



Influence of the activating solution composition on the stability and thermo-mechanical properties of inorganic polymers (geopolymers) from volcanic ash



Patrick N. Lemouagna^{a,*}, U.F. Chinje Melo^a, Marie-Paule Delplancke^b, Hubert Rahier^c

^a Physico-Chemistry of Mineral Materials Laboratory, University of Yaoundé I, and Local Materials Promotion Authority, MINRESI/MIPROMALO, P.O. Box 2396, Yaoundé, Cameroon

^b 4MAT, Université libre de Bruxelles, Avenue Roosevelt 50, CP 165/63, 1050 Brussels, Belgium

^c Dept. Materials and Chemistry, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium

HIGHLIGHTS

- NaOH promotes faster reaction rate while KOH promotes thermally stable materials.
- Fine particles favor the reactivity and the compressive strength development.
- Geopolymerisation of volcanic ash is not completely similar to that of metakaolinite.
- The volcanic ash geopolymers are relatively thermally stable up to 800 °C.

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ABSTRACT

The influence of the activating solution composition on the stability and thermo-mechanical properties of geopolymers made from a Cameroonian volcanic ash is investigated. NaOH, KOH solutions and silicate solutions with low modulus were tested.

The samples are cured at 90 °C and the mechanical strength increases up to 21 days. With NaOH the strength development is faster, with a dry and wet compressive strength respectively around 40 MPa and 20 MPa at 21 days. The largest particles only act as reactive filler while smaller particles dissolve in the activating solution as seen by SEM. Pure volcanic ash and synthesized materials consisted of mostly X-ray amorphous material with some newly formed crystalline phases. KOH specimens were found to be thermally more stable, shrinking less than 3% after heating till 1000 °C.

The obtained results suggest the possible use of the synthesized materials for building applications and low temperature refractories up to 700–800 °C.

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1. Introduction

Alkali activated cements such as inorganic polymers (geopolymers) have attracted growing interest in the recent years as a possible alternative for manufacturing structural materials, with the potential to contribute substantially to environmentally sustainable construction and building products [1–3]. These materials can be synthesized with a wide range of artificial or natural aluminosilicate materials and the relatively mild involved temperatures allow a flexible processability with the possibility to incorporate organic additives [1,4]. The obtained products are generally thermally more stable, with a much smaller CO₂ footprint than traditional Portland cements, and display good strength and chemical

resistance as well as a variety of other potentially valuable characteristics [2–8].

Geopolymer chemistry involves mechanisms such as dissolution of aluminosilicates (amorphous or semi crystalline) in a strongly basic medium, followed by polymerization of the dissolved species eventually with surface active groups to form a solid geopolymer structure [7–10]. The latter consists of chains and three dimensional networks made of various Q unit types of connected SiO₄⁴⁻ and AlO₄⁵⁻ tetrahedra [1,4,10]. The presence of alkaline ions such as Na⁺, K⁺, Li⁺ in the network is necessary to compensate the negative charge of Al³⁺ in IV-fold coordination [7,10].

Over the past two decades, extended work has been done on the influence of the composition of the activating solution on the reaction kinetics and products properties of metakaolinite and fly ash-based geopolymers [6–13]. Most of the work has however concentrated on thermally treated aluminosilicates. Very few studies have

* Corresponding author. Tel./fax: +237 22 22 37 20.

E-mail address: lemouagna@gmail.com (P.N. Lemouagna).

been reported on these parameters for volcanic ash based geopolymers, despite the huge potential availability of this raw material in several countries with past or present volcanism [14]. It is however clear that using minerals that do not need a thermal treatment to activate them has a large environmental and economic benefit.

The aim of this study was to investigate the influence of the activating solution composition on the thermo-mechanical properties of geopolymers made from a Cameroonian volcanic ash. NaOH, KOH solutions and silicate solutions with low modulus were tested. The reactivity of the systems was studied with Differential Scanning Calorimetry (DSC). The resulting products were characterized by Scanning electron microscopy (SEM), Infrared spectroscopy (IR) and X-ray diffraction (XRD). The products stability was assessed by dry, wet and wet-dry compressive strength measurements. Thermogravimetric analysis (TGA), thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA) were used to investigate the high temperature behavior of the different compositions.

2. Experimental

2.1. Materials

The volcanic ash used in this study was from Cameroon (Foumbot's Petponou site). The material was ground and sieved through a 400 μm mesh. The chemical composition of the volcanic ash as determined by X-ray fluorescence is presented in Table 1.

The sodium hydroxide, potassium hydroxide and amorphous silica pro analyses were used for the preparation of the activating solutions.

2.2. Geopolymer synthesis

The inorganic polymer formulations were obtained by adding, while stirring, volcanic ash into a solution obtained by dissolving in distilled water NaOH and/or KOH with or without amorphous silica, such as to obtain a $\text{M}_2\text{O}/\text{SiO}_2$ molar ratio of 0.30 for mixtures without amorphous silica. An introduction of 3 g of amorphous silica per 21 g of water (or 100 g of volcanic ash) in the mixture led to a $\text{M}_2\text{O}/\text{SiO}_2$ molar ratio of 0.28 for mixtures with amorphous silica. This has resulted in six compositions, three of them without amorphous silica named Va–Na, Va–Na + K, Va–K corresponding to mixtures containing added sodium, sodium + potassium and potassium hydroxide respectively. Their counterparts with amorphous silica were named Va–NaSil, Va–(Na + K)Sil and Va–KSil. For Va–Na + K and Va–(Na + K)Sil preparation, the molar amount of potassium and sodium added were equal. The water/ash ratio (by weight) was maintained at 0.21 for all mixtures. However, as the Va–K composition presented a lower viscosity, a water/ash ratio of 0.18 called Va–K0.18 was also prepared.

