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Alkali activated waste fly ash as sustainable composite: Influence of curing and pozzolanic admixtures on the early-age physico-mechanical properties and residual strength after exposure at elevated temperature

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ABSTRACT

Waste fly ash, referred in literature also as "weathered", represents a major management issue for coal-fired power plants. The low qualification of this relevant fraction of produced fly ash is not adequate for recycling in structural concrete. Non-structural applications may represent an economically feasible solution to maximize the recovery of coal fly ash from power plants. A potentially valuable recycling track may be represented by alkaline activation for the production of sustainable precast elements based on geopolymeric binders. In this work, three mineral admixtures, namely blast furnace slag, silica fume and metakaolin, were used to synthesize binary alkali activated binders whose major volumetric fraction was waste fly ash. Three curing temperatures (20, 40, 60 °C) were also considered. Early age kinetics and properties development were assessed by means of strength development and ultrasonic pulse velocity. Residual compressive strength after exposure at high temperature was also assessed in order to highlight typical geopolymeric thermal resistance which is generally observed for higher value raw materials. Furthermore, microstructural analysis was carried out by means of scanning electron microscopy. Silica fume exhibited an increasing detrimental effect (formation of agglomerates/partial foaming) with early age curing temperature, while blast furnace slag and metakaolin revealed to be effective admixtures without strict need of higher curing temperatures.

1. Introduction

Despite worldwide growth of investment related to renewable energies, coal-fired power plants still represent one of the major energy source for industrialized countries. At the same time, it should be considered that latest Figures suggest that the issue of complete recycling of coal fly ash (CFA) is not fully addressed [1]. Construction sector is only one of the potential market for CFA, which can be recycled for other relevant applications such as soil amelioration, production of ceramics, catalysis, metal recovery, etc. Due to management issues related to the very large amount of daily produced CFA, there is a major fraction whose recovery process is limited, determining several problems such as: lack of qualification process for recovery in construction sector according to international standards such as EN 197, EN 206, EN 413, EN 450, EN 13282, EN 14216, EN15368 [2–8]; very low reactivity or very large particles size (coarse fly ash); storage under aggressive conditions (wetting cycles). Waste fly ashes (WFA) are produced when the demand of CFA by the local market is lower than it would be required to consume the whole amount of fly ashes daily produced. CFA is produced at a rate of about 20–25 t/h from each unit of 660 MW and typically collected in a 2000 m^3 silo per each unit [9]. Generally, it can be estimated that the fly ash stocking capacity of a power plant does not overcome 4–5 days of full production. Hence, a very effective industrial interaction needs to be implemented to recovery the total amount of daily produced CFA. Furthermore, it can be estimated that up to 20 trucks per day are needed to transport CFA by each 660 MW unit [9]. Since this process is rarely set up, temporarily out-silo stocked fly ash are generated. The typical destination of WFA is landfill disposal depending on several

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factors: (i) costs and the feasibility of the drying process, which for such huge amount of by-product could be excessive; (ii) storage conditions in ready mix concrete plants, since their silos are designed to store dry powders; (iii) periodical oscillations in concrete consumption, with a typical decrease in coldest months. In those periods, the increase of WFA storage volumes is very large and more effective technological processes are needed in order to avoid landfilling.

Alkaline activation may represent an effective technology to maximize the recycled quantity of total CFA produced. Binders realized by means of alkaline activation are usually referred as alkali activated materials (AAMs). AAMs can be synthesized by means of alkaline activation of several solid precursors such as CFA [10–12], calcined clays [13–15], etc., allowing at the same time the reduction of environmental impact respect to clinker production and the achievement of valuable engineering properties, in terms of mechanical [16], environmental [17] and functional [18–20] performance. Dealing with alkali activated fly ash (AAFA), recently, Atiş et al. [12] reported results related to alkali activated class F fly ash achieving compressive strength values higher than 100 MPa. The perspective of recycling also CFA with lower commercial value by means of alkaline activation was evaluated by Mejia et al. [21], who studied the potential valorization of CFA with high content of unburned material (loss on ignition equal to about 14.6%).

This study deals with the alkaline activation of WFA characterized by low reactivity at early age. Starting from promising results of a previous study where only 20 °C curing temperature was considered [22], the present experimental program was designed in order to enlighten supplementary features. Particularly, the effect of higher curing temperatures, namely 40 °C and 60 °C was considered. Furthermore, analysis of mechanical properties, evaluation of residual strength after high temperature exposure and microstructure, were assessed.

