THE DEVELOPMENT OF BLENDED SUPPLEMENTARY CEMENTING MATERIALS CONSISTING OF HIGH AND LOW CALCIUM FLY ASHES

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ABSTRACT:
For overcoming the problems associated with the use of each type of fly ash (high and low calcium) in cementitious systems (low early strength, insufficient chemical resistance, expansion, etc), a development of new supplementary cementing materials consisting of blends of high and low-calcium fly ashes in various proportions was examined. Developing such blended pozzolans will result in facing with the mechanical and durability problems arousing from each of the two types when these are added separately into cementitious systems and concrete.

The blended pozzolans resulted from the mixing of a low calcium fly ash with a high calcium fly ash, both generated in great quantities in Greece. The fly ashes were selected so as to diverse on their active silica and calcium oxide contents. Various mixing proportions were adopted in order to find an optimum composition for the new pozzolan. The efficacy of the new combined supplementary material was examined in terms of active silica content, compressive strength and efficiency factor from the mechanical properties perspective.

Identification of hydration products was based XR Diffraction of the corresponding pastes, while microstructure development was monitored by means of a SEM. Comparison between the overall performance of the new combined fly ash systems and the initial fly ashes was attempted in order to explain individual contributions and detect possible synergistic effects related to the different fly ashes used.

INTRODUCTION

Acute environmental problems created by the irresponsible disposal of fly ash [1] and the anticipation that sustainability [2] in the construction sector can only be achieved via the increased utilization of such by-products, has led to an ongoing research for the full exploration of their properties. The majority of the fly ashes generated in Greece possess significant lime contents, being therefore characterized as high-calcium ashes. A respectable amount of low-lime fly ashes are also produced contributing to the great diversity of this material in the Hellenic area.

Despite the fact that advantages of both types of fly ashes are fairly well established, certain shortfalls that accompany each of them, especially when these are used as cement replacements, contribute to the skepticism with which they are still being handled by a part of the industry. In recognition of the significant differences in behaviour of 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]. This is a classification scheme that is expected to be implemented in the national standards of other countries producing different types of fly ashes during the forthcoming years.

In the literature there is plentiful information regarding the distinctions in the chemical and mineralogical composition between low and high calcium fly ashes and the effect that these factors have on their reactivity. It is low-calcium fly ashes for example that react slower, especially during the early stages of hardening, due to the higher presence of crystalline phases, which are considered chemically inert in concrete [4]. High calcium fly ashes on the other hand provide better early age strengths as a result of the cementitious compounds they possess. It is believed [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 [5].

Despite their increased reactivity and lower sensitivity to inadequate curing [6], high-lime fly ashes are generally less efficient in suppressing expansion due to ASR [7] and sulphate attack [8]. On the other hand, ashes of lower lime contents provide better resistance to ASR and sulphate attack and furthermore they usually guarantee better performance on the longer term. Concerning additional durability properties, such as carbonation and chloride penetration [9,10], both low and high calcium ashes seem to have a similar beneficial effect, with the latter presenting a slightly better resistance.

To deal with the mutual shortcomings of each type of fly ash, the majority of the researchers have attempted to produce ternary blends by introducing in the fly ash/cement matrix an additional highly reactive pozzolanic material, such as silica fume [11] and metakaolin [12]. These policies however in most cases result in substantial cost increases putting obstacles to their wider acceptance as a routine tactic in the concrete sector. Keeping this in perspective, and to additionally control the rate of hydration reaction, Naik et al. [13] prepared several mixtures of blends of class F and class C ashes. The constructed blends, that occupied 40% of the total cementitious material, showed either comparable or better results (in terms of both mechanical and durability properties) than either the reference mixture or mixture containing the class C fly ash solely.

In the present study, new supplementary cementing materials (SCM) were prepared from mixing two types of fly ashes in several proportions. The main objective was to demonstrate that contributions of each type of fly ash in concrete could compensate for the handicaps of the other, while maintaining the production cost at low levels. The efficiency of the new products was examined in comparison with both the control mixture and the corresponding mixtures containing each type of fly ash.

