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High-calcium fly ash as the fourth constituent in concrete: problems, solutions and perspectives

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Abstract

Even though Hellenic high-calcium fly ashes of different origin are widely used by the cement industry for the production of several CEM II types of cements according to EN 197-1, their systematic use in concrete still presents some difficulties. This inhibits the establishment of specifications for their addition. Main problems concerning the quality, are focused on variations in chemical and mineralogical composition, necessity for supplementary grinding, high proportion of free-CaO and periodically high proportion of SO_3 content.

These problems as well as the solutions, for every day use by the concrete industry, applied during the construction of a dam, are discussed, in this paper. To overcome these problems, untreated fly ash was cheaply upgraded by grinding at a specially designed ball mill, with simultaneously hydration, for the reduction of free-CaO.

Details also (i) for fly ash variations in relation to their origin, (ii) the grinding plant and (iii) the industrial production of fly ash, are given. Finally, in a separate chapter of this paper, aiming to explain the treatment of fly ashes followed during their industrial production, data of the mechanical strength of mixtures of cements incorporating fly ashes with different treatment, concerning their free-CaO and their fineness, are given.

Keywords: High-calcium fly ash; Concrete; Compressive strength; Fly ash treatment

1. Introduction

Fly ash is used extensively in concrete either as a separately batched material characterized as addition as it appears in EN 206-1 [1] or as an ingredient in blended cement (Type CEM II, IV of EN 197-1) [2]. It is used for economy, as it partially replaces an energy intensive material, the cement. However, now it is mainly approved to improve the properties of concrete used for many applications. Their main contribution, amongst others, is to the workability and the reduction of temperature rise in fresh concrete as well as to the durability and long term strength development of hardened concrete [3]. Factors such as the origin of the coal and the burning conditions, strongly affect their chemical and mineralogical composition, resulting in the production of different fly ashes, which are characterized as siliceous, silico-calcareous, or calcareous. These ashes have pozzolanic and/or latent hydraulic properties.

According to ASTM C618, two classes of fly ash are specified: Class F, is usually produced by burning anthracite or bituminous coal and class C is normally produced by burning sub-bituminous or lignite coal. Wide ranges exist in the content of the four principal constituents: SiO_2 (25–60%), CaO (1–35%), Al_2O_3 (10–30%) and Fe_2O_3 (5–25%). If the sum of SiO_2, Al_2O_3, and Fe_2O_3 is 70% or greater the fly ash is technically considered as class F. This lower limit must be covered also by all ashes incorporated in EN 450-1, dealing with ashes in concrete. These ashes, where compounds as $Al_2O_3SiO_2$ and $3Al_2O_32SiO_2$ are predominant, are reported also as low calcium fly ashes (LCFA), showing pozzolanic properties. In the case of class C fly ashes, which in general contain significant percentages of calcium compounds, the sum of SiO_2, Al_2O_3, and Fe_2O_3 is only required to be greater than 50% [3–5].

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Table 1
Fly ash chemical composition (%) from different thermal stations

	Agios dimitrios	Kardia	Ptolemaida	Amyntaio	Megalopolis
SiO_2	33–42	26–34	28–41	31–38	47–52
Al_2O_3	9–12	12–17	13–19	17–21	12–22
CaO	29–38	33–41	23–39	27–35	5.0–15
Fe_2O_3	5.0–6.0	4.5–5.5	4.0–7.0	2.5–4.0	5.0–10
TiO_2	0.7–0.9	0.2–0.5	0.2–0.5	0.7–1.2	–
MgO	4.0–6.0	2.0–6.0	2.0–4.0	3.0–5.0	1.5–3.0
K_2O	0.8–1.0	0.5–1.0	1.2–1.5	0.6–1.2	1.5–3.0
Na_2O	0.5–1.5	0.3–0.6	0.3–0.8	0.5–0.7	0.3–0.7
SO_3	4.0–9.0	6.0–8.0	4.0–8.0	4.0–9.0	3.0–5.0

2. The characteristics of the Hellenic HCFA

The production of ashes, in the year 2000, in Greece is more than 10×10^6 tons. 80% of this quantity comes from Ptolemais area in Northern Greece where the main deposits of Hellenic lignites are located In that area four thermal power stations with 15 thermal units have been constructed. The rest comes from the two power stations of Megalopolis in the central Peloponese. In Table 1 are shown the chemical variations in the main oxides of fly ashes coming from different Hellenic thermal stations. It is evident that fly ashes coming from Ptolemais area (as are ashes from Agios dimitrios, Kardia, Ptolemaida and Amyntaio) are mainly calcareous while the fifth, from Megalopolis area is siliceous.

