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ScienceDirect
Cement and Concrete Research 37 (2007) 877–885
Cement and Concrete Research

Improving the performance of ternary blended cements by mixing different types of fly ashes

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Received 9 February 2006; accepted 13 February 2007

Abstract

For overcoming certain drawbacks characterizing both basic types of fly ashes (of high and low calcium content), different ash intermixtures consisting of two types of fly ashes were prepared. The principal idea lying beneath the effort presented herein is that beneficial assets of the one type of ash could compensate for the shortcomings of the other. Compressive strength development, pozzolanic activity potential and nature of hydration products of all ternary cements were closely monitored and presented in comparison to the respective properties of the initial binary blends. Moreover, efficiency factors were calculated for all new systems and were further used to validate previously reported expressions describing Binary Fly ash-Cement (BFC) systems. In accordance with previous works, ternary fly ash systems examined here outperformed the respective binary systems almost throughout the curing period. Synergy between the different types of fly ashes was considered the main reason for the excellent performance of the ternary mixtures. Results obtained indicate that previously developed analytical expressions, correlating active silica of SCMs and *k*-values, can be applied in the case of multicomponent ash systems as well.

Keywords: Synergic action; Kinetics (A); Hydration Products (B); Blended Cement (D); Modeling (E)

1. Introduction

Since the mid-nineties, a significant increase in the production of blended cements incorporating Portland cement and two (in the case of ternary cements) or even three (quaternary) supplementary cementing materials (SCMs) has occurred. The advantages of these types of cements compared to the respective binary systems [1–3] motivated considerable research in this field. The principal aim of all of these efforts was to produce resource-efficient cement and concrete with tailor-made properties, based on the unique features of the third component in the mix, which in most cases compensated for the shortcomings of the pozzolan initially used. Therefore, several types of blended cements with various combinations of fly ash–silica fume, fly ash–slag, or slag–silica fume were rapidly developed and nowadays are commonly used in several countries [4,5]. However, there are still a number of shortcomings, associated with several SCMs that actually prevent ternary blended cements from being more universally applied. These include their higher cost relative to Portland cement (especially in the case of silica fume or metakaolin), the higher water requirement, and also, in some cases, the generation of greater amounts of heat (during hydration) leading to undesirable temperature rises in concrete [6–8].

Fly ash constitutes the primary SCM for the majority of the ternary blended cements that are designed and produced. This is not only due to its great global availability (over 600 tons annually) and low cost, but also due to the fact that is clearly the most tested and best quality-controlled SCM being utilized in the construction sector. Moreover, it has been repeatedly proved that despite its relatively slow rate of reaction [9], it generally provides improved workability [9,10], higher later-age strength [11–13] and superior resistance towards aggressive media [14–16] when it is added in cement and concrete. Materials such as silica fume [3,5] and metakaolin [1,7], possessing significant quantities of silica in active form, have been employed to

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doi:10.1016/j.cemconres.2007.02.017

compensate for the early strength loss and slow rates of reactions associated with class F and class C fly ash. In recognition of the fact that these tactics, although very effective, often resulted in substantial cost increases, a number of researchers attempted to develop ternary blended cements based on the two aforementioned types of fly ashes. Naik et al. [16,17] for example, prepared several mixtures of blends of class F and class C ashes. The constructed blends, representing 40% of the total cementitious material, showed either comparable or better results (in terms of both mechanical properties and durability) than either the reference mixture or the mixture containing only the class C fly ash. Recently, Antiohos et al. [18,19] prepared intermixtures, using a class F fly ash and a highly siliceous active class C fly ash, and replaced up to 30% by weight of cement. The encouraging results obtained were attributed to the synergy between the ashes used, given that no significant alterations in the nature of hydration products were observed. Other authors have attempted to develop fly ash mixtures and use them for stabilization or pavement construction purposes [20], emphasizing their excellent performance even without the use of any binding agents.

The work presented here, is part of a research programme dealing with the production and evaluation of ternary blended cements made with two types of fly ashes (of high and low calcium content). Since class C ashes are the paramount industrial by-product being generated in Greek power plants (almost 82% of the total annual ash production) and given the vast heterogeneity of this material, the authors selected two class C ashes, differentiated by the content of their principal reactive constituents. Quantities of each of these materials were used to produce ternary cement systems by incorporating a class F ash. The overall aim of this effort was to ascertain the improvement, mainly in terms of mechanical properties, in the performance of the final product due to its partial replacement by a range of fly ash intermixtures. Additionally, the authors wanted to establish optimum class C/class F blending ash proportions and cements replacement dosages for attaining superior products. Results from this study may constitute a supplementary basis for explaining the effect of active silica content of fly ashes in such systems, since this is the factor that contributes most to the strength development of fly ash-cement systems.

