Effect of slag on the improvement of setting time and compressive strength of low reactive volcanic ash geopolymers synthesized at room temperature

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Abstract

This paper presents an investigation on the effect of ground granulated blast furnace slag on the geopolymerization of low reactive volcanic ash. Volcanic ash was blended up to 50 wt% with slag at 10% intervals. The fresh geopolymer samples were cured at 25 and 60 °C for 3, 7 and 28 days. XRD, FTIR, TG and SEM were used for phases analysis. The results outlined that only 10 wt% of slag was enough to reduce the initial setting time of the geopolymer from more than 7 days to couple of hours (6.7 hours). At 25 °C, the 28 days compressive strength increased with the addition of slag in the system until an optimum value of about 85 MPA. This strength development was suggested to arise from a synergetic formation of C-A-S-H /N-A-S-H gel. At 60 °C, curing for periods longer than 7 days was not beneficial for strength development. These results are of interest for the valorization of low reactive volcanic ashes in the development of structural geopolymers, with related environmental and socioeconomic benefits.

Key words: Volcanic ash; GGBS; structural geopolymers; compressive strength; setting time

1. Introduction

Ordinary Portland Cement (OPC) is a commonly used building material across the globe, the use of which was found to be second after water [1]. With the need for new infrastructures mainly in developing countries, the global production of cement has reached 4.6 billion tons in 2015 [2]. However, OPC is also a high energy intensive material, with an additional concern related to carbon dioxide (CO₂) released during its production, currently accounting for 5-8% of global anthropogenic CO₂ [3–5]. These concerns have raised the pressure for the development of more environmentally friendly binders. Amongst these binders, geopolymers and alkali activated materials have emerged recently as a possible alternative with potential to partly replace Portland cement [6–16]. Alkali activated materials were defined as materials that encompass any binder system derived from the reaction of solid or dissolved alkali metal source with a solid silicate powder, while geopolymers are in many instances viewed as a subset of alkali activated materials where the binding phase is almost exclusively aluminosilicate with low calcium content such as calcined clay and low calcium fly ashes [17]. In this study, the term geopolymer will be used albeit slag with high Ca content was part of some compositions. Geopolymer chemistry involves the dissolution of aluminosilicate rich materials in the presence of an alkaline solution. The dissolved species made of aluminate and silicate units are then subjected to polycondensation reactions to form the geopolymer structure [10,18,19]. Amongst the potential natural aluminosilicates for geopolymer synthesis, volcanic ashes have been suggested to be one of the more efficient materials, because there is no need for calcination around 700 °C prior to their use, as in

the case of kaolin in the production of metakaolin based geopolymer [20,21]. Volcanic ashes are pyroclastic materials abundantly found in the world, mainly in regions with past or present volcanic activity [5,22]. In comparison to clay mining, volcanic ash mining presents less environmental concerns because they are readily available, with no need for open quarrying method as for the case in mining operations of common clays [22]. It is also noteworthy that many volcanic ash deposits are unexploited meanwhile their valorization can be of environmental and economic benefit [5,23,24]; hence, the interest of their valorization in the development of structural geopolymers. However, the practical use of many volcanic ashes for geopolymer synthesis has been found to require some heat (50-100 °C) necessary for hardening the geopolymer slurry in a reasonable time, and often for the development of acceptable strength [20,21,24]. This need is a drawback for their practical use in geopolymer synthesis because although this curing temperature is relatively low, the cost associated for a large-scale production will be significant. On the other hand, some aluminosilicate materials such as Ground Granulated Blast Furnace Slags (GGBS) were observed to be highly reactive for geopolymer synthesis, with potential to achieve a good reaction rate at temperatures as low as 0 °C [25]. GGBS is an industrial byproduct derived from pig iron. It has been observed to perform well in the development of cementitious materials [4,12].

The present paper investigated the development of geopolymers from a synergetic use of a low reactive volcanic ash and GGBS, for potential structural applications. The effect of slag addition is assessed on the setting time and the development of strength at ambient temperature (25 °C). For comparative study, some specimens were also cured at 60 °C. The effect of mixture composition on the 3, 7 and 28-days compressive strength and the

setting time was investigated. The products were also characterized by X-ray diffraction, scanning electron microscopy, thermogravimetry and Fourier transform infra-red spectroscopy.

