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Investigating the role of reactive silica in the hydration mechanisms of high-calcium fly ash/cement systems

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Abstract

High-calcium fly ashes (ASTM Class C) are being widely used as a replacement of cement in normal and high strength concrete. In Greece such fly ashes represent the majority of the industrial by-products that possess pozzolanic properties. Even thought the contribution of factors, such as fineness and water/binder ratio, on the performance of fly ash/cement (FC) systems has been a common research topic, little work has been done on examining whether and to what extent reactive silica of fly ashes affects the mechanisms occurring during their hydration.

The work presented herein describes a laboratory scale study on the influence of active silica of two high-lime fly ashes on their behavior during hydration. Volumes up to 30% of Greek high-calcium fly ashes, diversified both on their reactive silica content and silicon/calcium oxides ratio, were used to prepare mixes with Portland cement. The new blends were examined in terms of compressive strength, remaining calcium hydroxide, generation of hydration products and microstructural development. It was found that soluble silica of fly ashes holds a predominant role especially after the first month of the hardening process. At this stage, silica is increasingly dissolved in the matrix forming additional cementitious compounds with binding properties, principally a second generation C–S–H. The rate however, that fly ashes react in FC systems seems to be independent of their active silica content, indicating that additional factors such as glass content and fineness should be taken into account for predicting the contribution of fly ashes in the final performance of pozzolanic cementitious systems.

Keywords: High-lime fly ash; Active silica; Glass; Hydration kinetics; Performance prediction

1. Introduction

High-lime fly ashes are the main industrial by-product generated in Greek thermal power plants, representing the 80% of the total fly ash production. Despite the fact that natural gas has already been introduced in the Greek energy sector, the rate at which fly ashes will be derived, at least during the forthcoming years, is expected to steadily increase. This posts not only an additional environmental concern but primarily a necessity for their greater utilization in different market sectors. At the moment the utilization rate of this material in the construction sector is still impoverished (about 10%), since it is being handled with a lot of skepticism [1]. The major reason for this timidity is its rather peculiar chemical composition, which apart from being very diversified, is also characterized by high free lime and sulphur contents, factors that threaten the concrete's durability [2]. On the other hand, the self-cementitious properties of those ashes diminish their dependency from calcium hydroxide liberated from hydrated Portland cement and result in improved early strengths compared to low-lime fly ashes [3].

In the literature there is consensus that the use of fly ash not only achieves energy and material saving [4,5], but also imparts improved quality to the final product in terms of strength and durability [6,7]. Even thought the beneficial role of fly ash in cementitious systems has been fairly well established, the potential of this by-product has not been explored fully yet. Current research is emphasizing on the role of parameters that affect the behavior of fly ashes during the hardening process. Factors such as fineness [8,9], water to cementitious materials ratio [10], curing temperature [11] and

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alkalinity of the pore solution [12,13] have been thoroughly examined in an attempt to explain the reactivity of this material and relate its pozzolanic potential with the evolution of the hydration procedure. However, the majority of the published work is concerned with ashes bearing low to moderate calcium contents, overlooking a wide range of different fly ashes, those with high calcium content.

During the 80s, several workers highlighted the distinct behavior of Class C fly ashes during hydration. Marsh and Day [14] for example, compared the hydration of a Class C fly ash to a low lime fly ash, indicating that the combined CH [2] per unit weight of fly ash was substantially higher for the high lime one. Diamond [15] tested two high calcium fly ashes, the one with a surplus of crystalline free lime and the other with lime mainly incorporated in the glass phase of the ash. He concluded that the reaction is mainly located in the depolymerized fly ash glass. Later, Tishmack et al. [16] examined the potential influence of such ashes on ettringite formation. He deduced that the addition of high-lime fly ashes in cementitious systems favors the monosulfate phases rather than ettringite. Other authors [17,18] showed that the rate of heat development in blended cement incorporating different fly ashes increases with calcium content of fly ash. Finally, a very handy approach concerning Greek high-calcium fly ashes was attempted by Papadakis [19] who proposed a simplified scheme describing the reactions occurring when those ashes are added in hydrating Portland cement and applied mathematical expressions for the resulting products.

Notwithstanding the fact that hydration of fly ash/cement (FC) systems has been one of the subjects that attracted a lot of attention from numerous researchers, the challenge of associating its mechanisms with some of the characteristics inherent in the pozzolan remains of paramount importance. The present study aims at enlightening the hydration kinetics and microstructure development of cementitious systems that incorporate high-lime ashes by stressing out the role of one of their inborn parameters, reactive silica. Reactive silica is the main active constituent located in the glass phase of the fly ash [20] and the fraction of the total silica participating in the pozzolanic reactions [21]. In previous publications, the authors have pointed out the effect of active silica in the strength development of FC systems [22], while Antiohos et al. [23] proposed optimum lignite burning conditions for obtaining ashes rich in reactive silica. Lately, Papadakis et al. [24] after examining several supplementary cementing materials described a model for predicting the activity index and efficiency factor of a blended system by measuring the active silica that it contains.

The results presented herein are part of an ongoing research program that intends to correlate the active silica of high-lime fly ashes with the hydration kinetics of the corresponding fly ash/cement systems. The final target of this effort is to elucidate the mechanisms dominating during the hardening of the aforementioned systems, but also to designate if and to what extent active silica affects this procedure.

