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Evaluation of blends of high and low calcium fly ashes for use as supplementary cementing materials

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Abstract

The present paper outlines the results of a research attempt aimed at developing and evaluating the performance of ternary blended cements, incorporating mixtures of two different types of fly ash (of high and low calcium content). The main target of this study was to investigate whether and by what means, the introduction of a certain type of fly ash into a fly ash–cement (FC) matrix containing a different type of ash, can improve the performance of the initial binary system. For achieving this, new pozzolans were prepared by mixing, in selected proportions, a high lime fly ash with an ash of lower calcium content. The efficiency of the new materials was examined in terms of active silica content, pozzolanic activity potential, strength development, *k*-values and progress of the pozzolanic action by means of fixed lime capabilities. The results obtained demonstrated that the mixtures containing equal amounts of each fly ash were the most effective for moderate cement substitution, whilst for higher replacements the intermixture possessing the highest active silica content shows supremacy at almost all hydration ages. The superior performance of the ternary fly ash blends was mainly attributed to synergistic effects detected for all the ashes utilized. These were quantified in each case and almost linear correlations were obtained with the *k*-values of the most efficient ternary mixes.

Keywords: Hydration; Ternary blends; Amorphous material; *k*-value; Active Silica

1. Introduction

Continuous generation of waste by-products possessing hydraulic and pozzolanic properties, creates not only acute environmental problems, but additionally outlines a need for their greater utilization in different market sectors. The construction sector is clearly the one that, at the moment, absorbs the majority of such materials, by incorporating them in hydraulic binders as supplementary cementing materials (SCMs). Appropriate usage of these materials not only brings economical and ecological benefits, but also imparts technological improvements to the final product [1,2]. For fly ash in particular, it has been proved that despite its relatively slow rate of reaction, it brings forward improved workability [3], higher later age strength [1] and superior resistance towards aggressive media [4,5] when used as an additive in cement and concrete. What is more, advantages such as these accompany the final product even when fly ash replaces equal or more volume of cement [6,7].

Regardless of the fact that the benefits of the two main types of fly ashes (of high and low calcium content) are fairly well established, certain shortfalls associated with each type contribute to the skepticism with which this material is still treated by a significant part of the industry [8]. Recognising of the significant differences

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between the two types of fly ashes, Canadian Standards Association (CSA) recently revised the specification for fly ashes categorization, dividing them into three classes depending on their calcium content [3]. The aforementioned standard is actually the first that introduces a third category of fly ash, those with intermediate calcium content, stressing out the strong relation between the lime content of fly ashes and their future performance in a cementitious system.

In the literature there is an extensive body of information on the differences of the two types of fly ashes, with respect to their physicochemical properties, reactivity and behavior during hydration. It is low-calcium fly ashes for example that react slower, especially during the early stages of hardening, mainly due to the higher presence of crystalline phases, which are considered chemically inert in concrete [9]. High calcium fly ashes on the other hand react faster, are less sensitive to inadequate curing [10] and provide better early age strength. Moreover, high-lime fly ashes are generally less efficient in suppressing expansion due to ASR [11] and sulphate attack [12] than low-lime ashes. It is believed [1,3] that calcium substitution in the glass phase is generally increasing the reactivity of high-lime fly ashes providing for the formation of the calcium-silicate and calcium-aluminate phases in the absence of an external source of lime. It should be however pointed out that class C fly ashes differ from the class F ashes not only in that they contain more lime, but also the lime depolymerized glass phase [1].