2. Experimental set-up

2.1. Initial materials, characterization and preparation of ash intermixtures

Two high-calcium fly ashes (designated here as T_f and T_k) were selected from a total of eight ashes coming from Ptolemais area. The principal aim, during the selection process, was to use similar ashes that differed only in their reactive silica and calcium oxide contents; since these are of the main factors (along with fineness, active alumina and glass content) determining the pozzolanic activity and strength contribution of fly ashes [10,21,22]. Therefore, T_f contains unusually high reactive silica and rather moderate active CaO contents, whilst T_k is an ash of low active silica (inappropriate for use in concrete according to European standard EN 450–1 [23]) but very high active calcium oxide content. The third ash, of low calcium content (T_m) was from the Megalopolis area. A CEM I 42.5 type cement was used to prepare the binary and ternary fly ash cements. The oxide analysis of all the initial materials, and the physical characteristics fineness determined by laser granulometry and insoluble

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

	Materials							
	Cement	T_m	T_f	T_k	T_1	T_2	T_3	T_4
CaO	65.01	13.80	29.79	34.13	21.50	23.93	17.96	19.28
CaO_f	0.63	0.95	5.96	6.90	3.65	3.76	2.10	2.23
CaO_{re} [a]	n.a. [b]	9.42	21.52	26.33	14.76	17.88	12.56	13.64
SiO_2	20.28	51.36	36.92	29.73	44.08	42.16	48.00	46.55
SiO_{2re} [a]	n.a.	31.36	29.13	24.07	30.36	23.93	32.02	19.28
Al_2O_3	4.75	16.73	13.50	13.90	15.70	15.70	15.92	15.92
Fe_2O_3	3.76	8.75	7.06	6.49	8.75	7.14	8.92	7.77
MgO	1.61	2.26	2.69	3.56	2.45	2.80	2.36	3.01
SO_3	2.55	1.49	5.10	5.13	3.18	3.52	2.39	2.55
Na_2O	0.17	0.77	0.92	1.12	0.81	0.35	0.78	0.56
K_2O	0.35	1.52	0.50	0.68	0.93	1.10	1.26	1.31
LOI	2.31	4.86	4.36	4.03	4.61	4.45	4.71	4.65
IR (%) [a]	0.18	25.16	14.52	9.51	17.62	17.28	20.26	21.68
Glass content. S [c] (%)	n.a.	74.84	85.48	90.49	82.38	82.66	79.74	78.75
Blaine fineness (cm^2/g)	3.760	5.600	5.450	5.600	5.500	5.600	5.500	5.600
x' [d]		18.5	20.5	19.5	18.5	19.5	19.5	20.0
n [d]		1.06	1.04	1.10	1.07	1.06	1.08	1.09
Specific gravity	3.13	2.59	2.83	2.93	2.70	2.76	2.65	2.68

[a] The method specified in the European Standard EN-450 was followed for the estimation of the reactive silica and calcium oxide contents and the insoluble residue (IR) of the fly ashes.
[b] n.a.: not available.
[c] 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 – IR).
[d] x': position parameter, n: uniformity factor (based on Rosin Rambler Particle Size Distribution).

Table 2
Mix proportions applied for preparing the fly ash intermixtures

Fly ash (%)			
Intermixture	T_f	T_k	T_m
T_1	50	0	50
T_2	0	50	50
T_3	25	0	75
T_4	0	25	75

residue (using the procedure described in EN 450–1) are given in Table 1. The particle size distribution (PSD) of the ashes, were brought to similar fineness in an attempt to reduce the effect of fineness on the pozzolanic activity. This was accomplished by grinding them in a lab ball mill and monitoring of their specific surface. The process was terminated when the ashes reached similar PSD (as validated from the almost identical x' and n values given in Table 1) and same specific surface (approximately 550 m^2/kg Blaine).

After the ashes were brought to the required fineness, they were mixed in a rotating blender for half an hour to achieve homogeneity of the new blend. The new fly ash intermixtures were prepared by using various dosages of the high (T_f and T_k) and low (T_m) calcium fly ashes (see Table 2). The chemical composition and physical characteristics of the new blends are also given in Table 1. It should be noted that the blending procedure had a beneficial effect on the sulfate and free lime (CaO_f) contents of the blended fly ashes, as these either met (blends T_2 and T_4) the requirements stated in EN 450–1 'Fly ash for concrete' or approached conformation (blends T_1 and T_3). This is of special importance since excessive SO_3 and *f*-CaO contents of fly ashes are partly responsible for expansive reactions and cracking [24–26] that threaten the durability of structures made with blended cements.

2.2. Determination of the pozzolanic reactivity

The Chapelle test was used to assess the potential pozzolanic action of the raw and blended ashes [10,15]. In this accelerated test, a gram of each pozzolan is added into a dilute slurry of calcium hydroxide (reagent grade) and remains there for 18 h under hydrothermal conditions (100 °C). The solution is then filtered and the remaining quantity of lime in suspension is determined by titration. Results are expressed in grams of lime reacted per grams of pozzolan tested. Though quite reliable for comparing the pozzolanic potential of different materials [27,28] earlier studies [29] clearly demonstrate that the test cannot provide a completely dependable indication of the performance of the examined materials into a cementitious matrix under ambient temperatures. In this study, results were used to compare the potential reactivity of the ash mixtures with the respective ability of the raw materials.

