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Mechanical performances of weathered coal fly ash based geopolymer bricks

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Abstract

In this paper weathered coal fly ash has been used in polycondensation processes aimed at the production of geopolymer–based low temperature ceramic bricks. The ash has been employed both "as received" and after drying, showing favorable reactivity in any case. Different curing conditions with a variable period at 60 °C have been tested. Samples obtained have been characterized by measuring Unconfined Compressive Strength (UCS) and by SEM observations. Good strength values have been obtained with the systems tested. Furthermore, it has been found that mechanical performance increases as the time during which samples are kept at 60 °C increases.

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1. Introduction

In the last thirty years, new silico-aluminate inorganic polymers, named geopolymers by Davidovits in 1979 [1], have emerged as components of a new class of low-energy materials characterized by highly desirable chemical and mechanical properties. Such materials are now of great interest for a wide range of applications in several different sectors of engineering [2].

In the field of civil engineering, geopolymer-based materials are also referred to as "alkali-activated

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cements" or "chemically-bonded ceramics" obtainable starting from raw materials with low (or zero) CaO content.

The synthesis of geopolymers can be carried out by mixing reactive silico-aluminate materials with strongly alkaline solutions such as alkali metal (Na, K) hydroxide or silicate. In such reaction environment the silico-aluminate reactive materials are rapidly dissolved. A complex reaction mechanism follows in which solubilized silica and alumina condensate with the ultimate formation of a three-dimensional geopolymeric network [3]. This phase is crucial in relation to the final product properties that strongly depend on the degree of cross linking among the different silico-aluminate polymeric chains. To this regard, temperature is the most important process variable whose increase up to about 90-100 °C greatly improves cross linking in an amorphous structure. At higher temperature, up to 200 °C, zeolite-like crystalline products are formed [4].

The synthesis of geopolymers has been carried out starting from a wide variety of virgin raw materials such as metakaolin [5], clay [6] and other natural silico-aluminates [7] as well as industrial process wastes such as coal fly ash [8], lignite bottom ash [9] and metallurgical slag [10]. Among these wastes, coal fly ash is by far the most interesting one, due to its widespread availability all over the world. Although many different options can be put into practice for fly ash material recovery, only a small fraction of the about 450 Mton yearly produced is managed accordingly. Hence, the study of new proposals aimed at widening the possibilities to recycle coal fly ash is well worthy of consideration, especially as far as the manufacture of geopolymer-based materials is concerned. The reason for this is due to the fact that good quality building materials can be produced starting from a waste like coal fly ash.

In the light of these considerations it is not surprising that many papers can be found in the literature concerning the use of coal fly ash for the manufacture of geopolymeric binders [11] and ceramics [12]. Specifically, the former applications deal with the possibility to replace Portland cement in mortar [13] and concrete [14] formulations as well as in the stabilization/solidification of hazardous solid wastes [15].

Despite the good physico-mechanical properties of the above building materials and the environmental and economical benefits linked to the implementation of the related production processes (reduced CO_2 production and energy consumption, safeguard of natural resources), the commercial exploitation of the above management options is still very limited. The reasons for this are due to technical difficulties, commercial barriers and regulatory issues [16]. As far as the first point is concerned, the hindrance against large scale application of the geopolymer technology is the need to handle a strong alkaline solution of high hazardous potential, due to its corrosive and dangerous properties.

Barriers such as those outlined above may not exist if the possibility is taken into account to replace pre-cast concrete elements and ceramic bricks with geopolymeric hardened products to be manufactured in specifically designed industrial plants.

A host of performance properties, such as high compressive strength, rapid controllable setting and hardening, fire resistance without emission of toxic fumes, resistance to acid and salt solutions, low shrinkage and thermal conductivity, high surface definition that replicates mould patterns, makes geopolymer-based materials very suitable for the manufacture of masonry units [16]. To this regard, it is to be pointed out that, according to European regulation [17], the masonry units must be produced in compliance with certified values of some physical properties (size, density, …) and thus it is important that the ultimate products can be made with high technological and commercial confidence, as it is the case of geopolymer-based units.

In this work the possibility to produce bricks by geopolymerization of mixtures of low Ca coal fly ash by means of sodium silicate/NaOH solutions has been studied. Differently from the majority of the papers that can be found in the literature on this topic, the study has been focused on the possibility of using fly ash coming from wet storage, without drying. Storing fly ash into ponds is a worldwide common

procedure linked to the need of avoiding fine powders dispersion in the environment [18]. In the case under investigation, fly ash comes from a temporary storage basin which is periodically sprinkled with water. The resulting ash is of moist consistency with water content much lower than that would be given by pond storage. Then, expensive drying is not necessary and the ash water content can be accounted for in the preparation of the activating solution.