In order to deal with shortcomings of each type of ash, the majority of the scientific community has attempted to introduce a third (ternary) or even a fourth (quaternary) highly reactive pozzolan into FC systems. Silica fume [13], metakaolin [14] and rice husk ash [15] have often been employed to compensate for the handicaps of the binary FC systems. Although these strategies have proved effective, in most cases they result in substantial cost increases, a fact that inhibits their wider acceptance and application as routine practices. An extended search in the published work has revealed that only a few researchers have examined the performance of ternary ash blends in cementitious systems. Naik et al. [16,17] for instance have prepared several mixtures of blends consisting of class F and class C ashes, principally aiming to control the rate of hydration. The constructed blends, that occupied 40% of the total cementitious material, showed either comparable or better results (in terms of mechanical and durability properties) than either the reference mixture or the mixture containing the class C fly ash solely. Mulder on the other hand [18], has prepared mixtures of different fly ashes and used them as road base construction materials, indicating that they provide an excellent solution for stabilization purposes without the use of any binding agents.

The primary aim of the study presented herein, was to prepare and evaluate the performance of new SCMs consisting of two types of fly ashes generated in great quantities globally. The authors wanted to determine whether and to what extent contributions of each type of ash could compensate for the handicaps of the other. If the two types of fly ashes can assist each other, or even better interact synergistically, they may constitute an excellent solution for producing superior cementitious systems of relatively low cost.

2. Set-up of the research

2.1. Raw materials and production of the blended SCMs

Two different fly ashes, all supplied by the Hellenic Public Power Corporation, one with high calcium content (from Ptolemais area), designated here as T_f, and one with lower calcium content (T_m from Megalopolis area) were used as the raw materials. The high lime ash possesses unusually high reactive silica content, whilst T_m on the other hand is a typical siliceous fly ash with moderate calcium content. Prior to use, all ashes were ground in a lab ball-mill to the same fineness in order to eliminate the influence of this parameter on their pozzolanic reactivity. For preparing the paste and mortar specimens a normal setting cement (CEM I 42,5 according to EN 197-1) was used. The chemical composition and main physical characteristics of the fly ashes and cement used are given in Table 1. The new blended ashes were prepared by mixing several proportions of the initial ashes. The mixing took place in a rotating blender (no further grinding was performed) until homogeneity of the blends was reached. The proportions applied were 75% T_f and 25% T_m (blend designated as T_1), 50% T_f and 50% T_m (for blend T_2), and 25% T_f and 75% T_m (T_3). The measured physicochemical characteristics of the new blends are also given in Table 1 An initial observation, based on the data presented in Table 1, is that the blending procedure had a beneficial effect on the sulfur and free lime contents of the new ash intermixtures, as these either met the requirements stated in European Standard EN 450-1 [19], or in the worst case (T_1 blend) nearly conformed with those.

2.2. Pozzolanic reactivity of blended SCMs

The pozzolanic activity potential of the initial ashes and their blends was determined using the Chapelle test [20,21]. According to this test, dilute slurry of the pozzolan reacts with calcium hydroxide at 100 °C for 18 h. The remaining quantity of lime into the suspension is then determined by titration and results are expressed in grams of reacted lime per gram of each pozzolan tested.

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

	Cement	T_f	T_m	T_1	T_2	T_3
CaO	65.01	29.79	13.80	24.89	21.50	17.96
CaO_f[a]	0.63	7.96	0.95	5.83	3.65	2.10
CaO_{re}[b]	–	21.52	9.42	17.83	14.76	12.56
SiO_2	20.28	36.92	51.36	40.38	44.08	48.00
SiO_{2re}[b]	–	29.13	31.36	29.60	30.36	32.02
Al_2O_3	4.75	13.50	16.73	14.65	15.70	15.92
Fe_2O_3	3.76	7.06	8.75	7.50	8.75	8.92
MgO	1.61	2.69	2.26	2.56	2.45	2.36
SO_3	2.55	5.10	1.49	4.02	3.17	2.39
R_2O	0.52	1.42	2.29	1.63	1.74	2.04
LOI	2.31	4.36	4.86	4.52	4.61	4.71
IR (%)[b]	0.18	14.52	25.16	14.83	17.62	20.26
Glass content, S[a] (%)	–	85.48	74.84	85.17	82.38	79.74
Blaine fineness (cm^2/g)	3.760	5.450	5.600	5.450	5.500	5.500
Specific gravity	3.13	2.83	2.59	2.72	2.70	2.65

[a] The method specified in the RILEM Recommendations (TC FAB-67 Use of Fly Ash in Building) was followed for calculating the free lime (CaO_f) content and the content (in % by mass) of the LOI-free fly ash constituents soluble in hydrochloric acid and potassium hydroxide ($S = 100 - \text{IR}$).