2. Strategy

2.1. Materials for experimentation

A rapid hardening Portland cement (CEM I 52.5R according to European Standard EN 197-1) and two high-calcium fly ashes (from Ptolemais region) were used in this study. For reaching the goals set during the investigation, the ashes were selected so as to diversify on their active silica content and silicon/calcium oxides ratio. In particular, the fly ash designated here as T_f is rich in active silica while the second fly ash (designated as T_d) possesses less active silica but more calcium oxide. The ashes were also selected on the basis of their similar free lime contents so as to highlight the role of active silica during hydration and especially on the depletion of calcium hydroxide occurring in the corresponding FC pastes. Finally, in an attempt to incapacitate the physical effect of fly ashes on their pozzolanic activity, they were both ground prior to use in a lab ball mill, so as to obtain ashes of similar fineness. Generally, Greek high-lime ashes are relatively fine materials as received, so a few minutes grinding was sufficient for accomplishing the target set. The particle size distribution of the ground ashes is shown in Fig. 1. The chemical compo-

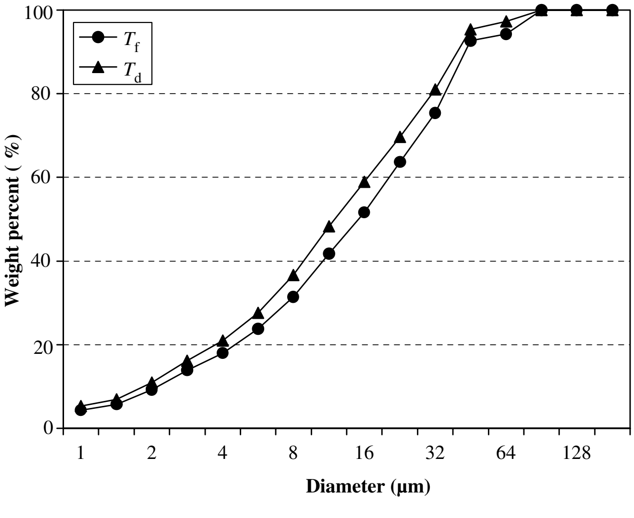

Fig. 1. Particle size distribution of ground fly ashes.

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[2] Cement notation chemistry is used throughout this paper, where: H: H_2O, C: CaO, S: SiO_2, A: Al_2O_3, F: Fe_2O_3, $\overline{S}$: SO_3, CH: $Ca(OH)_2$.

Table 1
Chemical composition (% by mass) and physical characteristics of raw materials

	Materials		
	Cement	T_f	T_d
CaO	65.01	29.79	34.13
CaO_f	0.63	7.96	8.93
CaO_{re}[a]	–	25.13	26.33
SiO_2	20.28	36.92	29.73
SiO_{2re}[b]	–	29.13	24.07
Al_2O_3	4.75	13.50	13.90
Fe_2O_3	3.76	7.06	6.49
MgO	1.61	2.69	3.56
SO_3	2.55	5.10	5.13
Na_2O	0.17	0.92	1.12
K_2O	0.35	0.50	0.68
LOI	2.31	4.36	4.03
IR (%)*	0.18	14.52	9.51
Glass content, S** (%)	–	85.48	90.49
Blaine fineness (cm^2/g)	3.760	5.450	5.600
Specific gravity	3.13	2.83	2.72

* IR: stands for Insoluble Residue of fly ashes according to EN450-1 standard.

** S: stands for Glass Content of fly ashes according to RILEM Recommendations (TC FAB-67), S = 100-IR.

[a] The method specified in the European Standard EN 450-1 was followed for the estimation of the reactive silica and calcium oxide contents and the insoluble residue (IR) of the fly ashes.

[b] The method specified in the RILEM Recommendations (TC FAB-67 use of fly ash in building) was followed for calculating the content of the LOI-free fly ash constituents soluble in hydrochloric acid and potassium hydroxide ($S = 100 - \text{IR}$).

sition and the main physical characteristics of the cement and fly ashes are listed in Table 1.

2.2. Active silica determination

European Standards EN 450-1 [25] and EN 196-2 [26] were applied for the determination of the active silica content of the fly ashes. Both Standards specify that active silica content is determined as the difference between the total silica and the silica present in the insoluble residue of the ash. Two measurements were performed for each specimen and the mean values are also given in Table 1.

2.3. Preparation of FC mortars and pastes

Mortar specimens were prepared to monitor the evolution of the compressive strength. Keeping the water-to-cementitious materials ratio (w/cm) and the cementitious materials-to-sand ratio stable at 0.5 and 0.33 respectively, mortars were constructed by replacing equal volumes of cement with each fly ash. Fly ash dosage varied from 0% (control specimen) to 30% by weight of cement. The dry materials were sufficiently mixed before they were cast into 40 mm × 40 mm × 160 mm prisms. One day after casting, the samples were stripped from their molds and the specimens were placed in lime-saturated water at 20 °C until testing. A Toni Tecknik compression machine with a loadcell of 0–300 kN and a loading rate of 2.4 kN/s was used during the compression test. At 2, 7, 28 and 90 days after mixing the specimens were removed from water and tested according to European Standard EN 196-1. For each age, three specimens of every mixture were tested and the mean value of these measurements is reported.

To simulate the paste in mortar and evaluate the hydration process, the corresponding paste samples were also prepared adopting the same proportions. The pastes were cured in water at room temperature. At the dates of testing (2, 7, 28 and 90 days) the samples were fractured into pieces. Nonchemically combined water was removed from the fractured samples by immersing them in acetone and diethylethere followed by drying to constant weight in a vacuum pump. Additional specimens were prepared for the first day, so as to have an integrated view on the early stage of hydration. After stopping hydration, all samples were ground so as to pass the 125-μm sieve, while representative fractured pieces were selected for microscopical examination. Both types of samples were sealed in polypropylene bags and stored in a dryer until they were tested.