2. Experimental

2.1. Materials

The primary raw materials used in this study were provided by local suppliers. The volcanic ash was from Petponoun in Foubot (West region of Cameroon). The ash was obtained after grinding of the volcanic scoria. The alkaline activator used was sodium hydroxide, which was produced by Xilong Chemical Company. The GGBS used in this study was provided by the Chengde Group Company, Beihai Guangxi, P.R. China. The oxide composition of volcanic ash and slag determined by X-ray fluorescence, and their particle size determined with an OMEC Laser particle size distribution, are presented in [Table 1](#) and [Figure 1](#) respectively.

Table 1: Chemical composition of the volcanic ash and slag

	Fe_2O_3	Al_2O_3	CaO	SiO_2	TiO_2	Na_2O	MgO	SO_2	K_2O	MnO
Volcanic ash	12	15.0	11	43	2.9	4.6	6.8	-	1.7	0.19
Slag	0.63	15.32	37.15	34.21	0.80	0.39	9.34	1.82	0.41	0.59

Figure 1: Particle size distribution of volcanic ash and slag

A non-corrosive alkaline activating solution with silica moduli ($R = \text{SiO}_2/\text{Na}_2\text{O}$) of 1.6 was prepared by dissolving solid sodium hydroxide in a commercial sodium water glass with $R=3.3$. In fact, sodium and potassium hydroxide solutions were classified as corrosive for skin when their modulus ($R = \text{SiO}_2/\text{M}_2\text{O}$ with $\text{M} = \text{Na}$ or K , R representing the molar ratio) is below 1.6 and irritating for the skin when this modulus is above 1.6 [26]. The prepared alkaline solution was sealed and stored for a minimum of 24 h prior to use.

2.2. Specimens preparation

The preparation of the fresh mixture was performed by mixing volcanic ash, GGBS and the alkaline solution of $R = 1.6$. The amount of volcanic ash substitution by slag was 0 to 50 wt% with 10 wt% interval. A composition made of 100 wt% slag was also prepared for reference. After preliminary investigation, the volcanic ash/water glass and

slag/water glass weigh ratio were maintained to 3 and 2 respectively. The details on the mix proportioning are presented in [Table 2](#).

Table 2: Mixture proportioning

No	Volcanic ash (g)	Slag (g)	Water glass solution R=1.6	Na/Al molar ratio	Percentage of Va substitution
1	90	0	30	0.62	0
2	81	9	31.5	0.65	10
3	72	18	33	0.68	20
4	63	27	34.5	0.71	30
5	54	36	36	0.73	40
6	45	45	37.5	0.76	50
7	0	90	45	0.91	100
8	90	0	45	0.92	0

The mixing process was performed for about 10 min, using an electric mixer at 750 rpm, until obtaining a homogenous paste. The samples were then casted in cubic alloy molds of 20×20×20 mm³, covered with a thin layer of plastic to facilitate the removal of the hardened paste upon curing. The alloy molds were vibrated on a vibration table for 2 min to remove air bubbles and sealed afterwards. The specimens were stored at 25 °C until the 3, 7 and 28-days compressive strength test. For comparative study, some specimens were also cured at 60 °C after their first day at 25°C. The sketch of the experimental plan is presented in [Figure 2](#).

Figure 2: Sketch of the experimental plan

2.3. Characterization method

2.3.1. XRD and FTIR analyses

The starting volcanic ash and the prepared geopolymers were examined by X-ray diffraction using a Rigaku Mini Flex 600 instrument with Ni-filtered Cu ($K\alpha$) radiation, a step size of 0.02° , operated at 40 kV and 15 mA, with a dwell time of 0.5 second and a 2θ range of 5 to 80° . The powdered samples were also pressed into KBr pellets for FTIR analysis using a Thermo Scientific FTIR spectrometer.

2.3.2. TG analysis

The TG analysis of the starting materials and the prepared geopolymers was performed with a simultaneous STA409PC TG/DTA. The measurement was performed in air, at a constant heating rate of 5 °C/min, from room temperature to 1000 °C.

2.3.3. SEM/EDX analysis

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) were used to analyze the microstructure of the powdered slag and volcanic ash and the surfaces of the synthesized geopolymer specimens with an S-3400N device (Japan Hitachi Limited Company). Specimens were impregnated using absolute ethyl alcohol and polished with SiC paper, then coated with gold before measurement.

2.3.4. Compressive strength testing

The compressive strength test was performed on specimens using a DNS100 universal testing machine. The displacement rate was set to 0.5 mm/min. The test was performed on specimens cured at 3, 7 and 28 days. For each composition, at least three replicate samples were tested, and the average strength was regarded as the representative value. The error bar in Figure 9 indicates the standard deviation.