The influence of particle size distribution on the reactivity and compressive strength was investigated by removing the coarser particles (about 40 wt% of the initial ash sieved at 400 μm) while sieving at 125 μm . The specimens made with this fraction and sodium hydroxide were named Va(<125 μm)–Na. All prepared mixtures made are summarized in Table 2.

The mixed pastes were placed in cylindrical plastic molds (50 mm height \times 25 mm diameter), then vibrated for 5 min to remove air bubbles before being cured at 90 $^\circ\text{C}$ for 7 and 21 days. The weight loss of the specimens was taken daily during the curing period.

2.3. DSC measurement

Differential scanning calorimetry was performed on a DSC instrument using Helium at 25 mL/min as a purge gas. The samples were mixed in small quantities (800 mg) with a spatula before placing in the sample pan. Reusable high pressure stainless steel sample pans were used. The sample (about 30 mg) was heated from 0 $^\circ\text{C}$ to 240 $^\circ\text{C}$ at 5 $^\circ\text{C}/\text{min}$. Temperature calibration was done with cyclohexane and indium. The latter was also used for enthalpy calibration. At least two measurements were performed for each formulation and the error on the reaction enthalpy was below 10%.

Table 1
Chemical composition of volcanic ash (major elements).

Oxide	Fe_2O_3	MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	SUM
Volcanic ash	12.7	0.19	2.9	11.3	1.7	0.89	43.2	15.1	6.7	4.5	99.2

Table 2
Mixtures composition.

Formulations	$\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar)	$\text{M}_2\text{O}/\text{SiO}_2$ (molar)	$\text{H}_2\text{O}/\text{solid ash}$ (weight)
Va–Na	4.84	0.30	0.21
Va–NaSil	5.18	0.28	0.21
Va–Na + K	4.84	0.30	0.21
Va–(Na + K)Sil	5.18	0.28	0.21
Va–K	4.84	0.30	0.21
Va–KSil	5.18	0.28	0.21
Va–K0.18	4.84	0.30	0.18
Va(<125 μm)–Na	4.84	0.30	0.21

2.4. Product characterization

The compressive strength of the samples was measured with a compression testing machine with a displacement of 1 mm/min. The results shown here are averages of three replicate specimens. At least nine specimens per composition were made for compressive strength measurements (three for the dry, three for the wet and three for the wet-dry compressive test). The dry compressive strength was obtained after curing the products at 90 $^\circ\text{C}$ for 7 or 21 days. For wet compressive strength, these specimens were immersed in water overnight and measured wet while the wet-dry compressive strength is for immersed specimens dried overnight at 40 $^\circ\text{C}$.

X-ray diffraction was carried out on powdered samples using a D500 diffractometer, generating a Cu $K\alpha$ radiation with an applied voltage of 40 kV and a current of 30 mA. XRD scans were measured from 2 $^\circ$ to 70 $^\circ$ 2-theta at a scan rate of 1 $^\circ/\text{min}$.

IR spectra were obtained with a 6700 FTIR instrument. For each spectrum, 32 scans with a resolution of 2 cm^{-1} were used in transmission mode on KBr pellets made with 1 mg of sample and 200 mg KBr.

EDS maps and scanning electron micrographs of polished samples coated with about 20 nm of carbon for secondary electron imaging were determined using a Scanning Electron Microscope with an acceleration voltage of 20 kV.

TGA analyses were performed with a TGA instrument under nitrogen flow of 25 mL/min. The samples were heated to 1000 $^\circ\text{C}$ at 5 $^\circ\text{C}/\text{min}$ and then cooled to 50 $^\circ\text{C}$ at 50 $^\circ\text{C}/\text{min}$.

For dynamic mechanical analysis a DMA 7 was used with a quartz expansion probe (diameter 3 mm). The purge gas was air at 50 mL/min. A static force of 250 mN and a dynamic force of 200 mN with an applied frequency of 1 Hz were used. The samples were cycled twice between 25 $^\circ\text{C}$ to 1000 $^\circ\text{C}$, while equilibrating for five minutes at the minimum and maximum temperature. The heating and cooling rate was 5 $^\circ\text{C}/\text{min}$. Cylindrical samples of about 4 mm in diameter and 10 mm in height obtained from geopolymer paste molded and cured at 90 $^\circ\text{C}$ for 7 days in small cylindrical tubes were used and placed between a platinum cup and lid for measurement.

3. Results and discussion

3.1. DSC measurement

The reactivity of all the mixtures and their DSC curves are presented in Table 3, Figs. 1 and 2. It appears that NaOH containing samples react faster than KOH ones with a peak maximum around 134 $^\circ\text{C}$ versus 187 $^\circ\text{C}$ for KOH. This trend is in agreement with previous reports on inorganic polymers from metakaolinite and silicate solutions [9,11]. The addition of amorphous silica in the mixture leads to a small delay in the reaction and broadened DSC curves. Removing coarse particles (40 wt% of ash particles above 125 μm) leads to an increase of reaction heat of about 30%, with a temperature reduction of the peak maximum of a couple of degrees when using sodium hydroxide as the alkaline activator (Fig. 1 and Table 3). For the potassium system a composition with reduced water content was also tested. This is possible due to the lower viscosity compared to sodium systems. Reducing the water/ash ratio (by weight) from 0.21 to 0.18 leads to an increase

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