2. Materials and methods

WFA was obtained by the power plant located in Brindisi (Italy) managed by ENEL (Italian Electricity Board). Commercial supplementary cementitious materials such as blast furnace slag (BFS), silica fume (SF) and metakaolin (MK) were used. Raw precursors (except SF for which technical report was considered) were dried and then submitted to quantitative chemical analysis performing X-ray fluorescence (XRF) by means of a Bruker Explorer S4 apparatus. Results of XRF analysis related to main oxides are reported in Table 1. Different particle morphologies were observed by means of scanning electron microscope (SEM) analysis. In Fig. 1, the particle morphologies of WFA (1000x), SF (5000x), BFS (5000x) and MK (5000x), were reported. WFA showed generally the coarsest particle size distribution, while SF exhibited typical high specific surface area. Finally, the typical flaky irregular particles of MK were detected.

The reference mixture was made by using only WFA as solid precursor (WFA1). Three types of binders were considered: 1) mixtures of WFA as the major component and BFS in addition percentages of 10 (BFS1) and 20% (BFS2) respect to the mass of WFA; 2) mixtures of WFA as the major component and MK in addition percentages of 10 (MK1) and 20% (MK2) respect to the mass of WFA; 3) mixtures of WFA as the major component and SF in addition percentages equal to 5 (SF1), 10 (SF2) and 15% (SF3) respect to the mass of WFA. In order to perform alkaline activation, a blended alkaline activating solution (AAS) was considered by combining 10 M NaOH solution with a Na_2SiO_3 solution of grade 3.2 (provided by Prochin Italia srl) in a mass ratio equal to 1:1. A separated mixing procedure was considered. For all the mixtures, fly ash was first mixed for 5 min with 10 M NaOH solution and left in contact for a total duration of 20 min. Then the supplementary cementitious material was added and, finally, sodium silicate solution was poured into the mixer. All mixtures were mixed for a time of about 5 min. The mass compositions of mixtures are reported in Table 2 and readapted from Ref. [22].

Table 1
Oxide composition of raw materials.

Oxides	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	MgO	LOI
WFA	44.3	20.2	10.5	8.1	0.5	–	11.30
BFS	35.16	10.76	1.40	0.14	41.91	7.68	1.78
SF	>85	–	–	–	–	–	<4.0
MK	51.20	43.98	1.12	0.54	0.075	0.091	4.0

Among the investigated mixtures, it can be observed that solution to precursor ratio is modified only by slight variations due to different percentages of pozzolanic additions.

The development of mechanical properties at early age was monitored by means of unconfined compressive strength (UCS) testing executed on paste samples with a Controls® 50-C1201/FR (max. load of 100 kN). Tests related to UCS were performed at 2 and 7 days. The tests were carried out on small cylinder samples of binder with diameter equal to 27.5 mm and length equal to 40 mm. All samples were slightly vibrated for about 1 min after casting and, then, cured for 7 days under sealed conditions at different early age curing temperatures, namely 20 °C, 40 °C and 60 °C, for the first 48 h. Afterward, the samples were cured for additional 5 days at 20 °C in a climatic chamber. For each paste, three cylindrical samples were tested. The ultrasonic pulse velocity (UPV) test was used as a non-destructive technique to monitor the stiffness evolution of the pastes, which is influenced by the following parameters: (i) amount of percolated solids; (ii) porosity; (iii) internal cracks of the matrix. The equipment used for the testing is a UPV tester compliant with BS EN 12504-4:2004 [23]. The samples tested by means of UPV were cured for 7 days under sealed conditions, at different temperatures, namely 20 °C, 40 °C and 60 °C. For each binding mixture, three cylindrical samples were tested.

Residual compressive strength was measured after exposure to a thermal load realized by means of a laboratory muffle. Measurements were carried out after initial (48 h) variable temperature curing and subsequent 26 days curing at 20 °C in a climatic chamber. The thermal program was designed taking into account the logarithmic cellulosic ISO 834 curve [24], which is defined by means of the following equation:

$$T = 20 + 345 \log_{10}(8t + 1) \quad (1)$$

where T is temperature expressed in °C and t is the time expressed in minutes. According to ISO 834 cellulosic curve, the material is exposed at about 842 °C after 30 min. In order to define a thermal load for AAMs here investigated, a thermal linear load was programmed by means of a laboratory muffle with maximum temperature equal to 840 °C reached after 30 min (see Fig. 2).

Microstructural analysis was carried out also on binder samples by means of SEM images. The images were taken after initial curing at variable temperature for 48 h and subsequent curing at 20 °C in sealed conditions until 28 days.

3. Results and discussion

3.1. Physico-mechanical properties

Results related to early age mechanical properties were reported in Figs. 3 and 4. At very early age (2 days curing, Fig. 3), due to waste nature of WFA, the reactivity in alkaline environment is very low. At