Hellenic ashes and especially those of Ptolemais origin are classified according ASTM as type C, e.g. into class with high proportion of CaO (HCFA). This classification must be attributed to the fact that in Hellenic ashes, compounds like $3CaO \cdot Al_2O_3$, $CaO \cdot SiO_2$, $4CaO \cdot Al_2O_3 \cdot SiO_2$ or sulfur–calcium–aluminates, are predominant [6–8]. The index $K = CaO + MgO + alkalies/SiO_2 + Al_2O_3$ fluctuates between 0.2 and 1.0 and that fact verifies that Ptolemais fly ashes have not only pozzolanic but also hydraulic behavior [8,9]. In all cases the sum of $Al_2O_3 + SiO_2 + Fe_2O_3$ is greater than 50% but less than 70% as have ashes which have been classified in type F. In all cases SiO_2 is greater than CaO_f and the greater this difference is, the more is the tendency for the pozzolanic reaction between the constituents of fly ash (mainly reactive SiO_2) and the $Ca(OH)_2$ produced during the hydration of the mineral phases of clinker. It must be emphasized that the mineralogical composition and especially the amorphous siliceous and aluminous phases, in relation to the fineness of fly ash, determine how fast this material can react with lime [4,6,10].

Eventhough, HCFA are classified as class C according to ASTM Standard C618 and Canadian Standard CSA-A 23.5, most of HCFA do not fully meet the requirements of the standards. There are no specifications in Europe for the use of HCFA in concrete similar to EN 450 for the LCFA. This makes their utilization difficult. However, under a tight control of the whole process of design–production–application, the use of HCFA is more beneficial than LCFA in terms of strength because the contribution of HCFA to hardening of cementitious phase is greater [7,8].

3. Difficulties on the systematic incorporation of HCFA in concrete

Eventhough there is a systematic and successful laboratory research concerning different fields of application [3,11], in Greece there is not a remarkable progress in fly ash utilization. This fact must be attributed to the high transportation cost as well as to the non-existence of norms covering their uses.

Beyond other uses, ashes are successfully tested in road construction, in several mortars, in cement groutings and in several environmental applications such as waste treatment, soils remediation and others.

The most significant and systematic use of ashes in Greece (only a percentage of 10%, that is about 1,000,000 tons/year) is that in cement industry, replacing cement clinker and aiming to the production of several CEM II types according to EN 197-1 standard. These ashes are interground with clinker and gypsum during the final grinding of cements [6,12–14]:

Focusing in the use of HCFA as additional component (fourth material) in concrete, we observe that, eventhough the technical and economical benefits and the relevant use in blended cements, in Greece their addition in large quantities, still presents some difficulties, mainly summarized to the following:

1. The inhomogeneity in the chemical and mineralogical composition, as they are by-products of a process aiming to the generation of energy and not to the quality of ash. These variations in chemical characteristics (especially in CaO, SiO_2 and SO_3 contents) are evident in Table 1. Fluctuations occur not only between the four power stations but also, as it is shown in Fig. 1, (where appear the mean annual values of Ptolemais power station), in the same station relating to the year of production. Remarkable differences, mainly in mineralogical characteristics, are also observed between ashes

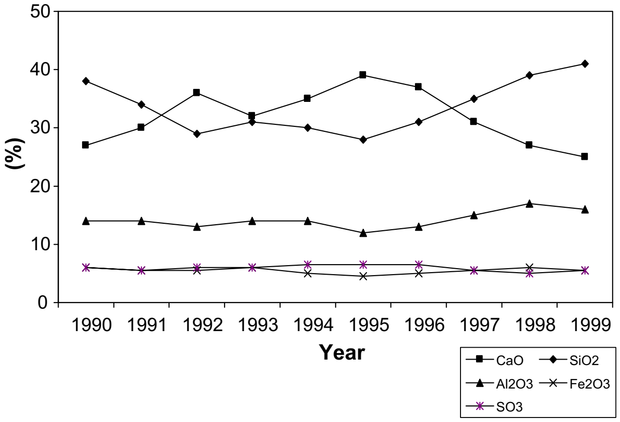

Fig. 1. Variation of main fly ash oxides of Ptolemais power station.

produced from the same lignite quarry but burned in different units of a power station. Except the lignite quarry and the temperature of combustion, the current situation of electrostatic precipitators also influences the quality, especially the granulometry, of fly ash.