[b] The method specified in the European Standards EN 450-1 and 196-2 was followed for the estimation of the reactive silica and calcium oxide contents and the insoluble residue (IR) of the fly ashes.

2.3. Compressive strength development and efficiency factors estimation

For studying the compressive strength evolution of the new SCMs, mortar mixes were designed by adopting a cementitious material-to-sand (Cm/*S*) ratio of 1:3, water to binder ratio (*w*/*b*) of 0.5 and 20% and 30% by weight cement replacement. Keeping the *w*/*b* ratio constant, a cement mortar without any fly ash (control) and two mortars incorporating the two initial fly ashes (also replacing 20% and 30% by weight cement) were prepared for comparison purposes. Details regarding the exact procedure followed are given elsewhere [22,23]. For each testing age (2, 7, 28, and 90 days after mixing) two specimens of each mixture were tested for compressive strength and the mean value of these measurements is reported. Based on the compressive strength measurements, efficiency factors (*k*-values) were estimated in order to draw conclusions regarding the effectiveness of each new cementitious material.

2.4. Evaluation of the hydration process

For studying the hydration evolution of the specimens made, pastes were prepared using a similar procedure with that described above, adopting a representative 20% cement replacement at the same *w*/*b* ratio and curing under water at 22 °C. At the day of testing, the pastes were removed from their batches and they were fractured into pieces. The crushed samples were immersed with acetone and diethylethere in order to terminate the hydration reactions and finally they were dried to constant weight in a vacuum pump overnight. After the specimens were brought into powder form (all passing the 125 μm sieve), thermogravimetric and differential thermal analyses (DTA) were carried out to monitor the progress of the pozzolanic reaction in each blend. The measurements were performed in a Mettler STARe 851/LF/1600 TG/SDTA. The samples were tested in a nitrogen atmosphere (50 ml min^{-1}) at a heating rate of 10 °C min^{-1} from ambient temperature to 1000 °C. The weight of calcium hydroxide in the samples (expressed through the abrupt weight loss occurring in the temperature region of 400–550 °C) and the quantity of free-portlandite transformed into calcium carbonate (due to possible carbonation during handling) were estimated and afterwards added to determine the total CH percentage in all specimens.

3. Results and considerations

3.1. Pozzolanic activity potential

The results of the Chapelle Test are given in Fig. 1, where they are plotted against the reactive silica content of each sample tested. It can be seen that low lime fly ash (T_m) exhibits the greatest pozzolanic potential, combining a significant amount of lime. Contrariwise, high calcium ash (T_f), presents the worst behavior, in terms of grams of combined lime. The activity of the intermixtures fluctuates between those of the initial ashes, confirming the positive influence of the T_m addition to T_f. From the figure it appears that active silica of the tested specimens determines, to a large extent, their pozzolanic activity, a fact that was somehow expected since amorphous silica is actually the fraction that participates in the pozzolanic reactions [22,23]. It should be pointed

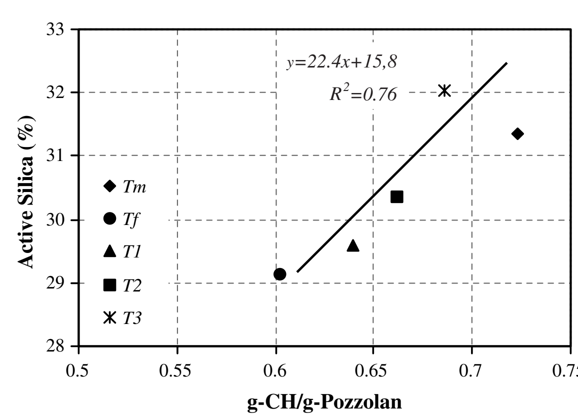

Fig. 1. Pozzolanic potential for initial and blended ashes in relation to their active silica content.