2.4. Monitoring hydration

2.4.1. Thermal analysis

Thermogravimetric and differential thermal analyses were performed in a Mettler STARe 815 thermal analysis device. Control and FC specimens were heated at a rate of 10 °C/min from 25 to 1000 °C in a N_2 surrounding atmosphere, kept constant at 50 ml/min. A platinum crucible with 70 μl capacity was used and mass of the examined samples ranged from 45 to 55 mg. Although this range of temperatures encompasses all the dehydration peaks that represent the products formed during hydration, only calcium hydroxide was quantified. The weight of remaining CH in the samples and the quantity of free-CH transformed into calcium carbonate (due to possible carbonation during handling of the samples) were estimated and afterwards added to obtain the total CH percentage in all specimens.

2.4.2. Powder X-Ray diffraction analysis

XRD patterns of the fly ashes and the hydrated samples were recorded using a Siemens D 500 X-ray diffractometer (CuKα radiation, 40 kV, 30 mA) in a scanning range of 5–65° in 2θ scale. The testing rate that was applied was 0.02°/s for all specimens. Identification of the hydration products was carried out by using a Diffrac-At Database. Table 2 presents the major crystalline compounds identified in the XRD patterns of the two fly ashes.

Table 2
Main crystalline compounds of fly ashes

	T_f ash	T_d ash
Quartz	✓	✓
Lime	✓	✓
Anhydrite	✓	–
Albite	✓	✓
Gypsum	✓	✓
Thernadite	✓	✓
Portlandite	–	✓
Calcite	–	✓

2.4.3. ESEM observation and EDX-analysis

XL 30 Philips ESEM was used for the microstructural investigation of the fractured specimens and the changes brought forward in the composition of cement hydrates by the presence of fly ash. The instrument was equipped with an energy-dispersive X-ray analyzer (EDAX) for the quantitative elemental analysis of the resulting phases.

3. Results and discussion

3.1. Compressive strength

The compressive strength results of all examined specimens are given in Table 3. The superiority of the sample with no fly ash addition (control specimen) at all ages is clearly manifested. This is mainly, if not entirely, attributed to the type of cement that was used (CEM I 52.5R), which contains an excess of C_3S grains with regards to the cements usually being replaced by pozzolanic materials (CEM I 32.5 or CEM I 42.5). Especially noticeable is the fact that during the early ages the variance in strength between the control specimen and the fly ash mortars is smaller than the corresponding one after one month of hydration, when the pozzolanic reactions are considered to have started [27]. The satisfactory early strength values observed for the high-lime fly ash mixes can be ascribed to their enhanced pozzolanic activity obtained by the grinding process that led to finer and more reactive particles, as well as to their self-cementitious character. On the other hand, a possible explanation for the low strength values that the fly ash mixes present after the first month of curing, can be given by the numerous calcium silicate grains of the Portland cement which apparently contribute more to the strength of the system than the fly ashes do. This is supported by the fact that at this age, increased replacement of cement by both ashes brings forward a subsequent increment in the strength difference between the FA and the control mortars.

Table 3
Compressive strength (MPa) of control and pozzolanic mortar specimens

RL (%)	FA	Curing time (days)			
		2	7	28	90
0	–	30.2	42.0	59.0	66.7
10	T_f	27.4	40.4	55.0	64.8
	T_d	28.7	41.4	52.5	62.8
20	T_f	26.3	38.4	52.1	62.5
	T_d	27.4	40.8	52.6	62.6
30	T_f	24.2	36.2	50.2	65.0
	T_d	25.6	39.1	52.7	63.7

Keys: RL: cement replacement level, FA: fly ash.

The influence of the fly ash replacement ratio on the strength development of all mixes is cited in Fig. 2. In the case of moderate cement substitution (i.e. 20%, Fig. 2(a)) the two fly ash mixes behave similarly, with CT_d mix attaining slightly higher strength values throughout the testing period. In the case of a substantial pozzolan addition (i.e. 30%, Fig. 2(b)), the system containing T_d fly ash outbalances the corresponding system with the high-siliceous active T_f ash, reaching a maximum

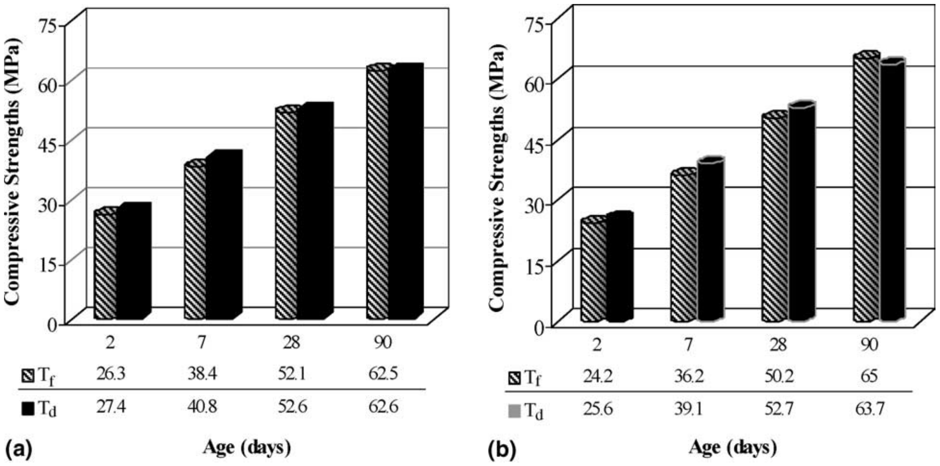

Fig. 2. Compressive strength values of fly ash mortars with hydration time for (a) 20% and (b) 30% cement replacement by weight.

strength variance after the first month of hydration. Given that the ashes were ground to similar fineness, this strength gap can be attributed to the higher active lime present in T_d ash. Calcium ions are easily dissolved from the ash particles into the pore solution during this period [28], accommodating the formation of calcium-aluminate and calcium-sulfo-aluminate phases whose filling properties [29] contribute substantially to the strength enhancement of the system.

