where F is the applied force and A is the initial cross-section area of the samples. Specimens were cylindrical with dimensions 31 mm in diameter and 62 mm in height. Sample surfaces were polished flat to avoid non-uniform loading.

SEM was carried out on a Hitachi S-4800 Scanning Electron Microscopy, coupled with an Energy Dispersive Spectrometer (EDS). Samples from hardened geopolymer mortars aged at least 28 days was carbon coated prior to analysis.

3. Results and discussion

3.1. *Characterization of fused volcanic ash*

3.1.1. *X-ray diffraction pattern of fused volcanic ash*

Fig. 4 shows the XRD pattern of fused volcanic ash (f-Z_G). XRD pattern of fused volcanic ash showed a broad hump between 30 and 45° (2θ) which are absent in the XRD pattern of the volcanic ash (Z_G) (Fig. 3). These differences are indications of higher amount of amorphous phase such as silica and alumina in the fused volcanic ash in comparison to the raw volcanic ash. The crystalline phases such as anorthoclase, diopside, nepheline, hematite and maghemite are found as well (Fig. 4). As shown in Fig. 4 a significant amount of crystalline phases in the starting volcanic ash (Z_G) reacted with sodium hydroxide pellets and was converted into sodium aluminosilicate after the fusion treatment. It is therefore reasonable to expect that the formation of sodium aluminosilicates will enhance the dissolution of Si and Al species from the fused volcanic ash (f-Z_G) in aqueous solutions. In particular, XRD pattern of fused volcanic ash shows that a significant amount of anorthoclase and diopside (around 35° (2θ)) was converted into soluble aluminosilicates. This is justified by the intensity of the peak of these minerals on the XRD pattern of fused volcanic ash (Fig. 4). The intensity of this peak decreases after fusion process. As also shown in Fig. 4 a significant amount of muscovite in the volcanic ash has reacted with sodium hydroxide pellets and was converted into soluble sodium aluminosilicate after the fusion treatment. It is suggested from this comparative study that alkali fusion process can effectively enhance the reactivity of volcanic ash for the geopolymerization.

3.1.2. *Amount of reactive phase in the starting and fused volcanic ash*

The dissolution of Si and Al species from solid source materials plays a crucial role in the geopolymerization. Although XRD can be used to estimate the reactive phase in the volcanic ash and fused volcanic ash, they do not reveal how readily these amounts of reactive phase are available for dissolution. Therefore, an alkaline dissolution (in NaOH 8 M) was employed to determine the amount of reactive phase in volcanic ash and fused volcanic ash. The amount of reactive phase in volcanic ash is equal to 29%. When sodium hydroxide pellets are heated with volcanic ash (NaOH/Z_G mass ratio of 0.7), the amount of reactive phase is higher (76%) compared to that of raw volcanic ash. This difference in the amount of reactive phase justifies the low compression strength, high shrinkage and long setting time observed in geopolymers from the starting volcanic ash [11,22,23]. The results obtained from the determination of the amount of reactive phase corroborate the result of XRD (Fig. 4) which showed a broad hump between 30 and 45° (2θ) with few broad peaks on the XRD patterns of fused volcanic ash indicating higher amount of reactive phase in the fused volcanic ash.

3.2. *Characterization of geopolymer mortars*

3.2.1. *Setting time*

The setting time of geopolymer mortars ranges between 7 and 15 min, as illustrated in Fig. 5. The setting time of geopolymer is important in practice because it establishes the time available for transport, placing and compaction of