out however, that the Chapelle test cannot provide any direct information about the rate of reaction of the same material under ambient temperatures in a cementitious matrix [21]. Therefore it should be taken into account only as an indication of the relative reactivity of the examined SCMs.

3.2. Compression test

Fig. 2(a) illustrates the compressive strength results for the control and fly ash specimens in the case of 20% cement replacement, as a function of curing time. It is apparent that the control specimen outperforms almost all of fly ash mixtures throughout the first month of the hydration process. This is in agreement with the theory on the slow evolution of the pozzolanic action, which mainly determines the strength development of the systems containing fly ash. However, during the same period and especially after the first week of hydration, all fly ash specimens are developing strength at a faster rate than the control. The only mixture that presents higher strength value than the control after four weeks of hydration is T_2, made with equal contributions from the two initial ashes. Somewhat surprisingly at the same age the strength values of the corresponding binary systems are noticeably lower. This is clearly an indication that a synergistic effect between the two ashes has taken place, possibly leading to a quicker initiation of the pozzolanic action.

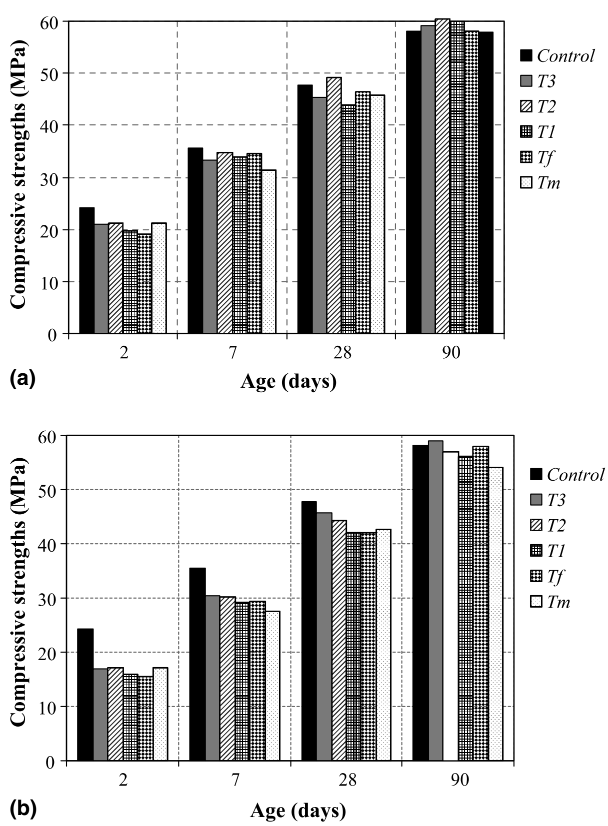

Fig. 2. Strength development of raw and blended fly ash-cement systems for (a) 20% and (b) 30% cement substitution.

High-lime ash T_f performs better than low-lime T_m during the early stages of hardening as a result of its higher active calcium oxide content, which participates in the reactions especially after the first two days. At that stage, the contribution of T_f in the ternary systems is critical, since those blends that incorporate more than 50% T_f (T_1 and T_2) outperform the ones with a lower T_f percent (T_3). At the end of the first month, T_2 blend has the higher strength than both the control mixture and the individual ashes, whilst the other blended specimens did not gain substantial strength, remaining lower than the individual ashes and the reference mixture. Conversely, after the next two months (at 90 days), the compression test revealed excellent strength values for all the blended fly ash specimens compared to the control specimen. The fact that at the same age the ashes consist of the blends are not performing evenly, provides a benchmark that at later ages even small contributions from each fly ash are effective in producing superior fly ash systems. The incorporation of a different type of fly ash in each constructed blend obviously did much to offset the synergetic effect that was also detected in previous hydration stages.