EXPERIMENTATION

Materials

Two different fly ashes, a high-calcium (designated as T_f) from Ptolemais region, and a low-calcium one (T_m) from Megalopolis, representing the diversity of fly ashes derived in Greek power plants were used in the present work. A normal setting Portland cement was used (CEM I 42.5R according to European Standard EN 197) during the construction of the mortar and paste specimens. The chemical composition both for the fly ashes and the cement used are given in Table 1.

Preparation of mortars and pastes

Mixing proportions and construction of new blends

Both fly ashes were ground prior to use in a lab ball mill in order to obtain ashes of similar fineness. The requirement set during grinding was that the 80% of the particles passes through the 45-μm sieve. Grinding of T_m fly ash proved to be more energy demanding since it consisted of more coarse particles in the as-received form. Therefore prolonged grinding was implemented in that case.

Table 1. Chemical composition of raw materials (mass %)

	SiO_2	Si_{re}*	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O
OPC	20.28		65.01	4.75	3.76	1.61	2.55	0.17	0.35
T_f	36.92	29.13	29.79	13.50	7.06	2.69	5.10	0.92	0.5
T_m	51.36	31.36	13.80	16.73	8.75	2.26	1.49	0.77	1.52
T_1	40.38	29.60	24.89	14.65	7.50	2.56	4.02	0.88	0.75
T_2	44.08	30.36	21.50	15.70	8.75	2.45	3.18	0.81	0.93
T_3	48.00	32.02	17.96	15.92	8.92	2.36	2.39	0.78	1.26

* The method specified in European Standard EN-450 was followed for estimating the reactive silica content (Si_{re}) of fly ashes.

When the ashes were brought to the required fineness, they were mixed in a rotating blender until homogeny of the new blend was achieved. The blended fly ash mixtures were prepared by using various dosages of the high (T_f) and low (T_m) fly ashes. 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 for the mix designated as T_3. The chemical composition of the new blends is given also in Table 1. An initial observation is that the blending procedure had a beneficial effect on the sulfate content of the blended fly ashes, as these either met the requirements stated in EN-450-1 'Fly ash for concrete' [14], or in the worst case (T_1) approached conformation with those.

Curing procedures and compression test

In order to study the compressive strength, mortar mixes with the new blends were designed by adopting cementitious material-to-sand ratio of 1:3, water to binder ratio (w/b) of 0.5 and 10-30% by weight cement replacement. Keeping the w/b ratio constant, cement mortar without any fly ash or activator was prepared as the control one. Additionally, one mix with no fly ash addition (control specimen) and two mortars incorporating the two initial fly ashes (also replacing 10-30% by weight cement), were prepared for comparison purposes.

The dry mortars were mixed in a mixer machine and then water was added. After sufficient mixing, they were cast in 4x4x16 cm mortar prisms and vibrated for 20 sec on a vibration table. The molds were stripped after 24 h, and the specimens were immersed in lime-saturated water at 20^{o}C, until testing. The testing ages were 2, 7, 28, and 90 days. For each age, two specimens of each mixture were tested for compressive strength and the mean value of these measurements is reported.

Pastes were prepared using a similar procedure, adopting a representative 20% cement replacement at the same w/b ratio and curing under water at 23^{0}C, in order to monitor the hydration process of the constructed systems. At the dates of testing, the samples were fractured into pieces. The hydration was stopped with the addition of acetone and diethylethere, followed by drying until constant weight in a vacuum pump. Finally, the specimens were placed into polypropylene bags and stored in a dryer until they were tested.

Efficiency factors

The concept of the efficiency factor (or simpler *k-value*) has been introduced as a way to predict the effect of fly ashes (and other supplementary cementing materials) on the compressive strength of Portland cement systems that incorporate them. In other words, 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) [15]. In this work, the efficiency factors were determined in order to draw conclusions regarding the effectiveness of each new blended cementing material.

Evaluation of the Hydration Process

XRD patterns of the hydrated samples were recorded using a Siemens D 500 X-ray diffractometer (CuK_a radiation, 40KV, 30mA) in a scanning range of 5 to 65^0 in 2θ scale. The testing rate that was applied was 0.02^0/min for all specimens. The identification of the products was carried out by using a Diffrac-At Database. A XL 30 Philips ESEM equipped with an energy-dispersive X-ray analyzer (EDAX) was used both for the microstructure and quantitative elemental analysis of the hydration products.