3. Results and discussions

3.1 XRD Analysis

The results of XRD patterns are presented in Figure 3: volcanic ash (a), geopolymer from volcanic ash (b), geopolymer containing 90% volcanic ash and 10% slag (c), geopolymer containing 70% volcanic ash and 30% slag (d), geopolymer containing 50% volcanic ash and 50% slag (e), geopolymer from 100% slag (f) and pure slag (g). Slag was mainly amorphous, with some crystalline reflection around 28-30 degrees. Meanwhile, the crystalline phases found in volcanic ash were mainly aluminian augite, $\text{Ca}(\text{Mg, Fe, Al})(\text{Si, Al})_2\text{O}_6$ (PDF no. 41-1483); sodium anorthite, $(\text{Ca, Na})(\text{Al, Si})_2\text{Si}_2\text{O}_8$ (PDF no. 20-528) and ferroan forsterite, $(\text{Mg, Fe})_2\text{SiO}_4$ (PDF no. 31-795).

Key :

▽ = aluminian augite, $\text{Ca}(\text{Mg, Fe, Al})(\text{Si, Al})_2\text{O}_6$ (PDF no. 41-1483)

● = sodium anorthite, $(\text{Ca, Na})(\text{Al, Si})_2\text{Si}_2\text{O}_8$ (PDF no. 20-528)

◆ = ferroan forsterite, $(\text{Mg, Fe})_2\text{SiO}_4$ (PDF no. 31-795)

Figure 3: XRD patterns of slag, volcanic ash and prepared geopolymers

It was observed after reaction of volcanic ash with sodium silicate solution that no new crystalline phases were formed. This indicates the amorphous character of the newly formed phase. Aside from that, the initial crystalline reflections of the ash were also present in the geopolymer, suggesting the difficulty of dissolving these crystalline phases in the alkaline conditions of the experiment. From the diffractograms (c, d and e), slag addition was found to mainly affect the XRD features of the geopolymer by reducing the intensity of the crystalline reflections. This was due to the relatively amorphous character of slag and the products resulting from alkali activation of volcanic ash/ slag system. Geopolymer resulting from slag (f) was mainly amorphous, with crystalline reflection of the starting slag around 28-30 degrees.

The amorphous fraction in volcanic ash and in other aluminosilicates were suggested to be more sensitive to geopolymer reaction, forming an amorphous geopolymer structure upon alkaline activation [9,27,28]. The presence of the starting crystalline phases in the prepared geopolymers is consistent with some previous studies on geopolymers from laterites [15] or volcanic ashes [20,27]. However, partial dissolution of the starting crystalline phases with possible participation in geopolymer reaction was also reported [15,28].

3.2 FTIR analysis

The infrared spectra of the volcanic ash, geopolymers and slag are presented in [Figure 4](#): volcanic ash (a), geopolymer from volcanic ash (b), geopolymer containing 90% volcanic

ash and 10% slag (c), geopolymer containing 70% volcanic ash and 30% slag (d), geopolymer containing 50% volcanic ash and 50% slag (e), geopolymer from 100% slag (f) and slag (g).

Figure 4: FTIR spectra of slag, volcanic ash and prepared geopolymers

The band around 460 cm^{-1} is ascribed to the bending vibration of Si-O [29,30]. The large band around $800 - 1200\text{ cm}^{-1}$ is ascribed to the stretching vibrations of Si(Al)-O groups usually observed on the spectra of volcanic ash, geopolymers and slag [9,13,30]. This band is common in aluminosilicates material and was suggested to be sensitive to the content of structural Si and Al [10].

The bands around $1400\text{ to }1500\text{ cm}^{-1}$ indicated the presence of O-C-O [30,31], usually ascribed to carbonation of geopolymer materials. The bands around $1640\text{ and }3440\text{ cm}^{-1}$ are attributed to water and correspond to the characteristic regions of O-H stretching and H-O-H bending in H_2O [15,31]. This water corresponds to either adsorbed or

trapped in the structure cavities of the geopolymer [32]. It is noted that the peaks are intensified in geopolymer samples in comparison to the starting slag and volcanic ash, due to increased trapped water molecules in the geopolymer structure.

3.3. Thermal gravimetry Analysis

The TG analysis of the volcanic ash, slag and resulting geopolymers are presented in Figure 5.

