



## In-situ carbonation of alkali activated fly ash geopolymer



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### HIGHLIGHTS

- Quick and superior properties are achieved in fly ash based geopolymers by in-situ carbonation.
- In-situ production of CO<sub>2</sub> induces dehydroxylation and mineral sequestration.
- Carbonates also mobilize the Al<sup>3+</sup> ions in the mortar which is essential for the geopolymerization process.
- Higher strength is achieved with lower bulk density of 1.56 g/cm<sup>3</sup>.
- The carbonation effect is justified by different characterization techniques.

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### ABSTRACT

This research work investigates the effect of in-situ carbonation on the properties and geopolymerization of alkali-activated fly ash mortars. The mortars were prepared from fly ash, sodium silicate, sodium hydroxide and different amounts of sodium bicarbonate. CO<sub>2</sub> produced by the decomposition of sodium bicarbonate during curing, was utilized for the fast and improved development of the geopolymer properties. After curing the samples were characterized by TGA-DTA, XRD, FT-IR and SEM in order to understand the effect of carbonation on the thermal behavior, phase composition, degree of polymerization and microstructure of samples. Geopolymers with 2 wt% of sodium bicarbonate shows higher compressive strength and Young's modulus compared to the sample without sodium bicarbonate. The thermal conductivity was found higher for carbonated geopolymer, whereas samples without carbonation show least conductivity.

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### 1. Introduction

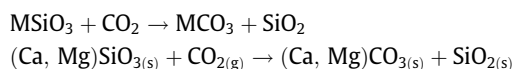
The term geopolymer was introduced in 1970 by Davidovits. Geopolymers are formed by the chemical reaction of aluminosilicates and alkali silicates to form a Si–O–T (T:Si or Al) network. During geopolymer curing, heat is evolved after 4–8 h which indicates that the geopolymerization reaction have been taken place [1,2]. Geopolymers are usually prepared by activating the aluminosilicates with alkali solutions and sets hardened with time, which may span over weeks for higher strengths. To decrease the hardening time and improve strength, different approaches have been proposed. Some researchers have enhanced the geopolymerization reactions by microwave curing, which creates thermal agitations deep down to the middle of the samples and creating less time to process the geopolymers [3,4]. Temuujin et al. have reported the processing of geopolymers at ambient temperature by introducing the slag or calcium rich sources [5]. The accelerated

carbonation of heavy metal wastes promotes rapid stiffening and result in production of monoliths. Carbonation is natural phenomenon where carbon dioxide from the atmosphere gets absorbed by the alkali activated cementitious materials with time and converts this to highly stable mass. This process of hardening is not new to mankind; even in the past hundreds of years ago this process was utilized. Carbonation not only enhances the structural strength but also immobilize the heavy hazardous metals in the waste matter [6]. But the process is slow because of low partial pressure of carbon dioxide in the atmosphere and also because of its low diffusibility to mass. Owing to low concentration and diffusion rate of atmospheric CO<sub>2</sub>, we intend to implement a new technique: in-situ production of carbon dioxide for the carbonation of the alkali activated mortar. In-situ carbonation can be done by adding sodium bicarbonate into the mortar, which decomposes between 150 and 200 °C and produce CO<sub>2</sub>. Similar process is also being used for core and mold hardening in steel making [7]. The CO<sub>2</sub> decreases the pH of the mortar because of its acidic nature, which is helpful in recession of pH from 14 to about 9, for the initiation of geopolymerization reaction and hardening by dehydroxylation of Si–OH

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group [6,8]. A similar process is extensively studied in literature in the name of CO<sub>2</sub> mineral sequestration as follow [9,10].



M is mono (Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>) or divalent (Ca<sup>++</sup>, Mg<sup>++</sup>) metal. This newborn silica is important in hardening mechanism of geopolymers. The optimal composition for geopolymer was found 73% fly ash, 18% water glass, 7% 14M sodium hydroxide solution and 2% water [10,11]. In this work, we intend to study the effect of in-situ carbonation by adding various percentages of sodium bicarbonate. The processing will be done in two steps; pre curing and post curing. The physical and chemical properties of the carbonated geopolymers were investigated and compared to non-carbonated geopolymer samples.

## 2. Materials and method

### 2.1. Materials

Fly ash (FA) was provided by coal fired power plant Federico II, Brindisi-Italy. 14M sodium hydroxide solution in water mixed with sodium silicate (9% Na<sub>2</sub>O, 30% SiO<sub>2</sub> and 61% H<sub>2</sub>O with specific gravity of 1.35 g/cm<sup>3</sup>) was used as alkali activating solution. Sodium bicarbonate (NaHCO<sub>3</sub>) was used in the form of powder.

### 2.2. Preparation of mortar

The fly ash, sodium silicate, sodium hydroxide solution and sodium bicarbonate were mixed in a ceramic jar and milled in eccentric ball mill with alumina balls as grinding media for 10 min. Water may be added later to enhance the workability but with care because excess of water is detrimental for the final properties. The mortar prepared was cast into polyethylene cylindrical molds of 3.6 cm diameter and 6 cm height. The molds were closed with lid and cured at 65 °C for 24 h. After curing, the samples were demolded and final curing was carried out at 150 °C for two hours at ambient atmosphere with 2° rise in temperature. The samples were named according to the weight percentage of sodium bicarbonate used and were prepared by changing sodium bicarbonate from 2% to 14% with a change of 1% in each next composition. But it was observed that samples with greater than 5% were remained as such; even after curing did not solidify. The sample with 5% was in semisolid form after pre-curing. The compositions of the slurries and sample IDs used, are given in the Table 1.