RESULTS AND DISCUSSION

Compression test

The results of the compression test in the case of 20% cement replacement are presented in Figure 1. The compressive strength values for the control specimen and the mixtures incorporating the two initial ashes are plotted against the values of the blended fly ash specimens.

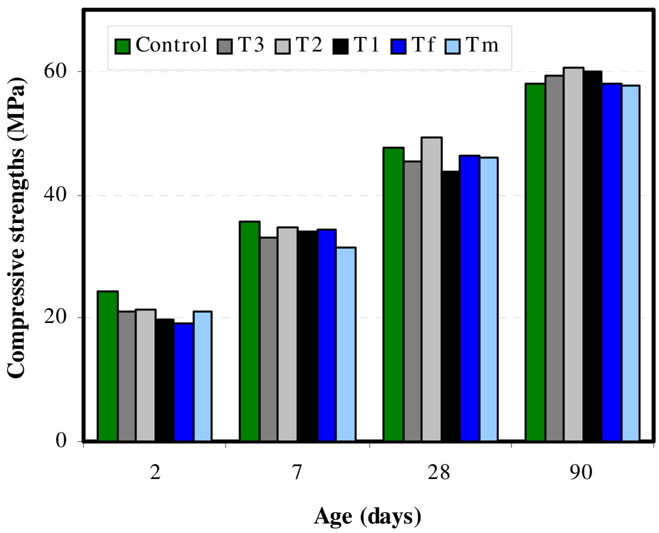


Figure 1 Compressive strengths with hydration age for 20% cement replacement

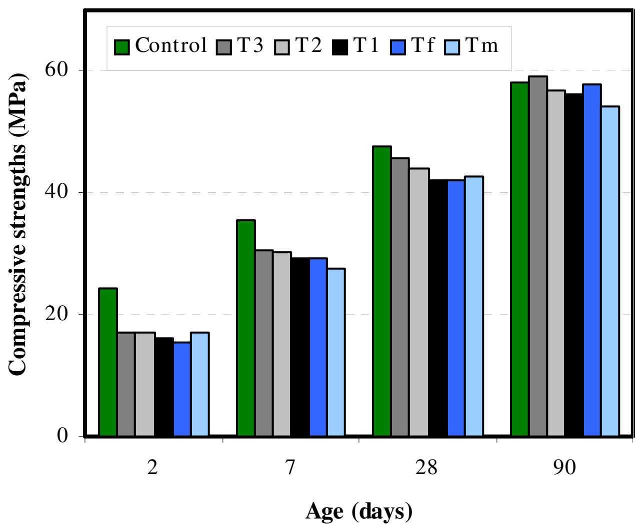


Figure 2 Compressive strengths with hydration age for 30% cement replacement

It is easily visible that during the first month of the hardening process, the control specimen (no fly ash addition) exhibited the highest value of almost all the mixtures tested. This is consistent with research establishments regarding the relatively slow evolution of the pozzolanic reaction, which mainly determines the strength development in fly ash-cement systems. The only mixture that presents higher strength value than the control after 4 weeks of hydration is T_2, constructed with

50% of class C T_f and 50% of class F T_m ashes. Somewhat surprisingly at the same age the strength values of the ashes that participate in the blend are noticeably lower. This is clearly an indication that a synergistic effect between the two ashes has taken place leading to a quicker initiation of the pozzolanic action.

After 2 days of hydration it is high lime fly ash T_f that exhibits the lowest strength value. This was unexpected since generally high calcium ashes behave better at early ages as a result of the hydration of their cementitious compounds. On the other hand, despite its low reactivity at this stage, low-lime ash T_m contributes substantially to the strength of the T_2 blend. Since the initial ashes were both ground to obtain similar finenesses, the superior performance of T_m ash cannot be attributed to that factor. However, the beneficial action of the filler effect [16] cannot be excluded, especially when the grain size distribution of T_m ash is improved due to prolonged grinding. It is clear that a small replacement (25%) of T_f ash by T_m ash at this age (blend T_3) induces positive consequences for the mix. However, the most efficient mix (T_2) contains respectable amounts of high-lime ash indicating that the synergy between the two different ashes occurs even at early ages.

