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Thermal cycling stability of fly ash based geopolymer mortars

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ABSTRACT

In this paper fly ash based geopolymer mortars have been prepared and their thermal behavior evaluated in order to assess the suitability of fly ash based alkali-activated binders for thermal energy storage in solar thermal plants. Different parameters, such as binder/aggregate ratio, percentage of fly ash replaced by slag, temperature and curing time, have been changed and optimized using the Design Of Experiments (DOE) approach. In order to estimate the thermal cycling stability of geopolymeric mortars at elevated temperatures, mechanical strength and weight loss of each sample subjected to different thermal cycles in the temperature range 150–550 °C were evaluated. Finally, thermal conductivity of some of the mixtures, selected on basis of the thermal stability test results, have been measured.

Fly ash based geopolymeric mortars remained stable after each thermal treatment and specimens treated at elevated temperatures retained acceptable compressive strength. The thermal stability was preserved also after repeated thermal cycles, proving that fly ash based geopolymers are suitable materials for thermal energy storage concretes.

1. Introduction

Geopolymers are hydraulic binders produced from the reaction of natural or synthetic silico-aluminate powders, often generated from industrial waste [1], in an alkaline environment (silicate solution and sodium hydroxide and/or potassium). Recently, geopolymers have been proposed in different applications, in the military and aeronautical field, as high-tech ceramic materials, thermal insulators, fire-resistant materials, protective coatings, refractory adhesives and hybrids inorganic-organic composites [2–7].

Geopolymers have been proposed also as a viable alternative to cement in concrete. In fact, in order to reduce the environmental impact of standard OPC concrete, the most employed material in the world after water, two routes can be pursued: 1) the use of eco-sustainable aggregates [8–12]; 2) the use of eco-sustainable binders, such as geopolymers [13–20]. A third option, the most environmentally friendly, is a combination of the first two.

Geopolymers also provide an opportunity to convert a variety of waste streams into useful by-products [20]. These materials show excellent thermal resistance (T > 1200 °C), even for long exposures to high temperatures [21,22]. Fly ash and blast furnace slag based concretes have been tested for thermal resistance up to 800 °C, evidencing a decay of the properties at temperatures higher than 600 °C [23,24]. Moreover, thermal resistance can be further improved using different strategies [18,25–28].

Fly ash and other natural and industrial by-products, currently disposed of as waste, have been researched as potential reuse opportunities [29–34] especially as a supplementary cementitious material in cement [35] and as a feedstock for geopolymers [36–42]. A recent paper concerning the numerical modeling of concretes for thermal energy storage (TES) [43] showed promising results on the use of fly ash based geopolymer concrete for this purpose.

In this paper, fly ash based geopolymeric mortars were prepared and characterized in order to evaluate their thermal behaviour under repeated thermal cycles. Low calcium fly ash and blast furnace slag were employed as aluminosilicate source and some different process parameters were changed, such as the binder/aggregate ratio, the percentage of fly ash replaced by slag, the temperature and the time of curing. One of the goals was to assess the suitability of fly ash based geopolymer binders for thermal

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energy storage (TES) in solar thermal plants.

This application requires not only resistance at high temperature, but also to prolonged thermal cycles [44]. Thus, the thermal behavior was assessed by monitoring physical-mechanical properties before and after thermal cycles, this approach being more representative of the actual operative conditions respect to thermal treatments constituted by a heating ramp, an isothermal step and a slow cooling.

In the present paper, mechanical strength, ultrasonic pulse velocity, weight loss and microstructural features of each mortar subjected to different step thermal cycles in the temperature range 150–550 °C, were evaluated. Applied testing conditions are much harsher than actual operative situation, where heating and cooling rates are slower. Thermal conductivity of selected mortars, based on the results of thermal tests, was also measured in order to assess the effective application of these materials.

2. Materials and methods

Geopolymeric mortars were prepared starting from fly ash with low calcium content (Class F – ASTM C 618) deriving from the combustion of coal. Fly ash (FA), supplied by ENEL (Brindisi, Italy) did not meet standard specifications EN 450 (EN 450-1:2012) for use in concrete thus potentially showing a lower pozzolanic activity [45].

Composition of FA is reported in Table 1. The alkaline solution was prepared mixing a sodium silicate solution (SS) (Na_2O 8.15 wt%, SiO_2 27.40 wt%) provided by Prochin Italia S.r.L. (Marcianise (CE)) with 10 M sodium hydroxide solution (N) prepared starting from NaOH in pellets (NaOH 98 wt%, J.T. Baker, "Baker analyzed") and bi-distilled water. The weight ratio SS/N/FA was 1: 1: 3, based on previous studies results [45]. The sand used as aggregate is a standard (UNI-EN 196-1:2016) siliceous sand.