The optimized fluid mixtures are simply cast into the mould and submitted to the curing treatment, without cold pressing [19]. After curing, the bricks have been characterized by Unconfined Compressive Strength measures and by SEM observations.

2. Experimental

2.1. Materials

The wet fly ash employed in this work was supplied by the ENEL SpA power plant located in Brindisi (Southern Italy). The water content was found to be 17 wt% after drying in oven at 105 °C until constant mass. The fly ash chemical composition was obtained by means of a Perkin-Elmer Optima 2100 DV ICP-OES apparatus. To do so, a weighed amount of fly ash was submitted to microwave digestion in a Perkin-Elmer Multiwave 3000 oven using a standard solution of HCl, HNO_3 and HF followed by H_3BO_3 fluoride complexation.

The fly ash particle size distribution was determined by means of a Malvern Mastersizer 2000 laser particle analyser.

The mineralogical composition was determined by means of X-ray diffraction analysis using a Philips PW1730 apparatus.

The sodium silicate solution was supplied by Prochin Italia S.r.l. with the composition SiO_2 27.40 wt% and Na_2O 8.15 wt%. Analytical grade sodium hydroxide from Baker was used in pellet form to get solutions of concentration 10 M and 14 M.

2.2. Samples preparation

Table 1 shows the complete set of polycondensation mixtures employed for samples preparation.

System 1.1 contains 1000 g of dry ash with additions of 200 g of the commercial sodium silicate solution and 250 g of 14 M NaOH solution. This composition has been designed on the basis of literature data and is expected to give hardened products of good physico-mechanical properties. The SiO_2/Na_2O molar ratio is 0.61 and the w/w ratio between water and total solids (including ash, SiO_2 and Na_2O) is 0.28. System 1.2 differs from the previous one inasmuch as the equivalent amount of wet ash is employed. The SiO_2/Na_2O molar ratio is kept constant while the water/(total solids) w/w ratio increases to 0.45. In system 1.3, wet ash is employed, but the addition of the commercial sodium silicate solution and solid NaOH are such that the SiO_2/Na_2O molar ratio is kept constant at 0.61, while the water/(total solids) w/w ratio is brought to 0.28, as for system 1.1.

The design criteria for systems 2.1, 2.2 and 2.3 is the same as for systems 1.1, 1.2 and 1.3, with the difference that 10 M NaOH solution is used with constant SiO_2/Na_2O molar ratio at 0.76 and water/(total solids) w/w ratio equal to 0.31 (2.1 and 2.3) and 0,49 (2.2). This set of systems shows a better workability in respect to the previous one.

Table 1. Composition of systems tested

Sys tem	Dry ash, g	Wet ash, g	Sodium silicate solution, g	NaOH solution, g	Solid NaOH, g	H$_2$O, g	SiO$_2$/Na$_2$O molar ratio	H$_2$O/(total solids) w/w ratio
1.1	1000	-	200	250 (14 M)	-	-	0.61	0.28
1.2	-	1205	200	250 (14 M)	-	-	0.61	0.45
1.3	-	1205	168	-	82	-	0.61	0.28
2.1	1000	-	244	306 (10 M)	-	-	0.76	0.31
2.2	-	1205	244	306 (10 M)	-	-	0.76	0.49
2.3	-	1205	244	-	92	9	0.76	0.31

A Hobart mixer was employed to homogenize the polycondensation mixture. Afterword, the mixes were poured into a series of cylindrical polyethylene molds of size d x h = 3 x 6 cm^2. The molded samples were cured 8 days according to four different curing schemes as follows: (a) the whole 8 days time at room temperature; (b) 1 day at room temperature, 1 day at 60 °C, 6 days at room temperature; (c) 1 day at room temperature, 2 days at 60 °C, 5 days at room temperature; (d) 1 day at room temperature, 7 days at 60 °C. After curing, the samples were de-molded, wrapped and stored at room temperature.

2.3. Samples characterization

Cured samples were characterized through the determination of several structural and physico-mechanical properties.

The structural characterization was carried out by means of scanning electron microscopy (SEM) using a FEI Quanta 200 FEG microscope equipped with an EDS probe for surface elemental analysis, while the mechanical characterization was carried out by testing the samples for their unconfined compressive strength.