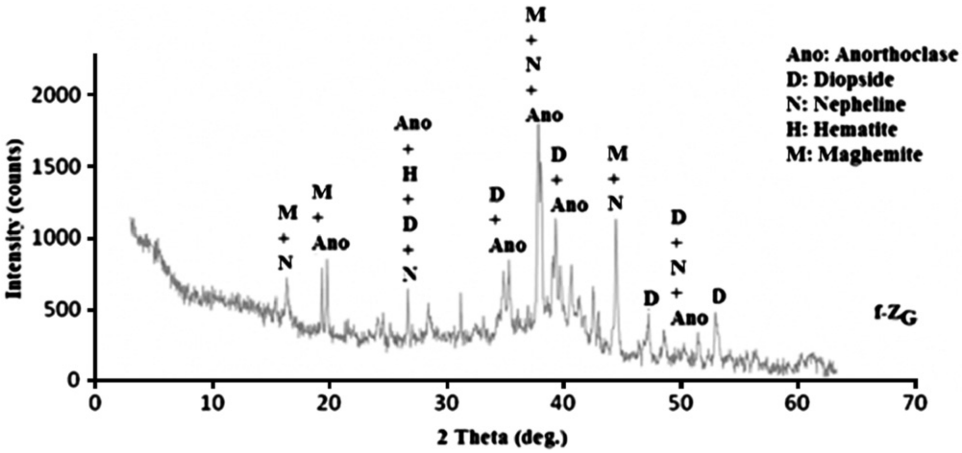

Fig. 4. XRD pattern of fused volcanic ash (f-Z_G).

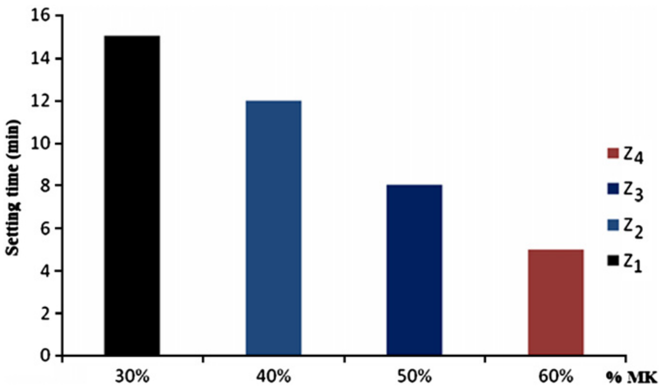

Fig. 5. Setting time of geopolymer mortars.

geopolymer. Fast setting time is the result of improved dissolution of the fused volcanic ash into sodium silicate solution; leading to improved polymerization and hardening of the gel phase [24, 25]. The relatively short setting time observed in the geopolymer cement obtained by fusion process actually show that the geopolymerization reactions including dissolution of amorphous aluminosilicates, formation and orientation of intermediate compounds and finally polycondensation reactions, are quite short. The excess of metakaolin in the fused volcanic ash could be likely responsible to the decrease of setting time. The addition of more metakaolin to fused volcanic ash favors the dissolution of alumina and silicate species, subsequently promoting the formation of $[SiO(OH)_3]^-$ and $[Al(OH)_4]^-$ intermediates, which enhance the polycondensation reaction and the formation of polymeric binder are promoted which result in a decrease in the setting time of the geopolymer mortars. The setting time of fused volcanic ash-based geopolymer mortars seems to be governed by the type of glass structure prevailing in the fused volcanic ash (Fig. 4). It appears that the setting time varies between 7 and 15 min; it decreases when the amount of metakaolin incorporated increase up to 60%. From these results, it appears that increasing the amount of metakaolin, increases the amount of reactive phase will result in a more rapid consolidation of the geopolymer. The excess of alkali in the fused volcanic ash certainly contributes to accelerate the release of reactive species such as Al and Si from the metakaolin added. The added MK also help to obtain a better workable geopolymer phase and, because the MK addition may mainly contribute to increase the Al and Si content of the mixture, then it was concluded that the decrease of the setting time is due to the increase of Al content (Table 2).

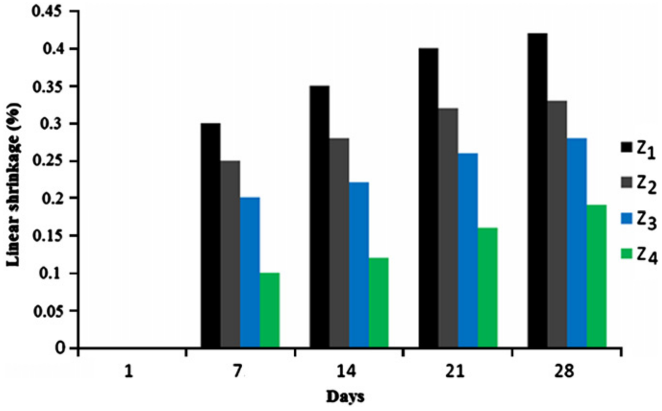

Fig. 6. Linear shrinkage of geopolymer mortars.