2. The necessity for supplementary grinding for better reveal of their pozzolanic and hydraulic properties. The retained on the 90 μm sieve is in the range of 15–20% while the relevant percentages on 45 μm sieve and 200 μm sieve are 45–60% and 3–5%. The additional, but not exhaustive, grinding until a retained of 200–30% on 45 μm sieve, is imposed to remove the glassy covering which agglomerates the fly ash particles and to create newly exposed surfaces which are more active. As it was observed, the coarser fractions are enriched in unburned carbon, which in the case of Ptolemais HCFA fluctuates in accepted limits (3–4%).

3. The elevated proportion of their CaO_f as its hydration causes soundness problems as well as significant temperature increase. Ptolemais fly ashes have a remarkable free CaO content (CaO_f) which fluctuates between 4% and 14% as it is shown in Fig. 2, where appear the mean annual values. The requirements for sound performance are more critical and serious as the amount and proportion of HCFA increases as part of the cementitious content of the concrete. Especially in the cases of mass concretes, as those for dams, any delayed hydration caused as result of conversion of CaO to $Ca(OH)_2$, needs to be virtually eliminated or significantly reduced, thus preventing early age temperature rises.

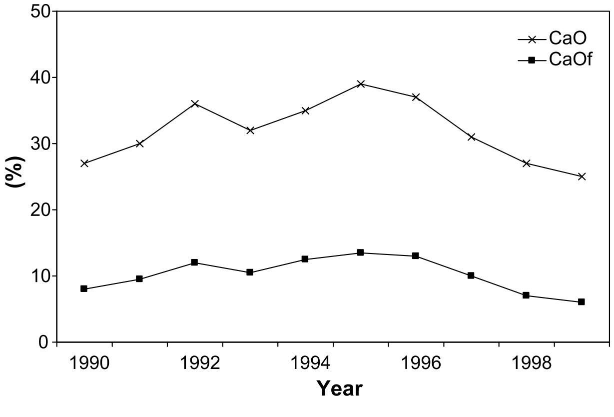

Fig. 2. Relation between total CaO and CaO_f in fly ashes of Ptolemais power station.

4. The periodically elevated proportions of SO_3 content. As it is shown in Table 1, SO_3 fluctuates between 4% and 9% and the upper limit of this range must be avoided because of expansion problems which may arise. Sulfates are mainly in the form of $CaSO_4$, coming from minimizing the released amount of SO_2, which is absorbed by the CaO, in the atmosphere. The best solution to overcome the disadvantages of elevated SO_3 content is to test the fly ash by continuous control of the soundness using the percentages that ash will participate in concrete, to establish an upper limit of SO_3 and to reject the quantities that they do not cover this limit.

4. The upgrade of Hellenic HCFA

Despite these negative effects, in 1992 Power Public Corporation (PPC) decided to go forward to the construction of Platanovrissi dam with the RCC technique and the use of 150,000 tons of Ptolemais fly ash as basic cementitious material (fourth ingredient in concrete mix) [15–17]. For overcoming the mentioned particularities of Hellenic fly ashes, PPC had imposed strict specifications for their upgrade. The basic requirement was the treatment of fly ash comprising simultaneous to their grinding, partial hydrolization for the conversion of the CaO to $Ca(OH)_2$. For the realization of this treatment a grinding plant was constructed, near Ptolemais Thermal Station. By this process the problems of high-CaO_f and supplementary grinding were simultaneously confronted.

In more details, for the four problems mentioned in the previous chapter, the relevant actions for the industrial treatment have been followed respectively:

(i) For the inhomogeneity problem, after a series of preliminary tests, two units of Ptolemais Station were chosen: One of them (the fourth unit) was the basic and had offered the 85% of rough (untreated) ash, while the other was supplementary. For minimizing the deviations of lignite quantities, these units were continuously fed with the same percentage from two lignite quarries. The acceptability of fly ash, mainly concerning CaO_f and SO_3, coming from these two units was tested every 2 h in continuous sampling in order to find the rate for their homogenization. During the construction of the dam (10/1995–4/1997) about 18,000 measurements have been carried out.