The unconfined compressive strength (UCS) was determined by means of a uniaxial compression Controls MCC6 testing machine.

3. Results and discussion

The chemical composition of the fly ash, on dry basis, is: SiO$_2$, 53.75 wt%; Al$_2$O$_3$, 28.12 wt%; Fe$_2$O$_3$, 6.99 wt%; CaO, 4.32 wt%; K$_2$O, 1.89 wt%; MgO, 1.59 wt%; Na$_2$O, 0.87 wt%. It is a typical composition of a low Ca coal fly ash, with silica being the most abundant compound. Then it is expected that will readily react in a polycondensation process.

X-ray diffraction analysis (not reported) shows that even the mineralogical composition is typical of a low Ca coal fly ash. In fact, it is highly amorphous with the presence of a small amount of Quartz and Mullite, evidenced by low intensity diffraction peaks.

The particle size distribution of the fly ash is showed in figure 1. The Sauter diameter is 6.4 μm, while the value of d$_{50}$ is 28 μm. In addition, only less than 10 % of ash particles have a size greater than 100 μm. These data are favorable in respect to reactivity in a polycondensation process.
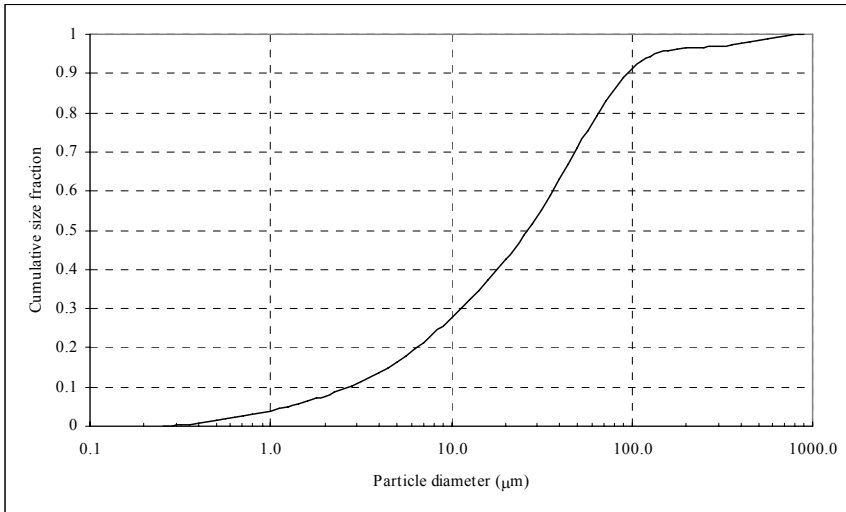
Fig. 1. Particle size distribution of fly ash

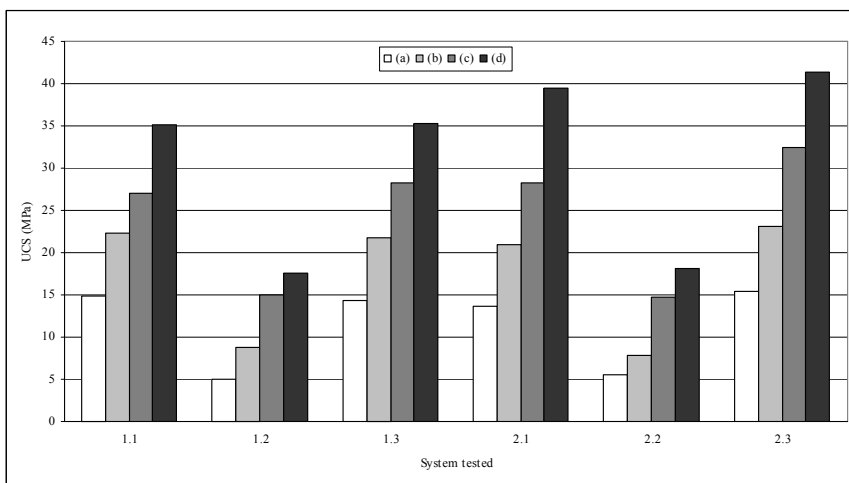Figure 2 shows the results of UCS determinations carried out in all the cases studied.

Fig. 2. Unconfined Compressive Strength (UCS) of the systems tested ((a), (b), (c) and (d) curing schemes)

The results shown are the average of three samples.