3.2.2. *Linear shrinkage of geopolymer mortars*

The linear shrinkage, as a function of the age of the hardened geopolymer mortars, produced from mixtures of the fused volcanic ash and metakaolin in mass percentage ranging between 30% and 60%, is presented in Fig. 6. The overall result indicates that the linear shrinkage is low (0–0.42%). From these data, high values of linear shrinkage are recorded with the test samples having f-Z_G/MK mass ratio of 70/30 (Z_1). Linear shrinkage originates from capillary tensions within the gel framework during geopolymerization. Thus, high shrinkage may be an indication of insufficient geopolymerization reaction [26]. Geopolymer mortars obtained from f-Z_G/MK mass ratio of 70/30 (Z_1) showed a high shrinkage (0.42%) suggesting a low geopolymerization rate. Since, there was insufficient geopolymerization, the excess solution in the geopolymer mortars migrates to the surface causing high shrinkage and cracks [27]. When the degree of disorder in the aluminosilicate source material is low, the reactivity of a blend of fused volcanic ash and metakaolin is low due to the low amount of metakaolin incorporated in the fused volcanic ash and this justified the high linear shrinkage of the resulting geopolymer mortars. The linear shrinkage of geopolymer mortars is high because the gel resulting from low amount of metakaolin incorporated in the fused volcanic ash was thinner than the one resulting from the activation of high amount of metakaolin added. It is therefore believed that, if excess water in the thinner gel is not consumed during the hydration process, free water will diffuse out of the matrices with time. Due to the considerable molecular size of water, the diffusion of water out of the matrices may leave behind more inner pores within the structure which may consequently induce more cracking throughout the matrices. The loss of water by evaporation of significant amount of water may also induce shrinkage. This shrinkage may be related to the fact that less aluminum is participating in the reaction. There is an excess in Na versus the stoichiometric ratio of Na/Al in the geopolymer phase (Table 2). Thus, high shrinkage may be an indication of insufficient geopolymerization reaction. The linear shrinkage of geopolymer mortars (Z_3, Z_4) is low because the degree of disorder within the structure of a blend fused volcanic ash and metakaolin is high due to the high amorphous phase in the metakaolin.

3.2.3. *Microstructure*

SEM micrographs of the geopolymer mortars Z_1, Z_2, Z_3 and Z_4 are illustrated in Fig. 7. The geopolymer mortars obtained from fused volcanic ash to metakaolin mass ratio