2.3. Compressive strength and efficiency factors

The effect of the different fly ashes (raw and blended) on the compressive strength evolution of the respective blended cements was monitored by applying the compression test according to EN 196–1 [30].

Specimens were prepared by replacing 20 and 30% by weight of cement by each fly ash blend. The dry materials were sufficiently mixed before they were cast into 40 mm × 40 mm × 160 mm prisms. Keeping the w/b ratio constant at 0.5, a cement mortar without any fly ash (control) was prepared for comparison purposes. 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. For each age (2, 7, 28 and 90 days after mixing), three specimens of every mixture were tested and the mean value of these measurements is reported.

Based on the measured strength values, efficiency factors were determined in order to draw conclusions regarding the effectiveness of the binary and ternary cements. The efficiency factor is defined as the part of the fly ash, which can be considered as equivalent to Portland cement, having the same properties as the concrete without fly ash (obviously $k=1$ for Portland cement) [31]. In a recent work [21] the authors reported, for the first time, analytical expressions that related active silica of artificial pozzolans with k-values of their respective cementitious systems. Thus, an additional target was to determine whether these expressions could be also applied in the case of ternary ash cements.

2.4. Identification of crystalline hydration products

Paste samples were prepared (blended SCMs replaced 20% by weight of cement) and examined by X-Ray Diffraction (XRD) after 7 and 90 days of hydration. The raw materials were first mixed thoroughly by hand, water was added (a w/b ratio of 0.5 was adopted) and mixing continued in a mixer machine using two different speeds. The samples were then cast in 40 × 40 × 20 mm^3 prisms and stored for 24 h under wet burlaps. The next day, the specimens were demoulded and cured under limewater at room temperature. At selected ages (7, 28 and 90 days), the samples were taken out of their batches and hydration was stopped with the addition of acetone and diethylether. After the pore water had totally exchanged with the organic solvents, the specimens were dried in a vacuum pump to remove any evaporable water that remained in the samples. Immediately after removing them from the vacuum pump, the dried samples were sealed hermetically into plastic bags. After crushing them into pieces, fragments from the core of the paste prisms were selected and pulverized into powder so as to pass the 90-μm sieve. XRD patterns of the hydrated samples were recorded using a Siemens D 500 X-ray diffractometer (CuK_a radiation, 40 kV, 30 mA) in a scanning range of 5 to 65° in 2Θ scale. The testing rate that was applied was 0.02^0/sec for all specimens and identification of the products was carried out by using a Diffrac-At Database.

3. Results and analysis

3.1. Chapelle test results

The results of the Chapelle test are plotted in Fig. 1 in relation to the reactive silica content of the materials used. Clearly, initial low-calcium fly ash T_m binds more CH than both

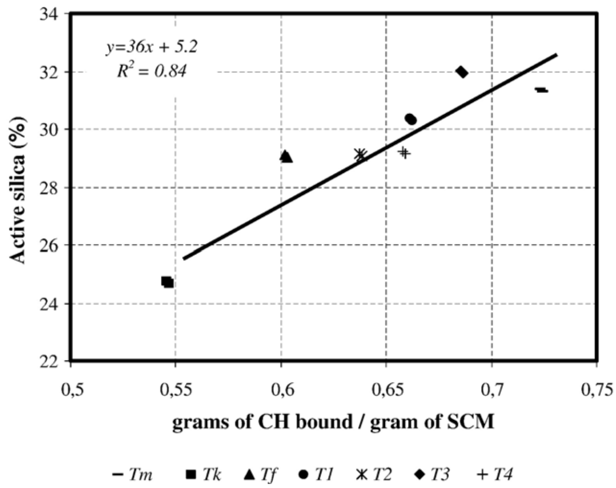

Fig. 1. Chapelle test results for initial and blended ashes in relation to their active silica content.

raw ashes of higher calcium content (T_f and T_k) binding more than 70% of the quantity added. On the contrary, both C classes fix less lime, with T_f ash being the most reactive, due to its higher active silica content. The active silica content seems also to designate the performance of the ternary ash systems, whose behaviour is between the activities of the ashes that constitute them. The plotted data show a significant correlation between the pozzolanic potential of fly ashes and their active silica content, a fact that was more or less expected since that is the fraction of the total silica contained in the ash that is participating in the pozzolanic reactions. Despite the fact that pozzolanic potential cannot be directly associated with the exact performance of a fly ash in a blended cement, it can be argued that the percentage of silica that it contains in its amorphous phase (therefore active in an alkaline environment) can be used to obtain an approximate image on its contribution in longer-term strength development [21,32–34].