The comparison between the results for system 1.2 with those for system 1.1 on one side and between the results for system 2.2 with those for system 2.1 on the other side, clearly shows that a great negative effect occurs when wet ash is employed instead of dry ash. Increasing the water/(total solids) ratio from 0.28 to 0.45 in the former case and from 0.31 to 0.49 in the latter case, causes a very strong reduction of UCS at any curing condition.

Such reduction ranges from 45 % (system 1.2 vs. 1.1, curing conditions (c)) to 66 % (system 1.2 vs. 1.1, curing conditions (a)).

The comparison of the results for systems 1.3 and 2.3 with those for systems 1.1 and 2.1, respectively, shows that the use of wet ash is not inherently unfavorable in respect to UCS development, provided that the compositional ratios are kept constant.

The other strong effect clearly evident from the data in figure 2 is the positive one due to higher curing temperature. In fact, UCS steadily increases when the curing time at 60 °C increases. This holds for any system; specifically the increase in UCS ranges between 2.4 times (system 1.1) to 3.5 times (system 1.2). These increases are so strong that reasonably good UCS values are reached even in the cases of those systems unable to develop satisfactory UCS at room temperature (systems 1.2 and 2.2).

The results of UCS determinations are corroborated by SEM observations, as reported in figures 3, 4 and 5.
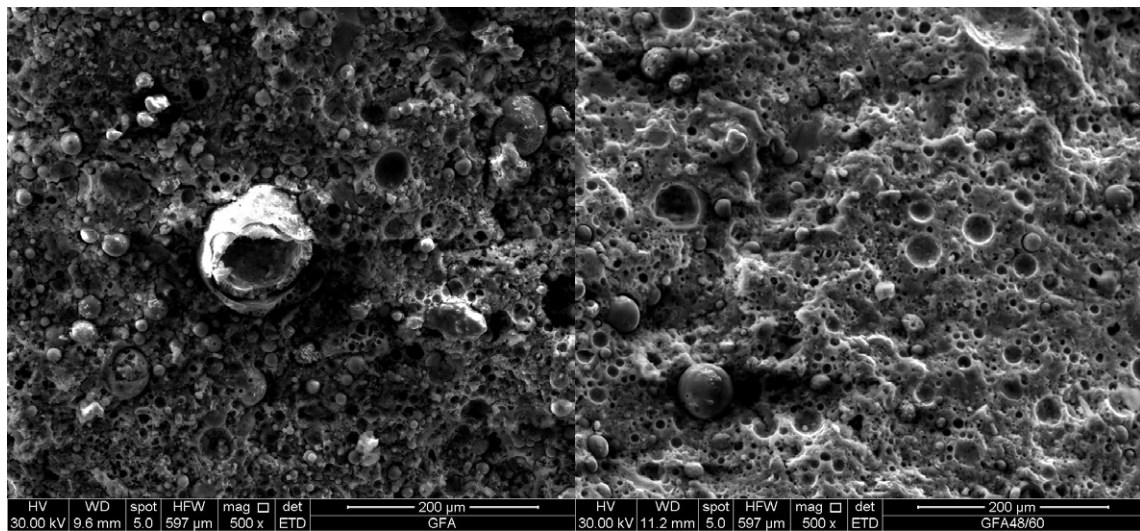

Fig. 3. Micrographs of system 1.1 subjected to curing treatment (a) (3a) and curing treatment (c) (3b)

Figure 3 shows two micrographs of system 1.1 cured under conditions (a) and (c). Curing at room temperature (Fig. 3a) gives rise to a scarcely compact structure in which many unreacted spherical fly ash particles are clearly seen. On the other hand, when curing is carried out according to conditions (c) (48 h at 60 °C), a much more compact structure is obtained, as seen in Fig. 3b. The cavities in this figure are ash particles imprints and not porosity voids.

Figure 4 is analogous to figure 3, but for system 1.2. In this case, curing at room temperature (Fig. 4a) has the effect to give rise to quite incoherent structure, while curing at higher temperature (48 h at 60 °C) increases, even if not dramatically, the system reactivity.