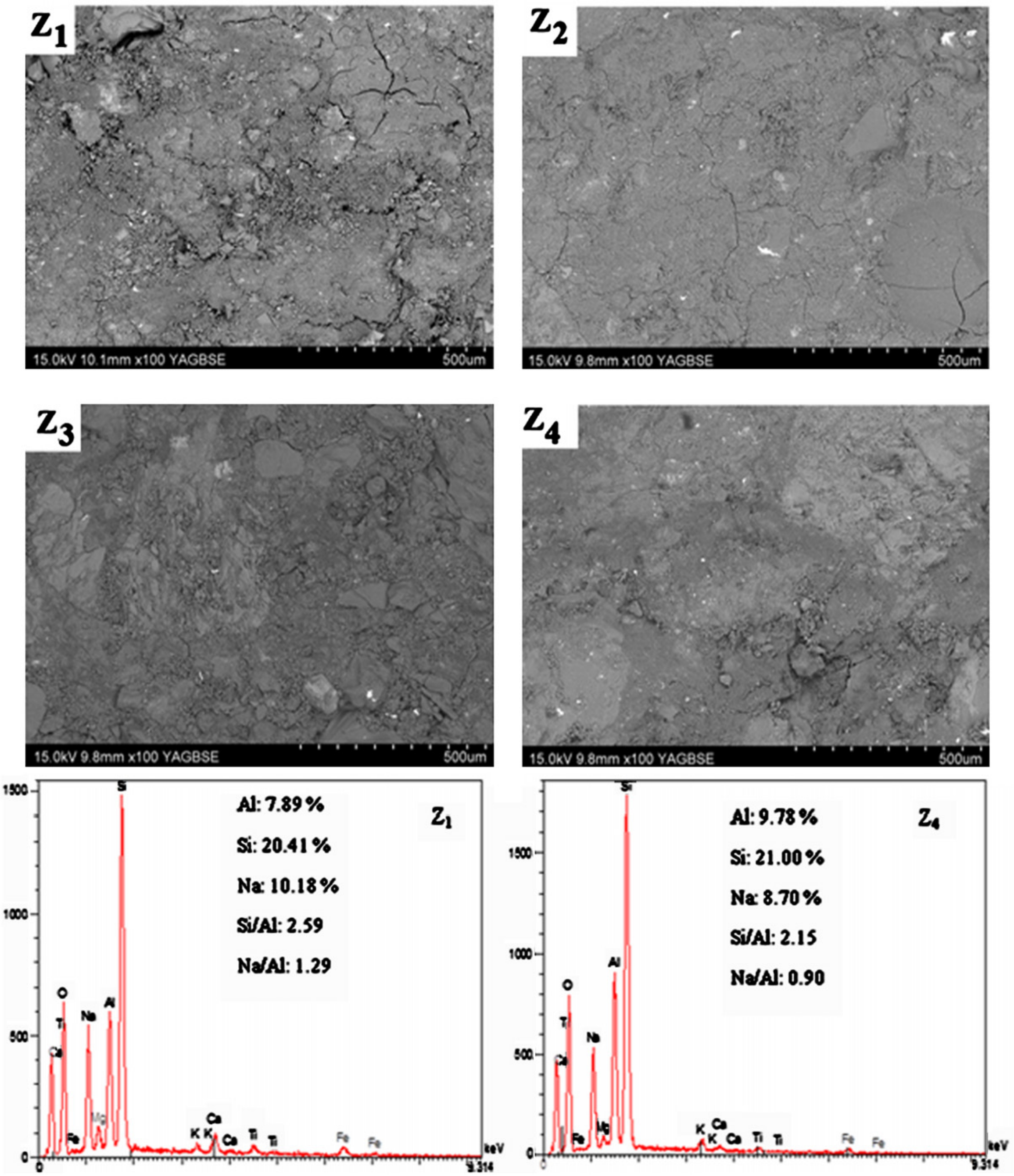

Fig. 7. SEM micrographs and EDS of some of the geopolymer mortars.

of 70/30 and 60/40 (Z_1 and Z_2) show more cracks. This result corroborate the result obtained by linear shrinkage which showed that, if excess water in the gel is not consumed during the hydration process, free water will diffuse out of the matrices with time. Due to the considerable molecular size of water, the diffusion of water out of the matrices may leave behind more inner pores within the structure which may consequently induce more cracking throughout the matrices. The geopolymer mortars (Z_3 and Z_4) show a more compacted structure than the other geopolymer mortars due to an amorphous feature of well-formed geopolymer mortars with fused volcanic ash/metakaolin (f-Z_G/MK) mass ratios of 50/50 and 40/60 demonstrating that a blend of fused volcanic ash and metakaolin could be used as an alternative source material for geopolymer synthesis. In fact, geopolymers synthesized from the fused volcanic ash with great content of amorphous phase (high metakaolin content) led to products with abundant amount of geopolymer phase (Z_3 and Z_4) without cracks. However, the presence of micro cracks, observed on SEM images, are weaknesses regarding the durability of the resulting construction material. More

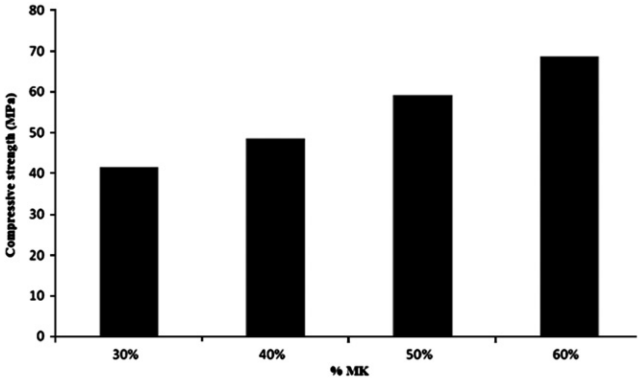

Fig. 8. Compressive strength of geopolymer mortars.

study is needed to dominate this fact. For instance, by applying longer mixing time than that used here (10 min).