Figure 5: TG curves of slag, volcanic ash and referred geopolymers

Volcanic ash presented almost no mass loss until 1000 °C. Slag was stable until 250 °C, temperature at which some mass loss was initially observed. The total mass loss of slag was about 8% at 1000 °C. At variance, inorganic polymers presented their major mass loss bellow 250 °C, with the values of mass loss of about 7%, 10% and 12% at 250 °C for inorganic polymers made from 10, 50 and 100% slag respectively. Hence, the substitution of volcanic ash by slag increased the mass loss below 250 °C. This is

ascribed to the formation of more geopolymer gel since the starting slag was almost stable until 250 °C. The mass loss below 250°C is then attributed to the reaction product of alkali activated slag, mainly CAS-H gel, agreeing with reported studies on alkali activated slag [8], as well as alkali activated volcanic ash [27], where the mass loss around 200 °C was attributed to the formation of CAS-H gel. At 1000 °C, the total mass loss of the inorganic polymer containing 10, 50 and 100 wt% slag was about 10, 16 and 19% respectively. These features of main mass loss below 300 °C are also like those observed on metakaolin based geopolymer [33,34].

3.4. Microstructural characterization

The SEM images of volcanic ash and slag powder are presented in [Figure 6](#). Slag particles ([Figure 6a](#)) were globally smaller than volcanic ash particles ([Figure 6b](#)), in agreement with their particle size information in [Figure 1](#). Volcanic ash particles were mainly composed of Al, Si and Ca elements, similarly to slag particles. However, the latter contained more Ca element.

Element Symbol	Element Name	Atomic Conc.	Weight Conc.
O	Oxygen	59.53	40.38
Ca	Calcium	23.48	39.89
Si	Silicon	9.39	11.18
Al	Aluminium	4.51	5.16
Mg	Magnesium	2.49	2.57
S	Sulfur	0.60	0.82

Element Symbol	Element Name	Atomic Conc.	Weight Conc.
O	Oxygen	69.44	54.87
Si	Silicon	13.06	18.12
Al	Aluminium	8.81	11.74
Na	Sodium	3.05	3.46
Ca	Calcium	2.61	5.16
Mg	Magnesium	1.43	1.72
Fe	Iron	1.03	2.85

Figure 6: SEM images of slag (a) and volcanic ash (b)

The SEM/EDS of composition made of 10% slag (a) and 50% slag (b) revealed a relatively homogenous distribution of Si, Al and Na element, ascribed to a good formation of inorganic polymer (Figure 7). However, from the analysis of the element maps, an incomplete dissolution of Mg rich particles is observed. Considering the ash mineral composition, the Mg rich particles are ascribed to ferroan forsterite.

Figure 7: SEM/EDS of composition made of 10% slag (a) and 50% slag (b)

The hard dissolution of forsterite ferroan bearing phase in the ash is in agreement with reported studies on volcanic ash based geopolymers [35]. The homogenously good distribution of Ca, Al and Si elements is ascribed to the formation of CASH gel.

The CASH gel of alkali activated materials was suggested to be highly stable as C-S-H gel of OPC systems in case of limited structural disorder and proper charge balancing during their synthesis [6]. Beside from that, an appropriate mixture of Ca rich aluminosilicate such as slag and Ca poor material such volcanic ash was suggested to be of potential benefit for the development of mechanical properties due to the formation of a synergetic mixture of CASH and NASH gel [36]. This is likely to be the case in the

present study, considering the positive effect of slag addition in the compressive strength presented in the next section.

3.5. Setting time and compressive strength

The setting times of the geopolymer compositions containing 10%, 30%, 50% and 100 wt% slag are presented in [Figure 8](#).

Figure 8: Initial and final setting time of referred compositions

It is worth pointing out that the initial setting time of the composition made of 100 wt% volcanic ash at 25 °C was above 7 days, hence about 25 times the value of 400 minutes (about 6.7 hours) of the initial setting time of the composition obtained by substituting 10 wt% volcanic ash by slag ([Figure 8](#)). When the amount of volcanic ash substitution by

slag increased from 10 wt% to 50 wt%, the setting time was further reduced, but now in a lesser extent. The setting time is an important parameter for binding materials. It should be reasonable to allow suitable time for mixing and shaping operation. However, when the setting time is more than couple of hours and days, the production efficiency is negatively affected. The use of the current volcanic ash to produce geopolymers for potential building application at 25 °C is highly hampered by the very long setting time and a low compressive strength. However, only 10 wt% substitution of volcanic ash by slag was enough to reduce the initial setting time to a reasonable time. Slag was found to have a short initial setting time (less than 15 min).

Hence, volcanic ash can also be used to extent the setting time of slag based geopolymer to a reasonable value.

The 3, 7 and 28-days compressive strength of geopolymers from the different compositions are presented in [Figure 9](#).