3.2. Compressive strength development

Compressive strength development of the pozzolanic mortars is shown in Fig. 2(a) for the case where fly ashes replaced 20% cement by weight. It is clear that the control specimen (no-fly ash addition) performs better than every fly ash specimen up to 7 days of hydration. This is consistent with previous studies which have shown that fly ashes do not contribute notably to the early strength development of cement systems [33–35]. However, after the first two days, pozzolanic systems are starting to develop strength at a faster rate than the control. In fact after 28 days of curing, all fly ash samples are either approaching or outperform the no-fly ash mortar. At this age, the intermixture prepared with equal contributions from high-calcium T_f and low-calcium T_m ashes (T_1) is the sample exhibiting maximum strength value. This is of special importance since, at the same age, the strength values of the corresponding binary fly ash systems (T_f and T_m respectively) are lower, indicating that synergy between the different ashes has taken place. It is postulated that this synergistic effect has done much to initiate earlier the pozzolanic reaction of the new blended system. Synergy is also detected in the rest of the intermixtures, which perform slightly better than their corresponding binary blends.

With continuous curing (at 90 days), an improvement in the strength performance of the pozzolanic samples can be detected. At this stage of hydration, the fly ash contribution to the strength of the mortars is greater than the one caused by the hydration of the cement minerals which have been replaced. The T_1 mixture is continuous to exhibit a slight superiority amongst all intermixtures tested, providing a guidepost that for moderate cement replacement levels, mixtures of high and low-calcium ashes in a ratio of 50:50 are very effective in terms of mechanical properties. The superiority of T_1 mixture with regard to the other intermixture containing equal quantities of different ashes (T_2), can be mostly associated (given the fact that fineness of all ashes is similar) with the greater amount of reactive silica contained in T_f, which holds a predominant role in strength development especially after the first month of a fly ash-cement system's hydration [33,34,36]. The fact that, at this stage, all fly ash intermixtures are performing better than the initial ashes (something that was not detected at 28 days) could be denoting that synergy between the ashes boosts with curing time.

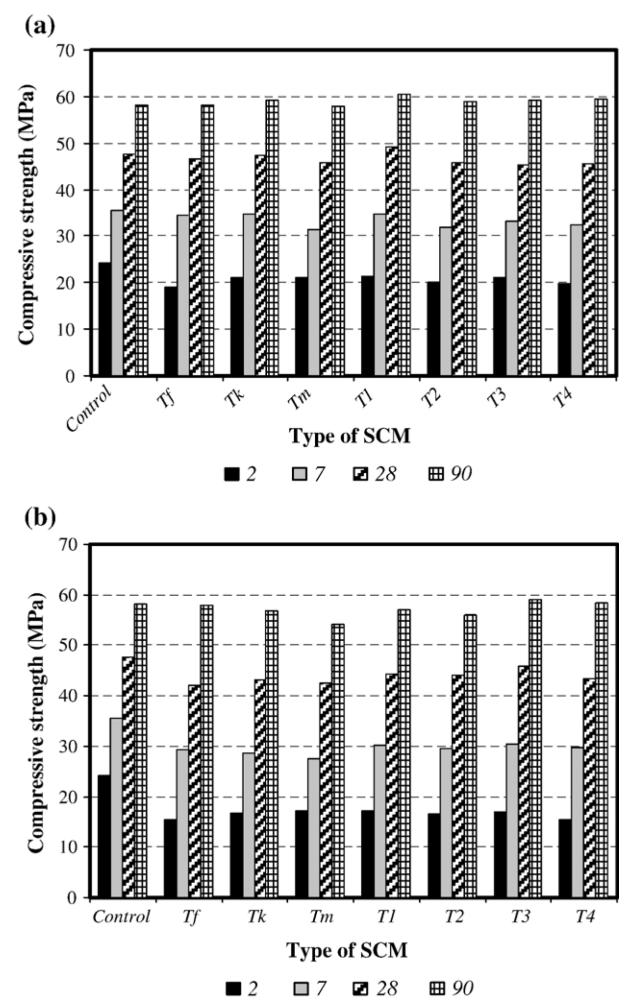

Fig. 2. Compression test results for (a) 20% and (b) 30% by weight cement replacement.

When 30% of fly ash replacement was used in the mixes (Fig. 2(b)), synergistic effects could still be detected between the ashes as early as from 2 days of curing. Even though strength development of the binary and ternary fly ash blends was further retarded due to the increased cement replacement, the intermixing procedure had clearly beneficial effects both on the early and later-age strengths of the binary systems. The superiority of the blended fly ashes continues up to the end of the testing period, when a dramatic strength improvement occurs in all fly ash specimens. Contrariwise to the results obtained when a moderate cement volume was substituted, the most efficient blends here are the ones with a substantial participation of low-calcium ash T_m, that is, T_3 and T_4 blends, with the former being slightly better possibly due to its excess of active silica. It can be postulated that when a fly ash acquires a more pronounced role in a cementitious blend (via its larger use), what governs the later-age strength development is the silica that it contains in its glassy phase, even if coming from a combined use of different reacting fly ashes.