In some of the mixtures, ground granulated blast furnace slag (GGBFS), supplied by Italcementi (Brindisi, Italy) whose composition is reported in Table 1, was added in replacement of fly ash.

The organization of the experiments was conducted using the Design Of Experiments (DOE) approach, considering a system of four factors that can change on three levels. DOE technique enables designers to control simultaneously the individual and interactive effects of many factors that could affect the output results for any design. The space of the experiments was explored using a fractional factorial design (an orthogonal array (L9) has been used [46]). The binder/aggregate ratio (B/A), the percentage of FA substituted by GGBFS (A), the temperature (T) and time of curing (t) were chosen as the active factors. The resulting matrix of experiments, containing the different levels used for each parameter, is shown in Table 2.

Solid raw materials, fly ash, sand and, eventually, blast furnace slag, were mixed and dry homogenized in a Hobart mixer for 5 min, then the alkaline solution was added to the dry mixture and mixed for further 10 min. The binder/aggregate ratios chosen were 1:0.75, 1:1 and 1:2. The mixtures were subsequently cast in cubic Plexiglas molds (5x5x5 cm), covered by a PVC film to prevent evaporation and cured at 25, 40 or 60 °C for 24, 48 and 168 h. After this period of curing, the specimens were removed from the molds and stored at room temperature. After 28 days, three specimens for each mixture were tested for compressive strength using a compressive strength test machine Controls (mod. MCC8) with a load cell of 300 kN.

The remaining specimens were subjected to thermal cycles as follows: three specimens for each mixture underwent a thermal treatment in air at five different temperatures, i.e. 150, 250, 350, 450 and 550 °C, using a Nabertherm HTC 03/15 oven. These temperatures were chosen to evaluate the behaviour of the mixtures at thermal levels similar or slightly higher than those experienced in a TES system [43]. The thermal treatment was performed according to the following procedure: each specimen, put in the oven at the specified temperature, was removed after 30 min, left on a refractory brick at room temperature for 5 min and subsequently its mass was measured. A Mettler Toledo XS105 Dual Range microbalance with an accuracy of ±0.1 mg was used. This procedure was repeated 8 times, for a total of 4 h of thermal treatment. In this way, it was possible to evaluate the thermal shock resistance of the material inasmuch as each specimen was subjected to a series of nine rapid heating and cooling cycles. Furthermore, at the end of each series of thermal treatments, the compressive strength of the specimens was measured. The apparent density of the specimens before and after thermal treatment was calculated by dividing the mass by the geometrical volume.

Mechanical properties of mortars were estimated also by ultrasonic non-destructive testing. The ultrasonic measurements were performed weekly during the 28 days of curing on each mortar using an ultrasonic pulse velocity (UPV) tester Matest mod. C368, in order to determine the time of propagation of pulses within the considered materials at different moments of curing.

The UPV test was used as a non-destructive technique to evaluate qualitatively the stiffness evolution of the mixtures, which is primarily influenced by the amount of percolated solids, the porosity and the inner cracks of the paste. Recently, an alternative technique, i.e. Acoustic Emission Technique, has been used for the same purpose [47].

Usually, the UPV results are correlated to dynamic elastic modulus of concrete. No theoretical correlation exists between UPV and strength, so ultrasonic testing is useful if intended as complementary tool. The equipment used for the testing is a UPV tester with microprocessor compliant with BS1881:203, EN 12504 part 4, ASTM C597, EN/ISO 8047.

Room temperature thermal conductivity was measured by using a Unitherm 2022 instrument, by Anter Corporation. This measurement was carried out on mortar discs (d = 5 cm; H = 1.25 cm) according to the guarded heat flow meter test method (ASTM E1530). Four specimens were employed for each mortar.

Furthermore, geopolymer samples were subjected to SEM observation to evaluate microstructural features. Freshly fractured surfaces were coated with gold and observed by a FEI Quanta 200 FEG microscope.

3. Results and discussion

In Table 3 the compressive strength (R_c) after 28 days of curing, the variations of mass ($\Delta\mathbf{m}$), density ($\Delta\boldsymbol{\rho}$) and mechanical strength ($\Delta\mathbf{Rc}$) of each sample after the 150°C- thermal treatment are reported.

Compressive strength of untreated samples was rather low

Table 1
Chemical composition of fly ash and slag (wt%).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	other oxides	SO_3	LOI
FA	53.7	28.1	6.99	4.32	1.59	1.89	0.87	2.54	–	4.53
GGBFS	35.16	10.76	1.40	41.91	7.68	0.14	0.11	0.92	1.92	1.78