Figure 5 is relative to the best system tested (3.1). It is clear that even at room temperature curing (Fig. 5a) the particles are well cemented to each other. In this case the higher SiO_2/Na_2O molar ratio in the activating solution may have played a favorable role [20]. Curing 48 h at 60 °C (Fig. 5b) further improves the compactness of the structure.
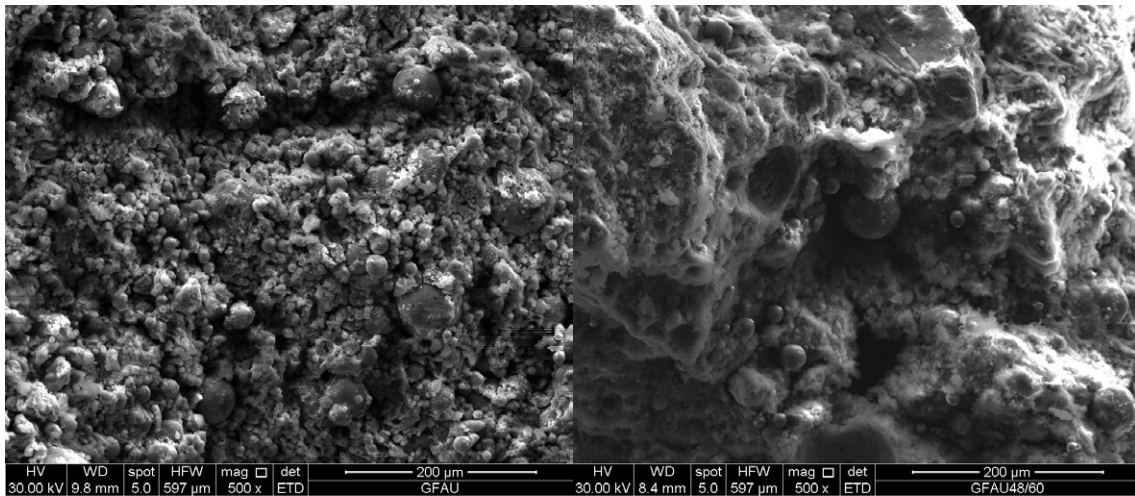
4. Conclusions

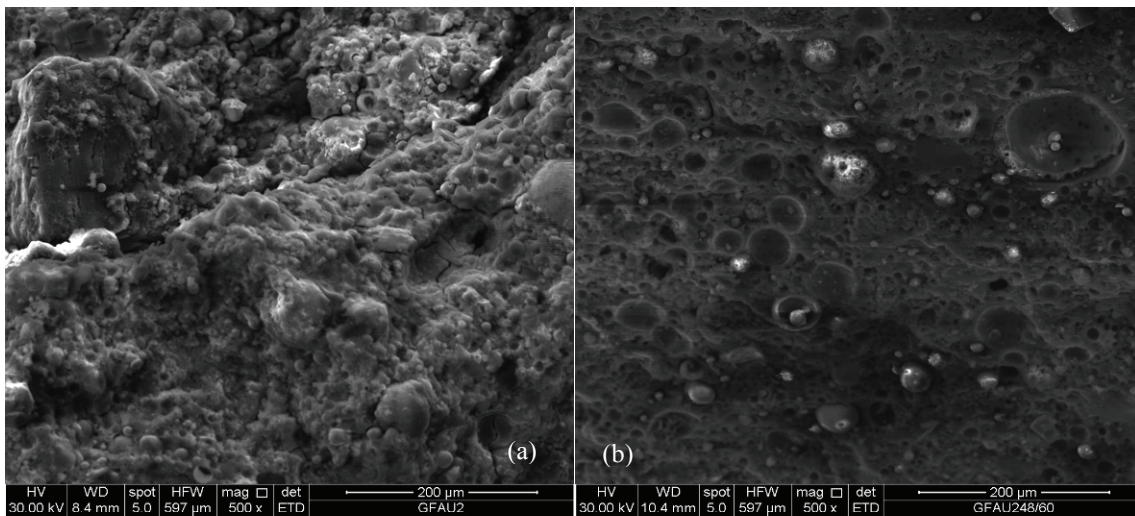Fig. 4. Micrographs of system 1.2 subjected to curing treatment (a) (4a) and curing treatment (c) (4b)

Fig. 5. Micrographs of system 2.3 subjected to curing treatment (a) (5a) and curing treatment (c) (5b)

When weathered fly ash is used after drying, the products performances are adequate for the manufacture of geopolymer based low temperature ceramics. If, however, weathered fly ashes are used wet (as received) without altering the additions of activating solutions, the polycondensation process suffers from the unusually high water content and poor mechanical performances are obtained.

Furthermore, if weathered fly ash is used as received and mix design takes into account its water content, an improvement of performances is obtained and results are similar to those offered by dry fly ash systems.

Finally, it has been observed that the curing conditions affect the results very strongly. Curing at 60 °C, even if for 24 h only out of 7 days, has a very remarkable effect on mechanical strength which can increase as much as 3.5 times.

Acknowledgements

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