Even though synergy between the ashes is still detected in the case of increased cement replacement (Fig. 2(b)), it becomes clear that fly ash systems retard the strength development, especially during the early ages. This is mainly attributed to the increased cement content substituted and the well-established retarding effect of fly ashes. The initial ashes are presenting a similar behavior to the previous replacement dosage, but the most efficient blend is the one with substantial participation of low-lime T_m (blend T_3). It is possible that a small participation of high-lime ash T_f reduced the period before the onset of the pozzolanic reaction leading to a notable strength increase at 28 days. Three months after mixing, a marked improvement in the strength performance of all the examined blends occurs. This is testified by the fact that T_3 blend outperforms the control specimen, whilst T_1 and T_2 are only slightly falling short of the control specimen. Especially noticeable is the fact that in the systems with an appreciable fly ash presence (i.e. 30%), the strength of the blended fly ash mixtures is proportional to their reactive silica content from 7 days and onwards. This becomes even more pronounced after the first month of hardening, where the noteworthy strength improvement of the T_3 blend over the control specimen is the result of its high reactive silica, which binds CH forming accessory pozzolanic C–S–H. This is in agreement with the findings of Antiohos and Tsimas [23], who observed that the role of reactive SiO_2 in the strength development of FC systems that incorporate high-lime ashes becomes especially predominant after the first month of the hydration process.

3.3. Efficiency factors

The efficiency factor (or k-value) 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) [25]. Briefly, in the case of mortars and concrete that incorporate supplementary cementing materials, the k-value derives from the following expression for the compressive strength (f_c) measured for the constructed systems [8,25]:

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

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 α a parameter depending mainly on time and curing. Using this equation and the strength values in Fig. 2(a) and (b), the efficiency factors of the new intermixtures were calculated and are presented in Table 2.

For 20% cement replacement, the values given in Table 2 verify the results obtained from previous research dealing with Hellenic fly ashes [8,21,25]. All studies seem to agree that the k-values are around unity during the early ages and they progressively exceed it as the hydration procedure evolves. This means that tested fly ashes could easily substitute for cement guaranteeing equal mechanical performance. In the present work, both initial ashes (T_f and T_m) have a k-value less than 1 at 7 days, but afterwards as fly ash is involved in the pozzolanic reactions, they reach unity. The beneficial role of the intermixing procedure is again highlighted through the concept of the efficiency factor. The fly ash mixtures present good early-age k-values and at 90 days they all exceed the corresponding values of the initial ashes used. It is of special importance to note that the k-value of the blend consisting of equal contributions from the initial fly ashes (T_2) is very close to unity after only seven days of hydration and has significantly exceeded unity three weeks later. From the dramatic increase of the k-value of the T_1 blend observed during the last two months of hydration, it becomes clear that a small incorporation of a class F fly ash in a matrix rich in class C ash can assist the strength development of such a system especially after the first month of hydration.

When the pozzolan dosage increases (i.e. 30%), the k-values of all systems are normally diminished. Cooperation between initial fly ashes in the blends is still effective, providing k-values that are comparable even with the ones that the initial ashes exhibited at a lower replacement level during the early stages of hydration. As the hydration progresses, the blends are tardily reaching unity due to pozzolanic reaction taking place. Blend T_3 (with surplus of low-lime T_m) takes over from T_2 and performs better especially after the first week, reaching an appreciable value of 1.03 at the end of the testing period. This manifests the ability of blended fly ash systems containing appropriate active silica contents to substitute equally for Portland cement even at high fly ash/binder ratios [23].