After four weeks of hydration, the strength superiority of CT_d mortar diminishes with regards to the CT_f system as a result of the significant increase of the latter's strength. During the following two months, the system incorporating the ash with high active silica (CT_f) not only outperforms the competitive mix (CT_d), but it exhibits the maximum strength of all fly ash specimens tested. This clearly indicates that active silica content plays a predominant role after the first month of the hydration process, providing at the same moment a guidepost that ashes rich in amorphous silica are more appropriate for use when replacing high volumes of Portland cement. This is in accordance with the findings of Ranganath et al. [30] who concluded that for lime-fly ash mixes, the influence of soluble silica in strength is more pronounced than the effect of fineness at later ages.

The aforementioned observation is also validated in Fig. 3, where the strength gain that the FC mortars exhibited after the first month of hydration is plotted against the replacement ratio applied. It is easily visible that the ability of T_f to provide additional strength to the system is strongly related to its high active silica content. This capability becomes even more pronounced as the ash replacement dosage increases. On the contrary, when the fly ash with lower active silica content (T_d) was utilized in the mix, the strength gain remained nearly constant reaching moderate values even at high addition levels.

3.2. CH contents and pozzolanic action rates

Thermogravimetric analysis (TGA) was mainly performed for the quantification of calcium hydroxide (CH) present in the control and FC mixes examined. Data reported in Table 4 depict the rather peculiar image that the CH contents of the FC pastes present. For both fly ashes and almost all replacement ratios, there is no evidence of calcium hydroxide depletion even after 28 days of hydration. In fact, the CH content of all specimens is continuously increasing with hydration age, as a result of the simultaneous production of CH from the acceleration of calcium silicate grains hydration in the presence of fly ash [28] and the rapid hydration of free lime present in both ashes. Even after the first month of hydration, when a considerable amount of fly ash particles are participating in the hydration reactions [31], calcium hydroxide is still produced in greater quantities than consumed in almost all samples.

It has been well established that the pozzolanic reactions are highly depended on the calcium hydroxide that exists on the cementitious matrix, thus primarily on the cement content in each mixture. Therefore, the CH contents that remained unbound in the systems were also calculated in unitary terms, that is, as a function of the cement mass in each mixture. Fig. 4 depicts the

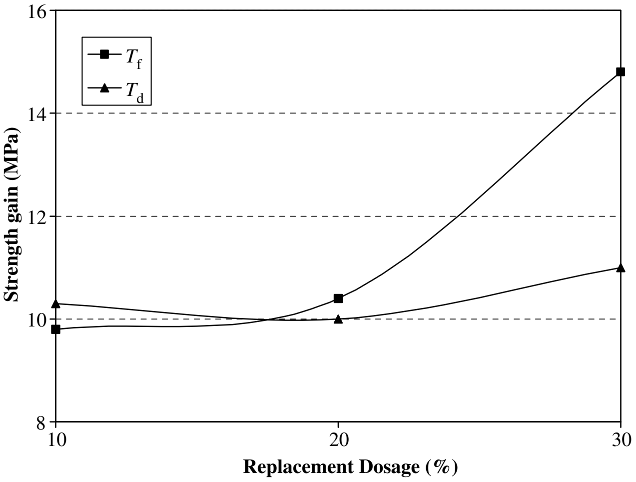

Fig. 3. Strength gain observed in FC mortars between 28 and 90 days of hydration in relation to the fly ash replacement ratio.

Table 4
CH contents (%) of control and FC pastes

RL (%)	FA	Curing time (days)				
		1	2	7	28	90
0	–	22.83	25.68	29.74	34.74	36.66
10	T_f	14.63	17.24	18.15	21.85	22.84
	T_d	19.68	21.44	22.92	26.80	28.19
20	T_f	13.72	17.89	19.95	22.38	20.73
	T_d	18.67	19.03	24.18	24.02	24.56
30	T_f	14.23	17.12	17.32	19.39	18.79
	T_d	16.07	20.57	21.31	22.86	21.36

Keys: RL: cement replacement level, FA: fly ash.

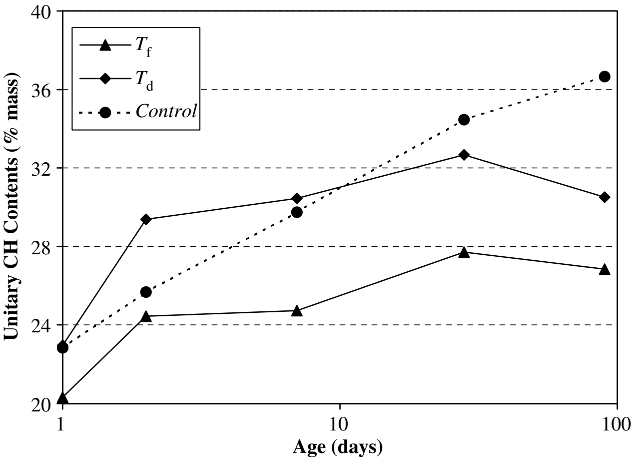

Fig. 4. Unitary remaining calcium hydroxide of FC pastes containing 30% fly ash with curing time.

unitary remaining CH content of the blends with 30% fly ash as a function of curing time. When expressed in this manner it becomes obvious that both FC systems present a similar behavior. However, the mix containing T_d ash generates greater quantities of CH compared to the control specimen during the first week of hydration as a result of its high-lime content that is diluted in the matrix. Despite the fact that more siliceous active T_f is clearly more effective in consuming available CH than T_d ash, the CT_f mixtures generate more calcium hydroxide than they bind during the first month of the hardening. It can be noted therefore that the apparent excess of portlandite in the pore solution of the cementitious matrix starts decreasing only when the CH-T_f or CH-T_d reaction evolves at faster rates. This desired acceleration seems to takes place after the first month of hydration. Silica present in the glass phase of the ash is increasingly dissolved into the matrix during this period forming new hydration products, principally a second generation C–S–H, by consuming available portlandite.

