



# Production and characterization of geopolymers based on mixed compositions of metakaolin and coal ashes



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## ABSTRACT

Mixtures of coal ashes from pulverized coal combustion (PCC) or fluidized bed combustion (FBC) and metakaolin were used to synthesize geopolymers. Upon full characterization of the raw powders (chemical and mineralogical composition), geopolymerization tests were conducted using an alkali aqueous solution of NaOH/Na<sub>2</sub>SiO<sub>3</sub> at different dilutions. The produced geopolymers were subjected to SEM analysis, as well as to leaching, thermal and mechanical tests. The final microstructure and the properties of the geopolymers indicate that FBC ash can be conveniently used as a partially reactive filler in combination with the metakaolin powder. The composite material has good thermal performance and compressive strength (~30 MPa) suitable for the building sector.

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## 1. Introduction

Ash content in the coal is somewhat high with respect to other fossil and renewable fuels, typical values being in the range 5–20% on mass basis with prevalent presence of quartz and kaolinite [1]. Thus, the ash disposal represents an important issue in the economy of a power station and dedicated coal boilers. The United States produce more than 110 million tons of coal combustion products per year [2], whereas an estimate for European Union is around 50 million tons [3]. Coal ashes are generally classified by international normative (e.g. European 75/442/EEC) as ordinary industrial wastes, although they may be geochemically unstable and environmentally unsafe [2]. Nevertheless, coal ash can offer to the society environmental and economic benefits, when properly managed without harm to public health, and can improve the competitiveness of the coal based energy power-plants.

Pulverized coal combustion (PCC) is the most common burning method used in coal-fired power plants. The combustion takes place at high temperature (1300–1700 °C) with formation of large flames. Due to high combustion temperature, the fly ashes from this process are mostly spherical in shape, the so called cenospheres, with high glassy phase content and also quite chemically reactive. PCC ashes are widely used as pozzolanic material for Portland cement partial replacement [4,5–6].

On the other hand, fluidized bed combustion (FBC) is a well-developed and effective technology for solid fuels, because of its

flexibility toward fuel properties and size [7]. Low-rank coals with high sulfur content can be burnt thanks to limestone addition. The process temperature is kept at moderate and well controlled levels (800–900 °C). The ashes produced in FBC can result enriched in “bed” constituents, such as silica (SiO<sub>2</sub>), lime (CaO) and gypsum (CaSO<sub>4</sub>). Furthermore they exhibit a higher amount of crystalline phase and quite irregular shape. Thus the usage as pozzolanic material is not straightforward.

Geopolymers are amorphous three-dimensional alumina-silicate binder materials, which were first introduced by Davidovits [8]. Geopolymers may be synthesized in the temperature range 20–120 °C by alkaline activation of alumina-silicates obtained from industrial wastes, calcined clays, natural minerals or mixtures of two or more of these materials. Theoretically, any aluminosilicate material can undergo geopolymerization under certain conditions. It has been reported that the microstructures and properties of geopolymers depend greatly on the nature of initial source materials, even though the macroscopic characteristics may appear similar [9–10,11].

In addition to the chemical composition, the thermal history of source materials also plays a significant role on determining the geopolymerization behaviours as well as the final properties of the products [12]. Previous research [10] has shown that geopolymers synthesized from calcined source materials (fly-ash, metakaolin) generally show higher compressive strength than those derived from classic non-calcined ones, suggesting that calcined source materials lead to higher geopolymerization degree. Among the aluminosilicate raw powders, metakaolin is the most reactive in alkaline conditions [13] but due to the largest volume of calcined industrial wastes, fly ash has been widely studied as a

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source material for geopolymer synthesis [14–19]; however, other classes of ashes should be considered for the increasing role of FBC of coal and coal plus biomass. Notably, the combustion in fluidized beds is characterized by a significant lower and well controlled temperature with respect to classical combustion systems. FBC ashes have received the attention only of few research groups [20–24].

The much lower amorphous fraction relying with the lower firing temperature would make FBC ash as an unfavourable raw material for direct geopolymerization. Nevertheless, FBC ashes contain a substantial amount of silica and alumina [25]; therefore, it is likely that they might also be utilized as an alternative source material or partially reactive filler for producing geopolymers suitable for building and construction (bricks or partitioning panels with fire-proof, refractory and passive cooling properties) [24,26].

In this paper, the synthesis of geopolymers of mixed composition using coal ashes and metakaolin was investigated. The metakaolin was taken as reference ingredient, whereas FB and PCC ashes were used in parallel tests of geopolymerization with alkali aqueous solutions of NaOH/Na<sub>2</sub>SiO<sub>3</sub> at different dilutions. The raw powders were fully characterized in terms of composition, microstructure and reactivity (namely Al and Si cations release by sodium hydroxide leaching). The stability in water, the mechanical properties and the thermal behaviour of the produced geopolymers were determined. The results are presented and critically discussed in the paper, also in term of equivalent CO<sub>2</sub> emissions.