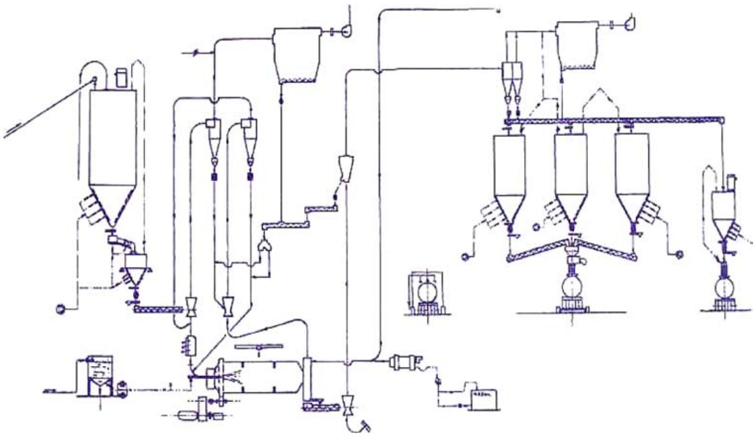

Fig. 3. The milling plant for the treatment of fly ashes.

(ii) For the supplementary grinding, a closed circuit (Fig. 3) ball mill ($D = 2.6$ m, $L = 12$ m) with the relevant equipment was constructed for through-put limits between 16.7 and 23 tons/h. The basic demand from mill was to grind the ash so that, independently on the variations of initial granulometry of fly ash, the final retained on 45 μm sieve will be 20–30% [17–19]. In Fig. 4a statistical data concerning R45 in daily samples during the construction of the dam appear [20].

(iii) Untreated fly ash has a CaO_f content which fluctuates in the range of 4–14%, with the most probable values measured in the range 6–8%. According to PPC specifications the max acceptable value for the suitability of fly ash was 3%. The choice of an intermediate value of free calcium oxide content is explained in details in the next chapter of the comparison of strength development between treated and untreated fly ashes. Water is sprayed into the mill, so that the most of the free lime is hydrolyzed to $Ca(OH)_2$ under hot moist conditions. Due to continuous ash variations, the suitable proportion of water to be added was automatically controlled by feedback from fly ash temperature. Mill temperature is thereby controlled by balancing heat removal, in converting excess water to steam with heat generated from reacting a variable lime content. It is essential that the mill must operate at a relatively high temperature (100 °C) to speed the reaction and to boil off surplus water. The water spraying system was designed for 5.0–12.5% water addition i.e. up to 48 l/min and much efforts have been done for the optimum angle in which the injected water meets fly ash. The ability of the mill for the proper reduction of CaO_f was controlled every 2 h and in the same time the appropriate corrections of the water injection were performed. In this level about 6000 measurements of CaO_f and fineness from the exit of the mill have were carried out. In Fig. 4b statistical data concerning the content of CaO_f in daily samples during the construction of the dam, appear.