Since one of the objectives of this work was to relate the reactivity of the used ashes with their active silica content, the CH measurements were also used to estimate the percentage of fixed lime in the pastes with a substantial pozzolan addition (i.e. 30%). The following equation (Eq. (1)) proposed by Paya et al. [32] was applied for determining the percentage of fixed lime in each case.

$$\text{Fixed lime }(\%) = \frac{(\text{CH}_c \cdot \text{C}_{\%}) - \text{CH}_\text{P}}{\text{CH}_c \cdot \text{C}_{\%}} \times 100 \tag{1}$$

where CH_c is the CH content of the control paste for a given curing time, CH_P is the CH content of the FC paste at the same age and $\text{C}_{\%}$ is the proportion of cement in the examined paste (obviously in this case $\text{C}_{\%}$ is 0.7). In Fig. 5 the calculated fixed lime values are plotted against hydration age for both ashes. In general, it is observed that fixed lime increases with curing time as a result of the evolution of the pozzolanic reactions. Negative values observed during the initial hydration stages of T_d ash are indicative of the higher quantities of CH generated in the CT_d system and also of the inability of its lower active silica content to act drastically during this period. It is at 28 days of hydration that fixed lime values become positive for both ashes with T_f binding more available lime. T_d ash begins to be active 90 days after mixing when the dissolution rate of the glassy silica it contains increases. Still at this age, T_f ash fixes more lime than T_d as a result of its higher active silica content.

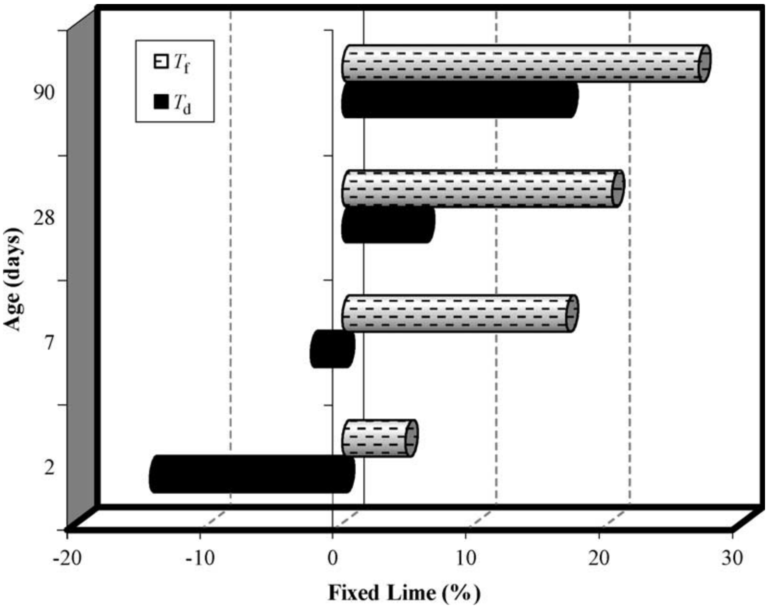

Fig. 5. Percentage of fixed lime with hydration age for FC pastes with 30% fly ash addition.

The major role that reactive silica of fly ashes holds during this stage of hydration is clearly supported by the data in Fig. 6, where the CH depletion (as this is expressed as the difference between the CH contents of the control paste and the CH contents measured in the corresponding FC pastes at a given curing age) of the control specimen after three months of hydration is associated with the fly ash replacement ratio. For all ash addition levels, T_f ash shows a greater ability of consuming portlandite than T_d ash. Given that the free lime contents of both ashes are similar, the superiority of T_f ash in this aspect can be attributed to its pleonasm of soluble silica and coincides with the previously presented enhanced strength gain during this stage. It should be emphasized however, that although a fly ash rich in active silica is expected to combine more CH than a fly ash with moderate active silica content, the rate at which this consumption is accomplished (Figs. 4 and 5) seems to be independent of the examined parameter. Confirming this initial observation though, requires additional experimental work using ashes representing a wider range of active silica contents and different types of cement.

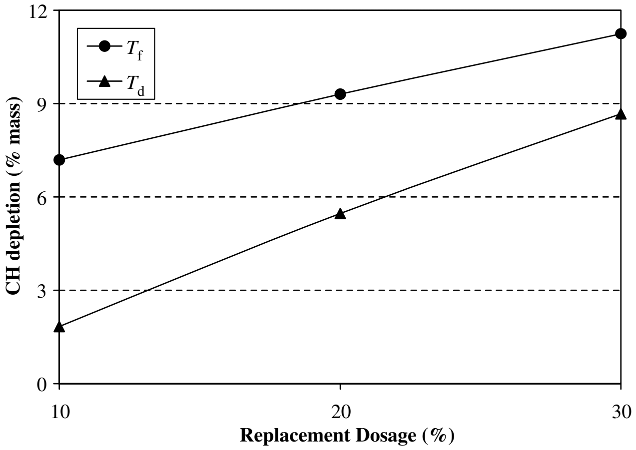

Fig. 6. Effect of fly ash replacement dosage on the depletion of calcium hydroxide present in the control mixture at 90 days curing.