3.4. Pozzolanic reaction evolution

Measuring, at a certain age, the quantity of calcium hydroxide (CH) generated and subsequently consumed in a pozzolanic cement matrix has often been employed as a way to monitor the evolution of the action of the pozzolan being incorporated in the examined system. Moreover, it is indicative of the rate at which pozzolanic materials are releasing their active constituents into the pore solution towards binding (or 'fixing') available lime. In the frame of this study, the CH measurements were used to calculate the percentage of fixed lime in the tested pastes. For this purpose, the following equation proposed by Paya et. al. [26] was applied for determining the percentage of fixed lime in each case.

$$\text{Fixed lime }(\%) = \frac{(CH_c \cdot C_{\%}) - CH_P}{CH_c \cdot C_{\%}} \times 100 \quad (2)$$

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 $C_{\%}$ is the proportion of cement in the examined paste (obviously here $C_{\%}$ is 0.8).

The fixed lime values of the FC systems containing the initial ashes and their intermixtures are presented

Table 2
Efficiency factors for raw and mixed fly ashes

Age (days)	k-values									
	SCM addition (% by cement weight)									
	20					30				
	T_f	T_m	T_1	T_2	T_3	T_f	T_m	T_1	T_2	T_3
2	0.67	0.81	0.72	0.82	0.80	0.63	0.71	0.65	0.71	0.70
7	0.92	0.72	0.89	0.94	0.84	0.73	0.65	0.72	0.76	0.78
28	0.92	0.88	0.75	1.09	0.85	0.76	0.78	0.76	0.85	0.92
90	0.99	0.97	1.12	1.15	1.06	0.99	0.82	0.91	0.95	1.03

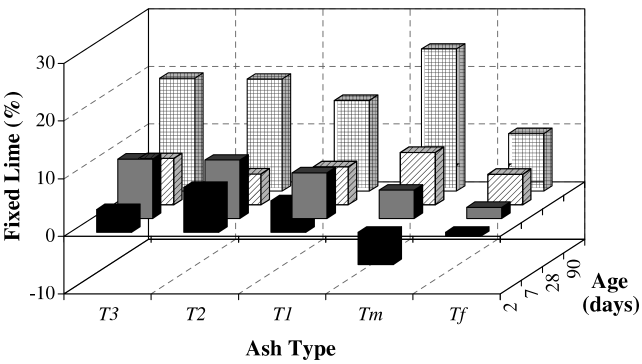

Fig. 3. Fixed lime values of fly ash specimens with hydration age.

as a function of the curing time in Fig. 3. In general, it can be observed that the fixed lime values are increasing with progressing hydration, as a result of the evolution of the pozzolanic action of all fly ashes tested. Negative values observed for both initial fly ashes during the very early stage of hardening, are attributed to their well-established inability to react from the beginning of the hydration process and also to the acceleration of the hydration of the cement grains that occurs during their presence [23,25]. On the contrary, after the same hydration period, all the new blended SCMs that are based on the initial ashes, are presenting positive fixed lime values, validating the previous remarks regarding the synergy taking place as early as two days after mixing. Up to the first week of curing, the ternary fly ash blends are outperforming the corresponding binary systems, with T_2 and T_3 being the most efficient in this respect. On the other hand, the SCM containing an excess of T_f exhibits the worst behavior, but it still binds more lime than the sum of the corresponding binary mixes, almost throughout the testing period. This is clearly depicted in Table 3, where the synergistic effect (SE factor), in terms of depleted lime, is quantified as the difference of the measured value and the theoretically expected in each curing stage that was investigated.

The ability of the ternary ash blends to fix lime seems to be retarded after the first month of hydration. In this stage, no synergy in fixing lime is detected (Table 3) between the ashes that consist of the new SCMs. However, the peculiar image that the ternary ashes present at this stage cannot be entirely associated with their inability to react fast, but it could be attributed to the simultaneous production (due to the participation of high lime ash in every blend) and consumption of CH. At 90 days, the intermixtures are fixing notable amounts of lime, confirming the predominant role of active silica at such an advanced hydration level [23]. Both T_1 and T_2 mixtures are binding more lime that was theoretically expected, with the latter showing supremacy in this respect. This provides an additional explanation of the previously presented strength superiority of the intermixture containing equal amounts of the two types of ashes (T_2 blend), at the end of the testing period.