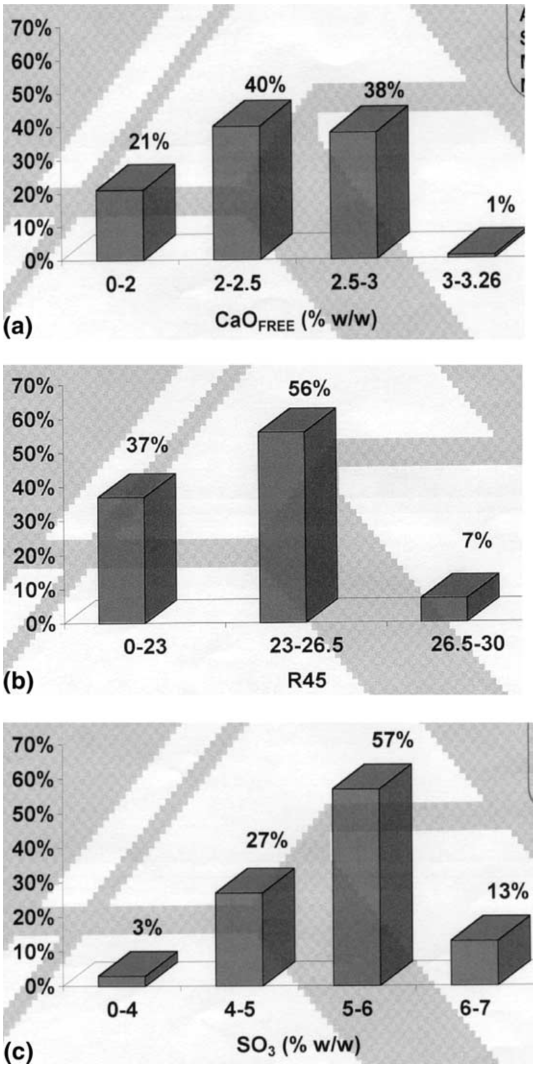

Fig. 4. Statistical data concerning the total milling plant production: (a) for CaO_f, (b) for granulometry—R45, (c) for SO_3.

(iv) For SO_3 content, max limit 7%, as well as control every 2 h, after special tests based on continuous sampling in the point of production, were established. A percentage of 20% of the samples led to the rejection of the relevant quantities of fly ashes in their untreated form, as the above limit was not covered. Additionally, expansion tests using Le Chatelier method were performed in daily samples of treated fly ash. The number of samples exceeding the limit of 10 mm was lesser than 1% and again the relevant quantities were no used for the dam. The undesirable expansion in the latter cases must be attributed to differentiations in mineralogical composition of fly ash. In Fig. 4c statistical data concerning the content of SO_3 in daily samples during the construction of the dam, appear.

The production of fly ash was completed into 19 months (October 95–April 97). In this period 135,000 tons of upgraded fly ash were produced and transported with 5500 silo vehicles for a distance of 380 km to the place of dam in Platanovryssi, on the Nestos river in North–East Greece. There, fly ash was mixed with CEM I cement at a rate of C/F = 20/80 and this mixture was applied for the construction of the main body of a RCC dam. This dam was the highest in Europe, having 95 m high, with a crest length of 270 m and a volume of 450,000 m^3. Until now (after 5 years), excellent results [21] concerning strength and other relevant properties have been obtained.

The above described milling plant is now able to treat raw fly ash according the specifications of the future uses in relation to any desired fineness (R_{45}: 50–15%) and to any desired CaO_f content between 12% and 2%.

5. Examination of fly ash treatment on the mechanical strength of cement–fly ash mixtures

In order to examine the influence of fineness and CaO_f content of industrial produced fly ashes on strength development in different proportions with OPC, six different fly ashes F1–F6 were produced. F1 refers to untreated fly ash and F2–F6 ashes are derived from F1 after industrial treatment in different conditions aiming to obtain the characteristics which are summarized in Table 2.

These six fly ashes were mixed with OPC (C) in proportion C:F = 80:20, while F3–F6 were additionally

Table 2
Characteristics of industrial produced fly ashes with different treatment

Fly ash code	CaO_f (±0.2%)	R45 μm (±1.5%)
F1	6.8	41
F2	6.8	22
F3	3.5	22
F4	3.5	11
F5	1.8	22
F6	1.8	11

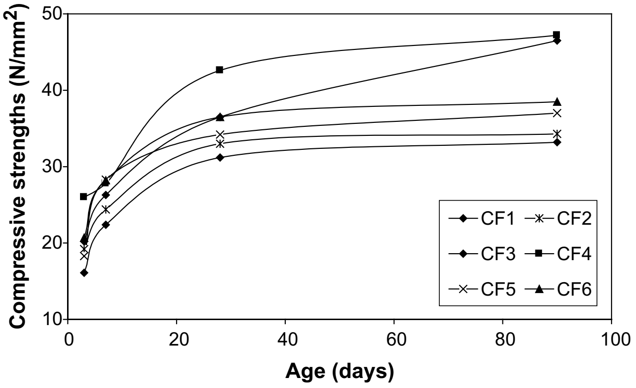

Fig. 5. Compressive strength of cement mixes with different fly ashes at a rate C/F = 80/20.