3.3. Identification of hydration products

For highlighting the influence of fly ash in the constructed systems, the authors mainly dealt with the identification of hydration products generated in the blends with a substantial pozzolan addition (i.e. 30% by weight of cement). In Figs. 7 and 8 the XRD patterns of both FC systems and the crystalline products formed with hydration age in each case are shown. Results testify the previous observations regarding the portlandite formed, and in particular its steady presence in the matrices throughout the testing period. It is possible therefore that the carbonate hydrates detected in both samples after 90 days are caused by the carbonation of a nontrivial part of unbound calcium hydroxide. Although the intensity of the calcium silicate peaks is getting relatively smaller with hydration age, the presence of alite and belite after 90 days indicates that the hydration of the two phases is not complete in both FC

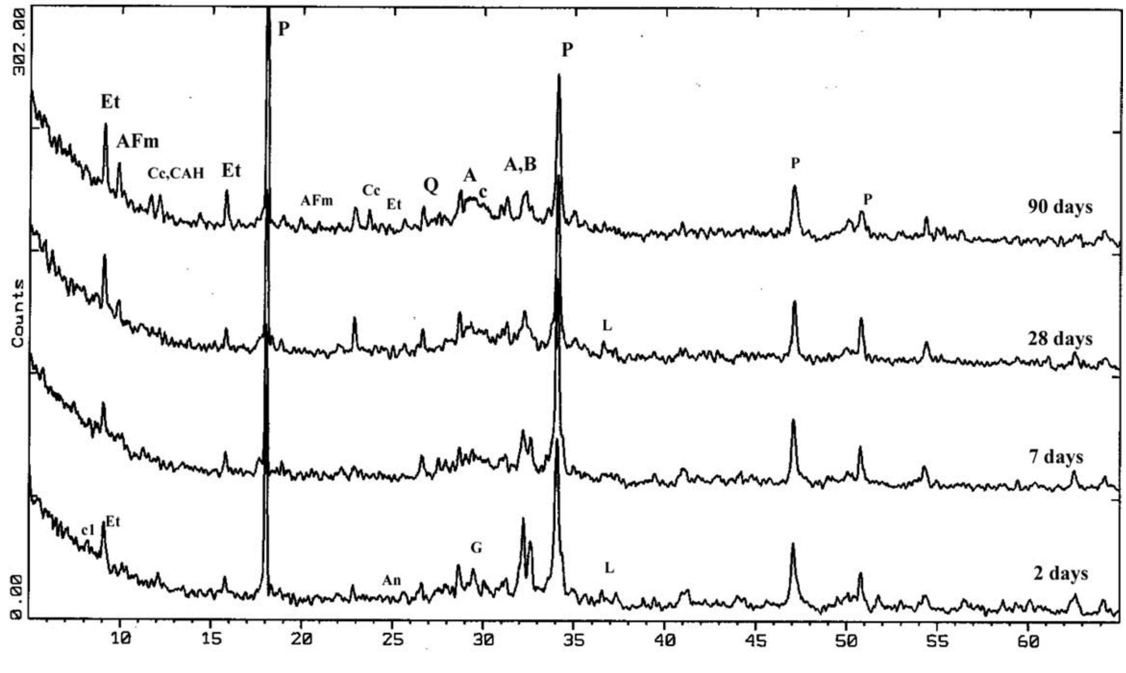

Fig. 7. XRD patterns of hydrated CT_f pastes. The following notations were used for the various minerals identified: Et: ettringite, AF_m: monosulphate, P: portlandite, Q: quartz, CAH: C_2AH_6, L: lime, c: calcite, Cc: $C_4A\underline{C}H_{11}$, G: gypsum, CAO(OH): $C_3ACH \cdot H_{18}$, A: alite, B: belite, An: anhydrite.