## 2. Experimental details

### 2.1. Materials

Alumino-silicate source materials for making geopolymer were:

- Metakaolin obtained via calcination at 750 °C for 2 h in a laboratory kiln with a heating ramp of 100 °C/h in static air of kaolin Argical-BS4 (AGS-Mineraux, Clèrac, France).
- Pulverized coal combustion fly-ash (PCC) obtained at high temperature (1200–1300 °C) from an ENEL SpA (Italy) power plant.
- Fluidized bed combustion ash of Polish coal (FBC) obtained from hot treatment at 850 °C.

The activating alkali aqueous solutions were NaOH/Na<sub>2</sub>SiO<sub>3</sub> solutions with molar ratios SiO<sub>2</sub>:Na<sub>2</sub>O = 2 and H<sub>2</sub>O:Na<sub>2</sub>O = 13.5 or 23.0, respectively named Na-Sil 13.5 and Na-Sil 23. NaOH/Na<sub>2</sub>SiO<sub>3</sub> solutions were prepared by dissolving NaOH pellets (purity >99%, Merck) into distilled water and adding fumed silica powder (99.8%, surface area = 255 m<sup>2</sup>/g, Sigma-Aldrich) or a commercial silicate solution (NaSil 38/40 R3.2, S.r.l. INGESSIL Industria Silicati) under magnetic stirring.

### 2.2. Raw powders reactivity

The reactivity of the powders for geopolymerization was assessed by testing the dissolution extents of Si and Al species from the solid source materials in sodium hydroxide, using a ICP-OES (Varian liberty 200). The leaching of the raw materials was conducted by immersing 0.5000(±0.0001) g of solid sample in 20 ml of NaOH 1 M solution in a glass beaker and stirring magnetically at room temperature. After 5 h of stirring, the solution was acidified, filtrated and diluted. Afterwards the ICP was employed to analyse the Al and Si concentrations in the solutions.

### 2.3. Preparation of geopolymer samples

Geopolymer samples were prepared by activating blends of different powders through mechanical mixing for 20 min at 100

r.p.m. of the alumina-silicate powders with the NaOH/Na<sub>2</sub>SiO<sub>3</sub> aqueous solutions. The powders were thoroughly mixed until uniform mixture was obtained and the resulting slurries were then placed in plastic test tubes.

Three types of geopolymer matrix were prepared by using metakaolin (reference matrix) or blending the alumina-silicate raw powders and an appropriate liquid/solid mass ratio was applied depending on the aqueous dilution (namely the molar ratio H<sub>2</sub>O:Na<sub>2</sub>O = 13.5 or 23.0) of the NaOH/Na<sub>2</sub>SiO<sub>3</sub> solutions and on the workability for each slurry. The reference metakaolin matrix was kept with an atomic ratio Si/Al = 2.0.

The curing method adopted was: test tube sealed for 24 h at room temperature and 24 h at 80 °C in a laboratory heater and test tube opened for 24 h at 80 °C in the heater.

### 2.4. Characterization and analytical techniques

The raw powders were widely characterized in terms of: chemical composition by ICP-OES; mineralogical composition through X-ray diffraction (XRD) (Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation,  $\lambda$  = 0.15406 nm); specific surface area by BET analysis performed using SORPTY 1750 (Carlo Erba Instrument, Milan, Italy); granulometric distributions by SediGraph 5100 (Micromeritics Instrument Corporation, Norcross, USA).

A non-isothermal Simultaneous Thermal Analysis (STA 409 Netzsch) was performed in air with a heating rate of 10 °C/min up to 1300 °C.

The morphological and micro-structural features of consolidated geopolymer samples were examined by SEM (SEM, Cambridge S360; EDS, INCA Energy 300, Oxford Instruments, Oxford, UK); samples non-conductive were coated using a gold sputter coater.

The maximum percentage of absorbed water (WS) reached after water saturation was measured after eleven days of the specimens into distilled water.

Samples stability in water was checked by complete immersion of cubic specimens (10 mm side) in distilled water at 25 °C for 11 days. Samples were preventively dried in a heater at 100 °C and, after cooling, their mass was measured. Sample were held by thin supports in order to avoid any contact with the bottom of the closed vessel. The mass of wet specimens were measured to calculate the percentage of absorbed water in the test period, while the weight loss percentage was calculated on the mass of the tested specimens after drying at 100 °C.

Thermal characterization was performed with dilatometer (DIL402E Netzsch) on 5 mm-long bars up to 1000 °C in static air (heating rate 10 °C/min).

Compressive strength tests were carried out on 5 cylindrical specimens (diameter: 10 mm, height: 20 mm) for each sample, using a Zwick Z050 testing machine (Zwick GmbH, Ulm, Germany). The crosshead speed was set at 1 mm/min. Nylon cylinders (h: 20 mm;  $\phi$ : 10 mm) put over a silicon rubber slab have been used as open-base moulds to produce samples suitable for compression strength tests. The cylindrical samples were obtained by filling the moulds with fluid cement pastes. The cylindrical samples were also machined to guarantee the opposite base faces flat and parallel.

## 3. Results and discussion

### 3.1. Raw powders reactivity

#### 3.1.1. Characterization of raw powders

The chemical composition of the raw powders is reported in Table 1. The aluminium and silicon percentage in PCC and FBC ashes

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