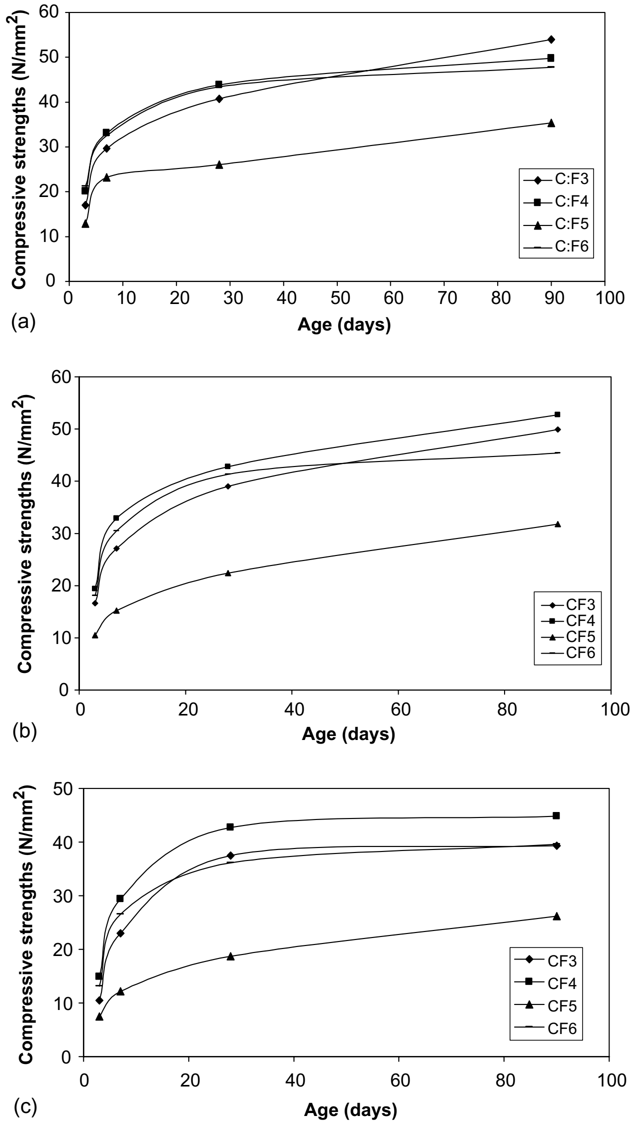

Fig. 6. Compressive strength of cement mixes with different treated fly ashes: (a) C/F = 60/40; (b) C/F = 40/60; (c) C/F = 20/80.