### 2.3. Samples analysis

Fly ash and geopolymer mortars were analyzed through X-ray diffraction pattern obtained using Rigaku diffractometer, with Cu K $\alpha$  radiations. Thermal properties of the geopolymers were investigated using thermogravimetric and differential thermal analysis simultaneously performed from 25 to 750 °C (Mettler Toledo, TGA/DTA). Apparent density was evaluated by helium Pycnometer while bulk density was measured through dividing weight by the bulk volume; calculated by measuring dimensions of the samples. The porosity was calculated from apparent density and bulk density using the following relation:

$$\text{Porosity (\%)} = (1 - \rho_b/\rho_a) * 100$$

whereby  $\rho_a$  and  $\rho_b$  are the apparent density and bulk density respectively. The particle size distribution measured using particle size analyzer. For the bonding characteristics, Fourier Transformation Infrared spectra were measured on ATR spectrometer (Attenuated Total Reflectance Spectrometer) with diamond crystal as a probe. Microstructure analysis of ash and geopolymer samples was carried out using Scanning electron microscopy.

Thermal conductivity was measured using modified transient plane source technique. Compressive tests were carried out using universal testing machine applying ASTM C109 standard protocol.

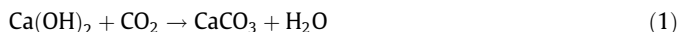
## 3. Results and discussion

### 3.1. Ashes analysis

The given fly ash contains 43% SiO<sub>2</sub>, 24.43% Al<sub>2</sub>O<sub>3</sub>, 15.14% CaO and 10.64% Fe<sub>2</sub>O<sub>3</sub>, 3.16% TiO<sub>2</sub>, 2.39% K<sub>2</sub>O and some traces of Cr<sub>2</sub>O<sub>3</sub>. The mean diameter of the particles was measured to be 28.68  $\mu\text{m}$  as shown in Fig. 1. SEM micrograph of fly elucidates the tiny spherical particles (cenospheres). These are lightweight, inert, hollow glassy sphere derived from coal combustion, which are formed due to melting of aluminosilicates and layering over gas bubbles or unburnt carbon particles. During activation process, this layer is dissolved and the unburnt carbon is exposes [11].

### 3.2. X-ray diffractography

Fig. 2 shows the X-ray diffraction patterns of geopolymerized samples. The major crystalline phase in all geopolymer samples is quartz. Beside quartz (JCPDS 40-1045), other phases like mullite (JCPDS 15-0776), belite (JCPDS 9-351), wustite (JCPDS 43-1312) and hematite (JCPDS 33-0664) were present. Traces of anorthite (JCPDS 89-1462), nepheline (JCPDS 35-424), illite (JCPDS 26-0911), hydroxyl sodalite (JCPDS 11-0401), microcline (JCPDS 19-392), C<sub>3</sub>AH<sub>6</sub> and C<sub>4</sub>AH<sub>13</sub> were also detected [4,12]. Although XRD does not give any direct indication of the geopolymerization reaction but through the formation of different phases, the effect of carbonation can be depicted indirectly. A broad hump correspond to amorphous glassy phase of geopolymer was detected for all the samples from 16° to 38°. Apart from these, a peak observed at 29.5° for carbonated geopolymers, indicating the presence of sodium polysilicate zeolite and CaCO<sub>3</sub>. This characteristic peak is absent in geopolymer made without bicarbonate (FG). Most of the calcium hydroxide and silicates readily transform to calcium carbonate [9,10,13].



Displaced SiO<sub>2</sub> (Eq. (2)), readily react with other silica networks and strengthen the structure. Carbonation is detrimental for the cement and other calcium based materials because of formation of CaCO<sub>3</sub>, which weaken the structure. But in geopolymers, the effect is opposite, where Si and Al are the main network former not the calcium. In addition to CaCO<sub>3</sub>, Na<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>·4H<sub>2</sub>O (sodium polysilicate zeolite) is also formed in carbonated samples, which is the pure crystalline form of zeolite but absent in non-carbonated sample. This indicates that the geopolymerization is more in carbonated samples compared to non-carbonated.

### 3.3. Thermogravimetric analysis

Thermogravimetric analysis is carried out to evaluate the thermal behavior of the geopolymer samples and is presented in Fig. 3. Geopolymer samples with sodium bicarbonate (FGB2–FGB5) show similar weight loss but quite different from the geopolymer without sodium bicarbonate (FG). The weight loss for the sodium

**Table 1**  
Compositions of geopolymers used.

Sample ID	Fly ash	Sodium silicate (%)	Sodium hydroxide 14M	Sodium bicarbonate (%)	Water
FG	73	18	7	–	2
FGB2	73	16	7	2	2
FGB3	73	15	7	3	2
FGB4	73	14	7	4	2
FGB5	73	13	7	5	2

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