3.3. Estimation of the efficiency factors and validation of analytical modeling expressions

It has been well established [21,31] that in the case of mortars and concrete that incorporate supplementary cementing materials, the efficiency factor, k, can be determined from the following expression for the measured compressive strength (f_c):

$$f_c = K\left(\frac{1}{W/(C+kP)} - a\right) \tag{1}$$

where K is a parameter depending on the cement type (here 38.8 MPa), C and P are the cement and fly ash contents respectively in the mortar (kg/m^3), W is the water content (kg/m^3) kept constant in all the mixes and a is a parameter depending mainly on time and curing. Using the above equation and compression test results, the efficiency factors of the examined systems were calculated and are presented in Table 3. In recent attempts with resembling ashes [18,19,21,31], the efficiency factors reported were below unity during the early hydration stages, but latter on, as their active constituents were involved into pozzolanic reactions, they reached and exceeded unity. All initial ashes tested herein perform, more or less, similarly, with high-calcium ashes exhibiting a slight superiority possibly due to the fact that they are involved earlier in the pozzolanic reactions (greater glass content than T_m ash). Regardless of the fact that T_f and T_k perform better than low-calcium T_m during the whole testing period, the intermixtures containing appreciable quantities of T_m outperform almost every binary system tested at both levels of cement replacement. In fact, the ternary ash cements present decent early-age k-values and at 90 days they all exceed the corresponding values of the initial ashes. This is an additional indication of the synergy developed between the different ashes in ternary systems. When the replacement dosage is increased (i.e. 30%) the k-values of all systems are normally diminished [19,21]. The fact that blends with substantial T_m (T_3 and T_4) exhibit k-values above unity at the end of the curing period clearly manifests the ability of blended fly ash systems having appropriate active silica contents to replace equivalent amounts of Portland cement even at high cement replacements, giving final products of the same quality.

Table 3
Efficiency factors of binary and ternary blended cements for 20% and 30% by weight of cement replacement

Age (days)	Efficiency factor						
	T_f	T_k	T_m	T_1	T_2	T_3	T_4
20%							
2	0.67	0.81	0.81	0.82	0.73	0.80	0.73
7	0.92	0.94	0.72	0.94	0.76	0.84	0.78
28	0.92	0.97	0.88	1.09	0.87	0.85	0.86
90	0.99	1.06	0.97	1.15	1.05	1.06	1.09
30%							
2	0.63	0.68	0.71	0.71	0.68	0.70	0.63
7	0.73	0.70	0.65	0.76	0.73	0.78	0.75
28	0.76	0.80	0.78	0.85	0.84	0.92	0.81
90	0.99	0.94	0.82	0.95	0.90	1.03	1.01

Table 4
Theoretically (based on Eq. (4)) calculated k-values compared to k-values based on experimental data

Age (days)	Synergic action (MPa)							
	SCM dosage (% by weight of cement)							
	20				30			
	T_f	T_2	T_3	T_4	T_1	T_2	T_3	T_4
2	1.25	−1.10	0.42	−1.30	0.85	−0.45	0.23	−1.58
7	1.75	−1.05	1.03	0.08	1.80	1.45	2.55	2.03
28	2.90	−0.90	−0.65	−0.75	1.85	1.25	3.33	0.57
90	2.55	0.55	1.33	1.38	1.00	0.40	3.95	3.65

In recent work [21] the authors reported, for the first time, analytical expressions that related the active silica content of artificial pozzolans with the k-values of their respective cementitious systems. The principal idea was to enable a first approximation of the future performance of those systems by knowing primarily the amount of silica present in the amorphous phase of the SCM. The authors concluded that for a SCM-system, k-value can be expressed as follows:

$$k = \left(\gamma_S W_{S,P}/W_{S,C}\right)(1-aW/C) \tag{2}$$

where γ_S is the weight fraction of the oxide SiO_2 in the SCM (given in Table 1), which contributes to the pozzolanic reactions (i.e. the ratio of active silica to the total silica in the SCM), $W_{S,P}$ and $W_{S,C}$ are the weight fraction of silica in the SCM and cement respectively and W/C is the water-to-cement ratio. By applying the above equation for the blended SCMs of the present work at 28 and 90 days of hydration (stages at which reactive silica is considered to have a more drastic effect) k-values were calculated and presented in Table 4, together with the respective measured values. It can be seen that, at both hydration stages, and for almost all intermixtures examined, the theoretically calculated values are in a good agreement with the experimental ones, in particular in the case of the T_2 and T_4 ternary ash cements. Maybe, this is due to the presence of a high-lime ash of normal active silica content instead of the unusually high present in the second high-lime T_f ash. To conclude, it can be argued that Eq. (2), formulated originally for simple binary SCM systems, can be also applied to ternary ash cements.