3.5. Quantification of the synergistic action

It is possible to calculate the increment observed in the compressive strength of the ternary fly ash systems due to the synergistic action between the two different types used. In the frame of this study, this was achieved by using the following equation:

$$SA = P_{(T_f+T_m)} - (W_f P_{T_m} + W_m P_{T_m}) \qquad (3)$$

where SA is the synergic action (in MPa) between the two types of ashes, $P_{(T_f+T_m)}$ the measured compressive strength (in MPa) of each ternary system prepared for a given age, P_{T_f} and P_{T_m} the compressive strength values of the corresponding binary systems of the same age (in MPa), and finally W_f and W_m the contribution by weight of each ash in the ternary blend. Using this equation and the compressive strength values presented earlier, the various SA factors were calculated and presented in Table 4, in relation to the SCM dosage and the curing period adopted.

The fact that the majority of the values plotted are positive indicates that for both replacement levels and for most ages examined, synergy took place between

Table 3
Synergistic effect factor (SE) in terms of fixed lime capability of the blended SCMs

Specimen	Curing time (days)											
	2			7			28			90		
	M[a]	*E*[b]	SE[c]	*M*	*E*	SE	*M*	*E*	SE	*M*	*E*	SE
T_f	−0.75	na[d]	na	1.95	na	na	5.29	na	na	10.01	na	na
T_m	−5.63	na	na	4.95	na	n.a.	9.09	na	n.a.	24.69	na	na
T_1	5.48	−1.97	7.45	7.89	2.70	5.19	6.59	6.24	0.35	15.76	13.68	2.08
T_2	7.81	1.09	6.72	10.12	7.53	2.59	5.38	7.23	−1.86	19.45	17.35	2.10
T_3	3.95	−4.41	8.35	10.31	4.20	6.11	8.05	8.14	−0.09	19.61	21.02	−1.41

[a] Measured fixed lime value (%).
[b] Theoretically expected fixed lime value (%) based on the sum of the measured values of the corresponding binary systems.
[c] Synergistic effect expressed as the difference of the measured and the expected values (i.e. SE = $M - E$).
[d] Not available.

Table 4
Quantification of synergic action between the initial ashes in ternary SCMs

Age (days)	Synergistic action (SA)					
	SCM dosage (% by weight of cement)					
	20			30		
	T_1	T_2	T_3	T_1	T_2	T_3
2	0.18	1.25	0.42	0.07	0.85	0.23
7	0.27	1.75	1.03	0.25	1.80	2.55
28	−2.55	2.90	−0.65	−0.13	1.85	3.33
90	1.97	2.55	1.33	−0.85	1.00	3.95

the ashes to further improve the efficiency of the pozzolanic systems with respect to the reference specimen and the corresponding binary systems. In previous attempts with ternary systems [15,27], it was shown that when a less reactive pozzolan, such as fly ash, is introduced in the matrix of a ternary system with silica fume or rice husk ash and metakaolin, a synergy occurs between these materials, thus the result obtained of an examined property (i.e. compressive strength) is higher than those that the respective binary systems exhibit. This is obviously the case here as well, where high lime ash probably reacts faster due to its higher glass phase (and given that the finenesses of the two ashes are similar) to improve the performance of the more crystalline low-lime ash also employed in the ternary SCMs. It is postulated that due to their physical effect, both finely ground ashes are accelerating the deflocculation of cement grains, which has been shown to be higher than that of the silica fume or rice husk ash particles [16,27]. This procures for the higher specific cement surface that comes into contact with water, leading eventually to the generation of more hydration products. The physical effect obviously enhances the chemical one (pozzolanic action of fly ashes), ultimately causing a higher calcium hydroxide depletion, formation of secondary hydration products, providing for the higher strength of the system. Moreover, it is possible that the instant hydration of free lime present in high-lime ash raises temporarily the alkalinity of the ternary systems, assisting the dissociation of the firm glassy chain of the low lime ash and subsequently the release of additional active centers (principally active silica) in the matrix. The possibility of such an 'internal activation' process taking place to offset the pozzolanic reactions could not be excluded, but it should be further investigated in resembling systems.