Figure 9: 3, 7 and 28-days compressive strength of referred compositions cured at 25 °C (A) and 60°C (B)

At 25 °C (Figure 9 A), it was observed that the composition made of 100 wt% volcanic ash was still soft and deformable by hand pressure after 7 days; therefore, the compressive strength test was only performed at 28 days for this composition. The compressive strength was found to increase with slag addition in the system until an optimum value of about 85 MPa after 28 days curing for specimens prepared with 50 wt% slag and 50 wt% volcanic ash. The composition made of 100 wt% slag presented a compressive strength of about 80 MPa at 28 day curing at 25°C. However, the 3 and 7 days compressive strength of the composition prepared with 100 wt% slag were about 70 and 75 MPa respectively, above the 3 and 7 days compressive strength of compositions prepared with 50 wt% slag and 50 wt% volcanic ash (about 45 and 60 MPa respectively). At 25 °C, the compressive strength was found to globally increase with the increase of curing time from 3 to 28 days for all the compositions. This was at variance with the

results of samples cured at 60 °C, where the optimum curing time was 7 days for compositions containing volcanic ash and 3 days for the composition containing only slag (Figure 9 B). Reasons for the decrease of strength with curing time at 60 °C are geopolymer gel dehydration and possible micro cracks formation resulting from the dehydration process as the curing time went on. Hence, at 60 °C or higher temperatures, there is no need to extend the curing time beyond 3 days for samples containing only slag and 7 days for samples containing both slag and volcanic ash especially when the curing environment is not saturated in water. These results are consistent with some reported studies on alkali activated materials. Indeed, for geopolymer or alkali activated systems, an increase of the mechanical properties with the curing temperatures is usually observed until a threshold temperature above which there is no strength-gaining [9,37,38]. This threshold temperature was found in some case around 60-70°C [38,39] for some metakaolin based geopolymers, 30-40°C for fly ash geopolymer-Portland cementitious system [37], 60-90°C for low calcium fly ash and volcanic ashes based geopolymers [9,20,37] and 40°C for slag based alkali activated materials [3]. Beyond this temperature, the time for a better dissolution of aluminosilicates becomes insufficient due to a rapid setting of the geopolymer gel formed at the surface of the undissolved particles [3,40]. High temperature curing may also reduce strength due to microcracks formation induced from rapid loss of water when the curing environment is not saturated in water [40]. The positive effect of slag substitution by volcanic ash observed in this study agrees with a reported study carried out by Robayo-Salazar et al. [41] on a Colombian volcanic ash. However, Onoue and Bier [42] observed slag replacement ratio to have little influence on flexural and compressive strengths on geopolymers made from a German volcanic ash.

These divergences are probably linked to the divergence in chemical and mineralogical composition of volcanic ash from diverse sources.

The compressive test and setting time results obtained in the present study suggest that some poorly reactive volcanic ashes could be mixed with ground granulated blast furnace slag or other suitable high calcium rich aluminosilicates to produce structural geopolymers with interesting properties at ambient temperature (around 25 °C). Indeed, moderate addition (8 - 24wt%) of calcium aluminate cement was also found to be beneficial for geopolymer reactions resulting in higher compressive strength [32].

The most important quality index of building materials such as building bricks is their compressive strength [43]. The optimum value of compressive strength obtained in this study (85 MPa) is above the one obtained in many geopolymers prepared from metakaolin or volcanic ashes [21,24,28,29]. These values are also above the minimum requirement for most building materials, including paving brick subjected to light traffic, requesting minimum compressive strength of 17.2–20.7 MPa [43]. The overall results are of great interest for the valorization of volcanic ash for building applications, with related environmental and societal benefits.

4. Conclusions

Geopolymers with very good mechanical properties were successfully prepared from a low reactive volcanic ash and slag at 25 °C. Slag addition was found to have a good effect on both setting time and compressive strength. The development of strength was ascribed to a synergetic formation of C-A-S-H /N-A-S-H gel. Only 10% of slag was enough to reduce the setting time of the geopolymer from more than 7 days to a couple of hours (6.7 hours) at 25 °C. The compressive strength was found to globally increase with the increase in curing time from 3 to 28 days for all the compositions cured at 25 °C, until an optimum value of about 85 MPA. At 60 °C, the optimum curing time was 7 days for compositions containing volcanic ashes and 3 days for the composition containing only slag. The overall results are very significant for the valorization of low reactive volcanic ashes in the development of structural geopolymers, with related environmental and societal benefits.

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