For comparison to the calculated Si/Al and Na/Al ratios, EDS measurements for Z_1 and Z_4 are presented in Fig. 7. The measured ratios are consistent with the calculated ones (Table 2). It must be noted that the EDS measurements are punctual and done without reference and all this justified the observed differences.

3.2.4. *Compressive strength*

The compressive strength of the geopolymer mortars are presented in Fig. 8. It is shown that the compressive strength increases (41.5–68.8 MPa) with increasing metakaolin incorporated up to 60% by weight. High amount of metakaolin (60%) in the fused volcanic ash increases the amount of reactive phase content in the aluminosilicate allowing the dissolution of silicon and alumina that improves the polycondensation phenomena and the formation of polymeric binder and thus increasing the compressive strength of geopolymer mortars. These results indicate that the addition of metakaolin to fused volcanic ash for production geopolymer improves the compressive strength. In order to explain these results, it is important to note that metakaolin has a considerably smaller particle size and high specific surface than fused volcanic ash. When dissolution takes place therefore, it is anticipated that metakaolin will be more reactive than fused volcanic ash due to smaller particles size and high specific surface area of metakaolin. Subsequently the viscosity of the initial suspension with more metakaolin will be higher than the one with more fused volcanic ash. The relatively low compressive strength of geopolymer mortars obtained from less metakaolin (30%) addition may be due to the excess sodium hydroxide contained in the fused volcanic ash. According to Maragkos et al. [28] an excessive amount of sodium hydroxide in the fused volcanic ash inhibits the polycondensation phenomena and the formation of polymeric binder decreasing the compressive strength of the geopolymer. The Si/Al ratio for the geopolymer containing 60% of metakaolin is smaller than that of geopolymer containing 30% of metakaolin (Table 2 and Fig. 7). It is then expected that the leaching of alumina in the geopolymer matrix obtains from a mixture of fused volcanic ash and 60% metakaolin added is more important than in the geopolymer containing lower amount of metakaolin (30%). The higher ratio of Si/Al results in geopolymers with lower strength and higher elasticity [29]. The compressive strength measurements correlate with the results from linear shrinkage measurements, setting time and scanning electron microscopy.

4. Conclusion

This work showed that enhancing the reactivity of volcanic ashes by alkali fusion and balancing the Na/Al ratio through metakaolin addition, all volcanic ashes could be used as an alternative source material for geopolymer synthesis. XRD pattern of fused volcanic ash showed that a significant amount of muscovite, anorthoclase and diopside were converted into soluble aluminosilicates. This further showed that fused volcanic ash have a higher content of reactive phases compared to raw volcanic ash and this suggest that alkali fusion is an effective means to enhance the reactivity of all volcanic ashes for the geopolymerization. The excess alkali in the fused volcanic ash can be consumed by the addition of metakaolin. It is found that fused volcanic ash to metakaolin mass ratio play a significant role in the geopolymerization via alkali fusion method. The setting time of fresh geopolymer mortars and the linear shrinkage of hardened geopolymer mortars decrease when the amounts of metakaolin added increase while the compressive strength of hardened geopolymer mortars increase with increasing MK added. The optimal geopolymer mortars reached a reasonably high 28-day compressive strength of 68.8 MPa for the f-Z_G/MK ratio of 40/60. The addition of metakaolin to fused volcanic ash favors the dissolution of alumina and silicate species, subsequently promoting the formation of $[\mathrm{SiO(OH)_3}]^-$ and $[\mathrm{Al(OH)_4}]^-$ intermediates. The polycondensation and the formation of polymeric binder are promoted, resulting in an increase of the compressive strength of the geopolymers. The method discussed in this study may provide a new approach for an effective recycling of all volcanic ashes for the production of value-added geopolymer materials.

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