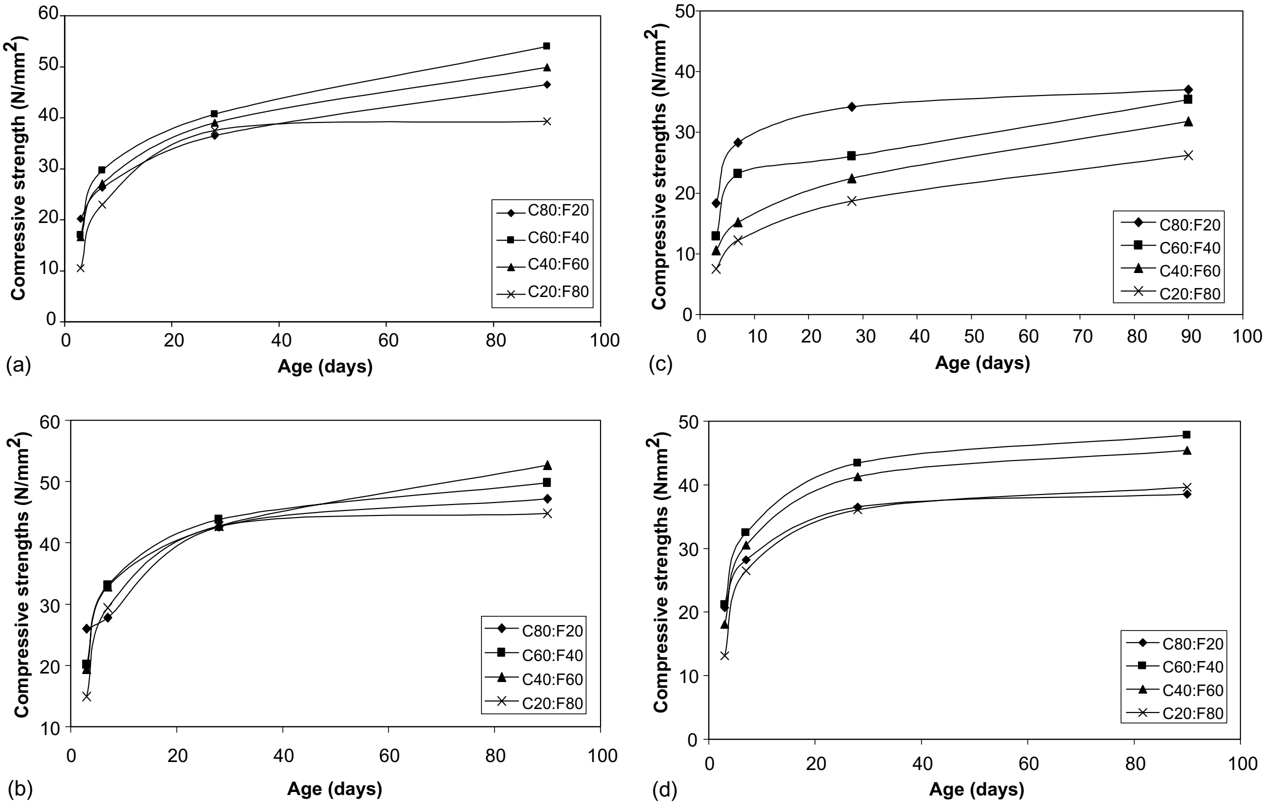

Fig. 7. Compressive strength of cement paste mixtures with treated fly ashes at different rates: (a) CF3, (b) CF4, (c) CF5, (d) CF6.

mixed with OPC at percentages varying from 40% to 80%.

Compressive strength (3, 7, 28, 90 days) were measured in all mixes according EN 196.1.

Fig. 5 shows the compressive strength of cement mixes with different fly ashes at a rate 80/20. In all cases of treated fly ashes, strength development showed better results comparing to untreated fly ash (CF1). The results obtained from the compressive strengths test showed, as it was expected, the positive effect that fineness has in strength development (CF2 > CF1, CF4 > CF3, CF6 > CF5). From the same samples derives also that intermediate CaO_f values, as are in the case of CF3 and CF4, show the best results (CF3 > CF5, CF4 > CF6), verifying that a moderate amount of CaO_f is essential for the initial activation of high-calcium fly ash. On the other hand samples of the higher CaO_f (as are CF1, CF2), showed less compressive strengths compared to CF3,CF4 due to the formation of $Ca(OH)_2$ in large quantities.

As the percentage of HCFA increases (Fig. 6a–c), the following are observed:

1. In all cases, even at proportions C:F = 20:80, strength development showed better results compared to untreated fly ash C:F1 = 80:20. Only CF5 mixtures have shown in all cases very low strength, indicating that values of CaO_f near 3.5% are the optimum. In the case that CaO_f is less than 2%, the mixture must be additionally ground (CF6 > CF5), in order to be sufficient activated and to express its hydraulic properties. The optimum values of CaO_f are also verified in the same figure as the curves representing CF3 and CF4 show better results concerning compressive strengths.
2. Comparing the curves of Fig. 7, where strength development is plotted against mixture proportion, we observe that in all cases (except F5 mixtures) the proportion between C:F = 60/40–40/60 gives better results. This must be attributed to the increased proportion of active silica which finds sufficient quantity of CaO_f and $Ca(OH)_2$ giving secondary CSH which is added to the primary one coming from the hydration of cement phases. The latter, in the case of mixture C:F = 20:80, is not sufficient to contribute significantly in strength up to 90 days.

6. Conclusions

1. It is possible to upgrade high-calcium fly ashes by a cheap method consisting to simultaneous to their grinding, hydration with a automatically controlled water spraying system.
2. By suitable adjustment of mill operation parameters, it is possible to obtain several qualities of treated fly

ashes. This differentiation is concerned to their fineness as well as to their CaO_f.

3. Industrial experiments showed that best results concerning strength development, in mixtures of OPC and high-calcium fly ashes are obtained when CaO_f is in the range of 3–3.5%, while ashes with CaO_f <2% need more grinding. A proportion in mixtures with OPC 60/40–40/60 gives very good results concerning strengths up to 3 months.

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