3.4. Quantification of the synergic action

In an attempt to quantify the synergic action detected between the ashes used throughout the curing period the following equation was used [19]:

$$SA = P_{(\mathrm{T}i+\mathrm{T}j)} - \left(W_i P_{\mathrm{T}i} + W_j P_{\mathrm{T}j}\right) \quad (3)$$

where SA is the synergic action (in MPa) occurring between two different ashes in a ternary blend, $P_{(\mathrm{T}i+\mathrm{T}j)}$ the measured compressive strength (in MPa) of each ternary system prepared for a given age, $P_{\mathrm{T}i}$ and $P_{\mathrm{T}j}$ the compressive strength values of the corresponding binary systems at the same age (in MPa), and finally W_i and W_j the proportion by weight of each ash in the ternary blend. Using the above equation and strength data presented in Figs. 2(a) and 3(b), the SA-factors were estimated in each case separately and are given in Table 5 in relation to the cement replacement ratio adopted and curing age examined.

The fact that in the majority of the samples tested the SA factor values are positive testifies that the strength of these ternary ash cements is greater than the strength that the

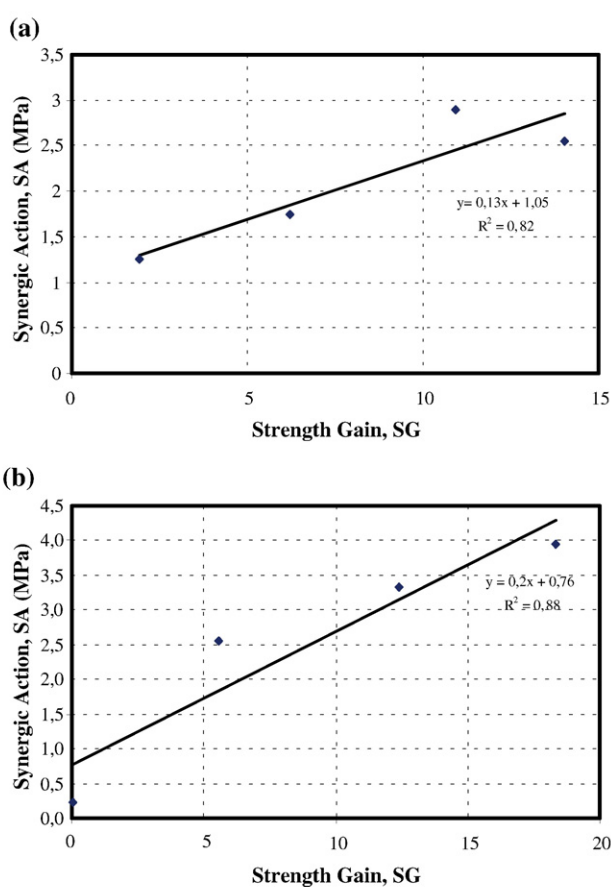

Fig. 3. Strength gain (SG) versus synergic action (SA) values for (a) T_1 and (b) T_3 ternary cements.

Table 5
Quantification of synergic action between the initial ashes in ternary ash blended cements

Pozzolan	*k*-value			
	28 days		90 days	
	Calculated	Measured	Calculated	Measured
T_1	1.08	0.90	1.15	1.10
T_2	0.87	0.87	1.05	1.06
T_3	0.85	0.95	1.06	1.16
T_4	0.86	0.87	1.09	1.06

respective binary fly ash-cement systems exhibited at the same ages. This is in accordance with the results obtained by Isaia et al. [36,37] who demonstrated that when the property (here compressive strength) of a ternary blended cement is higher than those of the respective binary systems, at a given age, this is almost entirely attributed to a synergy that has taken place between the two pozzolanic materials that co-exist in the mix. When comparing the performance of the four different ternary cements, it can be easily seen that in all cases of cement substitution and throughout the curing period applied, the synergy is more pronounced in the intermixtures containing high active siliceous T_f ash. On the contrary the presence of the other high-lime ash T_k, especially for a moderate cement replacement (i.e. 20%), seems to impede synergy with T_m ash even after the first month of hydration. When the same intermixture replaced a greater amount of cement (i.e. 30%) the situation differed notably since the SA values of the T_2 and T_4 specimens easily exceeded zero (no synergy) after the first week of curing. This indicates that synergy is favored by the increasing presence of the two different pozzolans in the cementitious matrix and at the same time provides a guidepost for the higher replacement of Portland cement by such fly ash intermixtures, regardless of the quality of the fly ash. Curing time seems to be an additional parameter that aids synergistic effects between the two types of ashes is, since the only case when the SA values of all ternary cements (for both replacement levels tested) are positive is after an extended curing period of 3 months.

The role of the synergic action (SA), developed between the ashes, in the mechanical performance of the ternary blended cements is highlighted in Fig. 3(a) and (b), where the SA values of the most efficient intermixtures (that is, T_1 for 20% and T_3 for 30% cement replacement respectively) are plotted against the strength gain values that the corresponding ternary blended cements exhibited during the hydration period examined. For estimating the strength gain (SG) of the blended cements, compressive strength data were inserted into Eq. (4) given below [38]:

$$\mathrm{SG}_i = R_i - \left(R_\mathrm{c} \cdot \frac{C_\mathrm{cem}}{C_\mathrm{poz}}\right) \quad (4)$$

where R_i the compressive strength of the pozzolanic specimens at a given age, R_c the compressive strength of the reference mixture at the same age, and C_cem and C_poz the proportions by weight of cement and sum of cement and pozzolan in each mixture respectively.