The determinative role of the synergic action in the performance of the new blended SCMs is validated in Fig. 4, where the SA values of the most efficient fly ash intermixtures (for the two cases of cement replacement applied) are plotted against the *k*-values they exhibited in each stage where hydration was terminated. It can be seen that both for T_2 and T_3 blends, which were proved to be the most efficient for a cement replacement of 20% and 30% respectively, almost linear relationships were established between the examined parameters. It could be argued that this is an additional indication that the synergy taking place between the ashes (expressed through the calculated SA values) is a deciding factor for the superior mechanical performance (expressed through the *k*-values) of these SCMs.

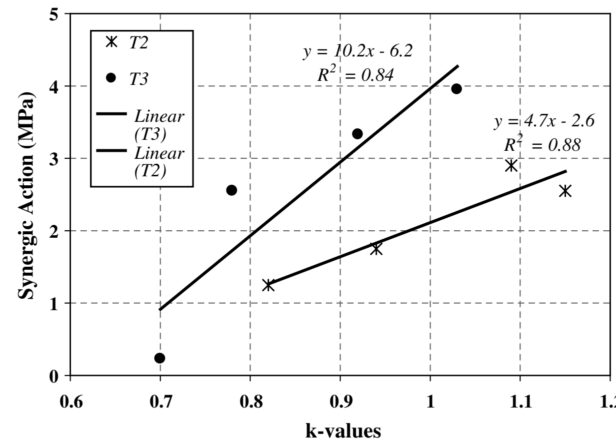

Fig. 4. Correlation of synergic action and efficiency factors for the most efficient SCMs in each case of cement replacement.

4. Concluding remarks

In the content of this study it was shown that intermixtures of high and low calcium fly ashes results in an effective, environmental friendly and relatively cheap cementitious material to deal with mutual shortcomings associated with each type of ash. Notwithstanding the fact that their pozzolanic activity potential was found to fluctuate between the values of the initial ashes, mechanical strength results of the ternary blended cements were far more encouraging since they exhibited superiority both compared to the initial ashes and, from the first month onwards, to the no fly ash specimen. The intermixture prepared with equal contributions from each fly ash was found to be the most effective for moderate cement substitution (i.e. 20%), whilst for higher replacements applied, the intermixture possessing the highest active silica content shows supremacy especially after the first week of curing. Mechanical performance of the tested ternary specimens outperformed the sum of the corresponding binary systems, at almost all ages, indicating that synergic action took place between the raw materials.

Synergic action (SA) was quantified in each case separately and was found to be decisive on the strength gain of the examined ternary systems. Almost linear correlations were established between the SA values and the efficiency factors of the best performing specimens throughout the curing period. Synergy is also validated by the measured fixed lime capabilities of the ternary ashes, which were proved to be greater than the ones theoretically expected, both during the early and later stages of hydration. The synergic effect is highly depended on the physical action of fly ashes, which by promoting the deflocculation of the cement grains accelerates the generation of hydration products. Physical effect obviously enhances the pozzolanic action of fly ashes (chemical effect), which might be accelerated by the 'internal activation' caused by instant hydration of free lime present in high lime ashes. The continuous formation of secondary (pozzolanic) hydration products contributes to the strength superiority and the pore size refinement of the system, improving the overall performance of the final product.

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