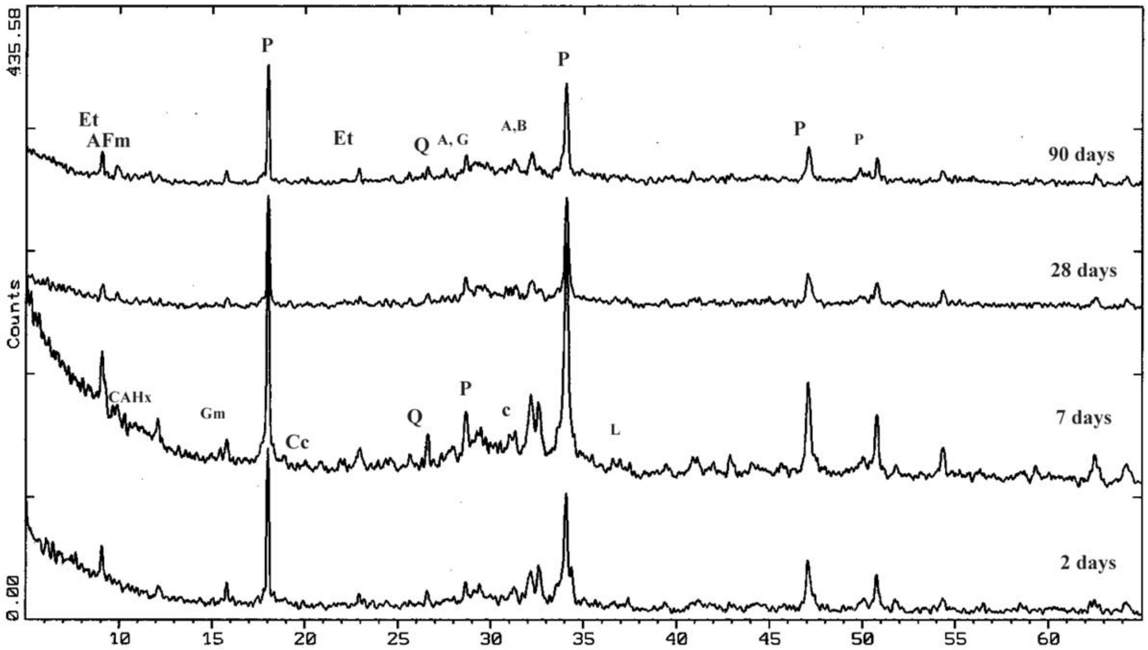

Fig. 8. XRD patterns of hydrated CT_d pastes. The following notations were used for the various minerals identified: Et: ettringite, AF_m: monosulphate, P: portlandite, Q: quartz, CAH_x: C_3AH_x, L: lime, c: calcite, Cc: $C_4A\underline{C}H_{11}$, G: gypsum, A: alite, B: belite, Gm: gismondine.

systems. This fact indicates that additional CH will probably be produced even after the first 90 days of hydration, appointing therefore a necessity for utilizing ashes (CH consumers) rich in soluble silica.

A noticeable difference related to the formation of hydration products in the tested blends, is the generation of AF_t (ettringite) phases and its subsequent transformation to AF_m (mainly monosulfate) phases with curing time. Ettringite is formed as early as in 2 days in both mixes as a result of the reaction of Ca^{2+} ions that live in the pore solution, with the aluminate rich fly ash phases. Later on, a significant intensification of AF_m peaks is observed, accompanied by the production of several calcium aluminate hydrates (C_4AH_{13} and C_2AH_6). In the literature there is agreement that the production of AF_m phases, principally monosulfate, is the outcome of the AF_t conversion due to increasing dissolution of aluminate ions from the fly ash glass [19,31]. However, this is not the case here, as the AF_m peaks seem to grow independently of the AF_t ones. This is clearer in the CT_f blend, where especially after the first month of hydration a simultaneous intensification of the peaks representing the aforementioned phases is observed. A possible explanation for that could be the presence of anhydrite in T_f ash. This observation is consistent with the work of Tishmack et al. [16], who noted that ettringite formation increases with increasing anhydrite levels. However, a synergetic effect caused by the carbonation of interlayer sulfate groups in monosulfate causing a delayed ettringite formation cannot be excluded, especially when carbonate hydrates ($C_4A\underline{C}H_{11}$) are observed at this age.

The consistent production of pore-filling AF_t and AF_m phases, even at late stages, obviously contributes to the final strength of the CT_f system and provides an additional explanation for the superiority of this blend at later ages. The visible absence of peaks in the XRD patterns correspondent to the main hydrates, C–S–H, implies the poor crystallinity of both the initial gel and the 'pozzolanic' C–S–H formed afterwards.

3.4. ESEM test

ESEM examination verified the results reported in previous sections and provided an image of the microstructural development of the tested blends. In this approach, special attention was given in the FC mix that presented the best behavior at the end of the curing period, that is the system containing 30% by weight T_f ash. Fig. 9(a) shows the microstructure of the paste at 2 days of hydration. Unreacted fly ash particles (points marked with A) retaining their smooth and spherical shape are distinguishable, while some others have already been covered by hydration products (mostly CH, point B). Rodlets present in the matrix (points C) indicate the presence of ettringite. At this age the fly ash particles act mainly as additional nucleation sites, promoting the precipitation of hydration products formed and therefore accelerating the hydration of calcium silicate phases of cement.

The numerous voids visible in the structure of the blend at 2 days decrease substantially after 5 days, leading to a more compact morphology (Fig. 9(b)). At