In both cases reasonable, almost linear, correlations were established between the plotted parameters, indicating that synergy is, to a great extent, responsible for the strength superiority of the examined cement systems. This coincides with relating work [19] that correlated linearly the SA factor with the efficiency factors (*k*-values) of resembling fly ash intermixtures. It can be argued that the simultaneous presence of two finely ground ashes is accelerating the deflocculation of cement grains [10,36,39]. This procures for the higher specific cement surface that comes into contact with water, leading eventually to the generation of more hydration products. The pozzolanic (chemical) effect of the ashes is obviously enhanced by the physical one, causing higher calcium hydroxide depletion and subsequently greater generation of secondary strength-providing hydration products. The possibility of an ongoing 'internal activation' process (due to instant hydration of free CaO in high-calcium ashes and temporal raise of alkalinity) that could be stimulating synergy is still under investigation [18,19].

3.5. Nature of crystalline hydration products

X-Ray Diffraction was used to detect possible changes in the hydration products caused by theuse of ternary mixtures. XRD patterns of the initial binary systems were examined and presented in comparison with their respective ternary systems both during the first (1 week) and later (12 weeks) stages of the curing process. Fig. 4 shows the XRD patterns of the binary (containing T_f and T_m) and corresponding ternary fly ash-cement pastes at 7 days after mixing. Main hydration products observed for all specimens at this age are portlandite, ettringite, AF_m and C_4AH_{13}. Portlandite is continuously produced in all samples, indicating the absence of pozzolanic reaction at such an early age. Any differences detectable between the initial fly ashes (such as variable intensity in the quartz and gypsum peaks) are mainly attributed to differences in their mineralogy. No other significant differences could be detected in the nature of the hydration products. An important observation, that possibly denotes that synergic action between the raw ashes has not developed yet, is that the intensity of the various peaks is highly depended on the participating percentage of each ash in the blends. For example, when the contribution of T_f ash was increased in the blends (from 25% in T_3 to 50% in T_1 blend) an intensification of the AF_t and portlandite peaks was observed as a result of the excess of sulfur and free lime contained in this ash. Contrariwise, intensity of crystalline silica (Quartz) diminished due to the reduction of T_m participation in the same blends.

90 days after mixing, some changes in the XRD patterns of the specimens (Fig. 5) are seen. For instance, the decrease of the portlandite peaks indicates the progress of the pozzolanic reaction (the consumption of CH by active silica of fly ashes), whilst carbonate hydrates are also appearing in all blended samples. This may be due to partial carbonation of the samples occurred during handling (after terminating hydration). Even thought calcium silicate peaks are relatively smaller, the presence of alite and belite after 90 days indicates that the hydration of the two main cementing phases is not yet complete. Ettringite and AF_m peaks are not only increasingly generated, but contrary to what is stated in the literature [10,40] the AF_m peaks seem to grow not in expense but along with the ettringite ones. According to Taylor [41], ettringite could persist because of a reaction with CO_3^{2-}, which reacts with monosulfate in the presence of $Ca(OH)_2$ to produce ettringite and hemicarbonate. Further reaction with CO_3^- causes the hemicarbonate to be replaced by monocarbonate and, ultimately the AF_m and ettringite phases are destroyed. In the context of this paper, this is not the case, since both phases persist until the end of the testing period. The fact that this phenomenon

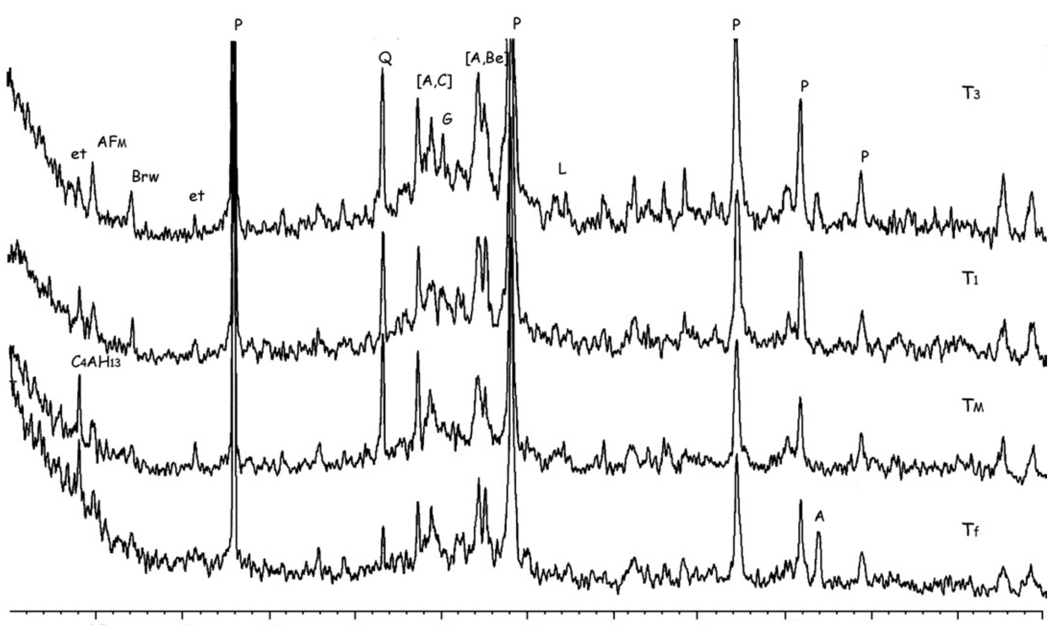

Fig. 4. XRD patterns of hydrated pastes after 7 days of hydration. (The following notations were used for the various minerals identified: et: ettringite, AFm: monosulphate, P: portlandite, Br: Brownmillerite, Q: quartz, L: lime, C: calcite, G: gypsum, A: C_3S, Be: C_2S).

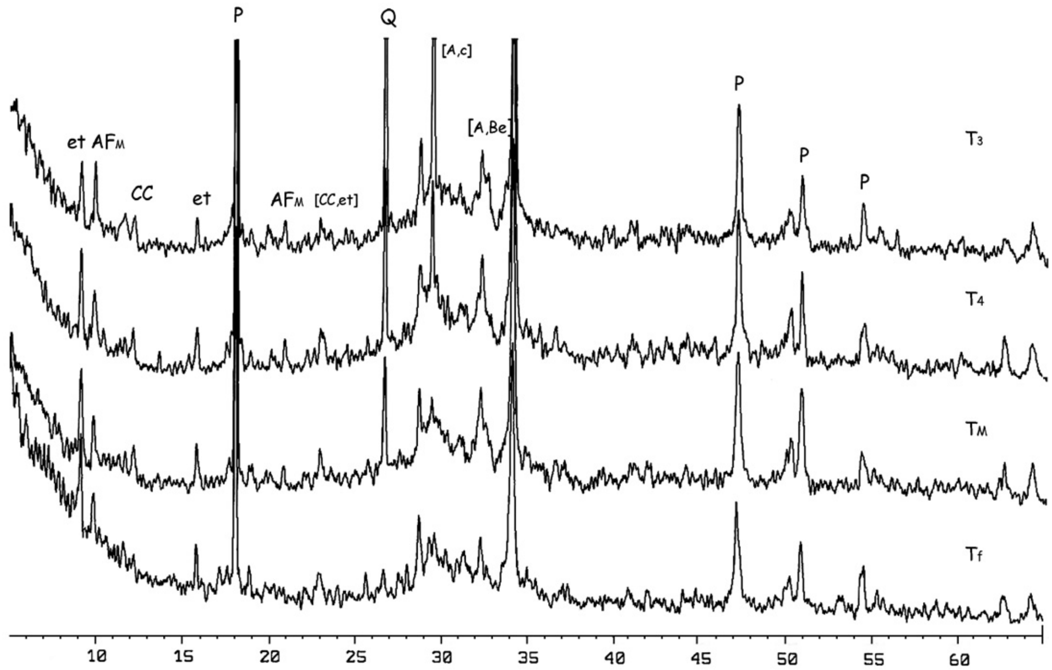

Fig. 5. XRD patterns of hydrated pastes after 90 days of hydration. (The following notations were used for the various minerals identified: et: ettringite, AFm: monosulphate, P: portlandite, Q: quartz, Cc: C_4A C H_{11}, C: calcite, G: gypsum, A: C_3S, Be: C_2S).

is more pronounced in the constructed blends constitutes an additional indication of the combined action of the initial ashes. The consistent production of pore-filling AF_t and AF_m phases, even at such advanced ages, contributes to the final strength of the ternary systems. The absence of any significant changes in the nature of the formed hydration products, with respect to those formed during the hydration of the respective binary systems, affirmed that synergistic action between the ashes is the main reason for the superior quality of the ternary ash cements.

4. Conclusions

The major conclusions derived from the present investigation can be summarized as follows:

1. The effect of blending different ashes resulted in improvements of the mechanical properties of the respective binary systems almost throughout the curing period.
2. It was demonstrated that blends with equal contributions from each fly ash (50:50 ratio) were found to be the most effective for moderate cement substitution, whilst at advanced cement replacements the apodosis of the intermixtures (especially after the first week of hydration) is highly depended on their active silica content.
3. Previously reported expression, correlating active silica of artificial pozzolans with *k*-values of binary cementitious systems, was validated in the present work for the case of multicomponent ash (ternary) blends. Using such an expression can lead to a relatively safe approximation of the future mechanical performance of the final product.
4. Since no significant alterations in the nature of hydration products were detected, the superior performance of the ternary blends was mainly attributed to synergistic effects between the utilized ashes. Results evidenced a combined synergic action between the different ashes possibly initiated by physical and chemical (pozzolanic) mechanisms.
5. Synergic action (SA factor) was estimated and almost linear correlations were established with the strength gain of the respective ternary blended cements.

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