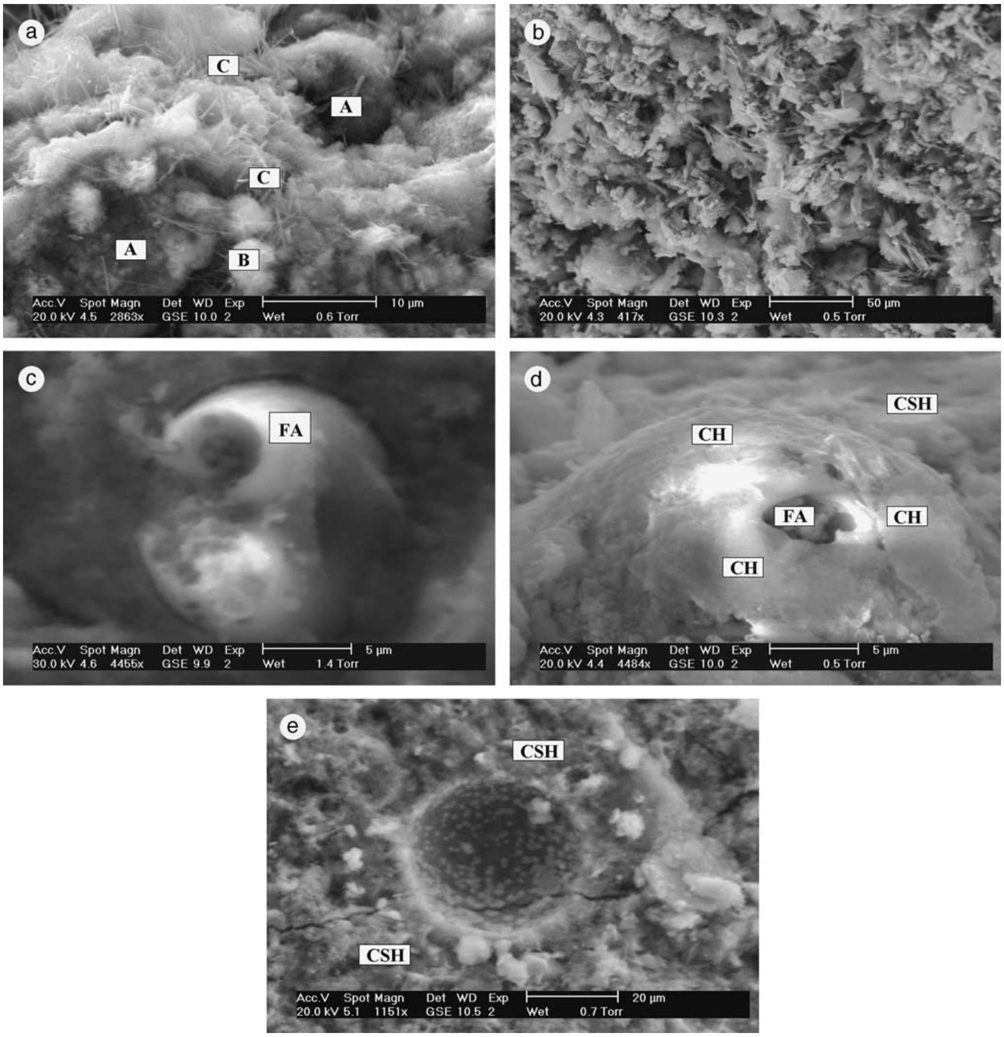

Fig. 9. (a) ESEM image of the blend with 30% T_f addition after 2 days of hydration. (b) Seven days of hydration. (c) Reacted fly ash particle at 7 days of hydration. (d) 28 days of hydration. (e) 90 days of hydration.

this age, fly ash particles have been encapsulated into the matrix of hexagonal calcium aluminates, AF_t phases and monosulphate formed. The formation of this network is to a large extent ascribed to the high sulfur content of fly ash. The strong presence of Na^+ and K^+ ions in the hydration products implies that dissolution of alkalies by some fly ash particles has taken place. X-ray mapping and elemental distribution analyses on a reacted fly ash particle at this age (Fig. 9(c)), revealed the high presence of alkalies and Ca^{2+} ions in the exterior glass hull of the ash confirming that these species are available from the ash particles from the very early ages. During the same analysis, silica was detected in the interior glass matrix of the ash particle. This indicates that glassy silica is not readily dissolved into the matrix. There is a need for the exterior glass shell of fly ash to be broken down, so as silica will run freely in the pore solution, leading to the formation of products with binding properties. The dense cluster formed by the generation of monosulfate reinforces the already present ettringite, providing an explanation for the satisfactory early age strengths. This is consistent with the work of Diamond [33] who monitored the hydration of resembling high-lime fly ash/cementitious systems.

One month after mixing, breaking of the fly ash glass has progressed leading to the formation of a flocculent C–S–H gel that surrounds the majority of the particles. This is an indication that pozzolanic reaction is evolving and that part of the amorphous silica in the ash is released into the matrix, combining available portlandite and forming a second generation C–S–H, improving the strength of the system. Numerous fly ash particles on the other hand, have been completely covered by hydrated lime crystals (Fig. 9(d)). From the early 80's, Grutzeck et al. [34] noticed that extensive surrounding of fly ash particles by CH, results in a dramatic limitation on the reactivity of the particles. This possibly accounts for the strength loss of the fly ash systems at this age when compared to the control sample.

After 90 days the paste structure has further densified (Fig. 9(e)), a fact that corresponds to its higher strength. Silica from the ash particles is increasingly dissolved, joins the pore solution, reacts with still available calcium hydroxide, and provides additional pozzolanic C–S–H. The binding properties of this gel supplement the filling effect of the ashes than remain intact, leading in a subsequent decrease of the pores in the paste. Ettringite and monosulfate were also detected during the XRD test. Obviously these phases continued to develop and needle crystals crossed each other to form an improved and frame microstructure.

4. Concluding remarks

When incorporating high-calcium fly ashes in cementitious systems, the soluble silica present in the ashes significantly affects their hydration. This effect seems to be substantial especially after the first month of the hardening process, when silica is dissolved in the matrix to form additional cementitious compounds with binding properties, principally a second generation C–S–H. Active silica was found to be critical both in the strength development and in the CH depletion of such blends especially after the first month of the hardening process. Increased replacement of cement by a high-siliceous reactive fly ash was found to accelerate the strength of the system and the formation of hydration phases, proclaiming that such ashes are more appropriate for replacing high volumes of cement. A synergetic effect that upgraded the final performance of the examined systems was related to the persistent appearance of AF_t and AF_m phases even at later ages, attributed largely to the mineralogical composition of high-calcium fly ash.

It is well known that the reaction of fly ash is not uniform since some particles react faster and to a greater extent than others that remain almost intact. Although ashes rich in active silica are generally more preferable, this does not excludes the possibility of achieving greater reaction rates and superior performance when utilizing different ashes. In other words, the rate with which fly ashes react in resembling systems, seems to be independent of the active silica content. For ultimately confirming this remark, additional research work must be conducted, since the present results are deeply associated with the cement type used. The present research group works in this direction and findings will be published shortly.

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