The hydration of the cementitious compounds of high-lime ash T_f seems to occur during the next 5 days, accounting for the remarkable strength gain evident after 7 days of hydration. At that stage, the contribution of T_f ash in the blends is critical, since those blends incorporating beyond 50% T_f (T_1 and T_2) outperformed the ones with a limited T_f participation (T_3).

At the end of the first month of the hardening process, T_2 blend has exceeded the strength values of both the control mixture and the individual ashes, whilst the other blended specimens are not gaining substantial strength, remaining lower than the individual ashes and the reference mixture. In the contrary, during the forthcoming months (at 90 days), the compression test results exhibited excellent strength values for all the blended fly ash specimens compared to the control specimen. The fact that at the same age the ashes that consist the blends are not evenly performing, provides a guidepost that at elevated 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.

At increased cement replacement (Fig. 2) the situation differs substantially. Despite the fact that synergistic effects are still detected, it is clear that the individual ashes used as well as their intermixtures retard the strength development, especially during the early ages. This is mainly associated with the increased cement content substituted in that case and the well-established incompetence of fly ashes to act drastically from the beginning of the hydration period. The initial ashes (T_f and T_m) 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.

After 3 months, a dramatic improvement in the strength performance of all the examined blends occurs. This is testified by the fact that T_3 blend outperforms the no-fly ash mixture at this age, whilst T_1 and T_2 blends are only slightly falling short of the control specimen. Especially noticeable is the fact that in the systems with an appreciable cement replacement, the strength of the blended fly ash mixtures is proportional to their active silica content from 7 days forward. 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 active silica, which binds CH forming accessory pozzolanic C-S-H. This is in agreement with the findings of Antiohos et al. [17], who observed that in the case of high-calcium fly ashes, the role of reactive silica in the strength development of fly ash-cement systems becomes predominant after the first month of the hydration process.

To sum up, it must be pointed out that none of the constructed blended fly ash systems at any age presented the worst behavior. Generally, it can be deduced that at moderate fly ash additions, the blend that incorporated equal amounts of two different fly ashes exhibited the best behavior at all ages of hydration. On the contrary, when the fly ash contribution became more substantial (30% by weight cement replacement), the role of soluble silica in each fly ash blend was highlighted, providing for the strength superiority of T_3 blend at the age of 28 days and beyond.

Efficiency factors

For estimating the *k*-values, the procedure described by Papadakis et al. [18] was followed. 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:

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

where K is a parameter depending on the cement type (here 38,8MPa), 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, the measured values of the compressive strength given in Figures 1 and 2, the *k*-values for the new blended SCM of the present work were calculated and are presented in Table 2.

Table 2. Efficiency factors (*k*-values) for initial and blended fly ashes

	***k*-values**									
	SCM dosage (% by cement weight)									
	20					**30**				
Age (days)	**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

In previous attempts [19] dealing with Greek fly ashes the reported *k*-values were around unity during the early ages and they progressively exceed it as the hydration procedure evolved. This means that up to a certain level, those fly ashes could easily substitute, equivalently, for Portland cement. However, those values were calculated for a moderate level of cement replacement (i.e. 20% by weight). For a similar pozzolan addition applied here, the results given in Table 2 verify the aforementioned conclusions. 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. None of the constructed fly ash blends presents the smallest value during the early stages of hydration. In the contrary, the blends present decent 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 amounts of the initial fly ashes (T_2) is very close to unity after only 7 days of hydration and has significantly exceeded unity 3 weeks later. Furthermore, a small incorporation of a class F fly ash in a matrix redundant with class C ash (case of T_1 blend) can assist the strength development of such a system especially after the first month of hydration. This is clear from the dramatic increase of the *k*-value of the aforementioned blend during the last two months of the procedure.

When the replacement dosage increases (i.e. 30%), the *k*-values of all systems are normally diminished. Co-operation between initial fly ashes in the blends is still efficacious, 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 impressive 1.03 factor at the end of the hydration period. This manifests the ability of blended fly ash systems owing appropriate active silica contents to substitute equal amounts of Portland cement even at high cement replacements, providing final products of the same quality.

Identification of hydration products

For investigating the role of the newly formed hydration products in the performance of the constructed blends, their XRD patterns were examined in comparison with the corresponding ones of the initial ashes at the same testing ages. Indicative images for the early (7 days) and later (90 days) stages of hydration are given in Figures 3 and 4 respectively.

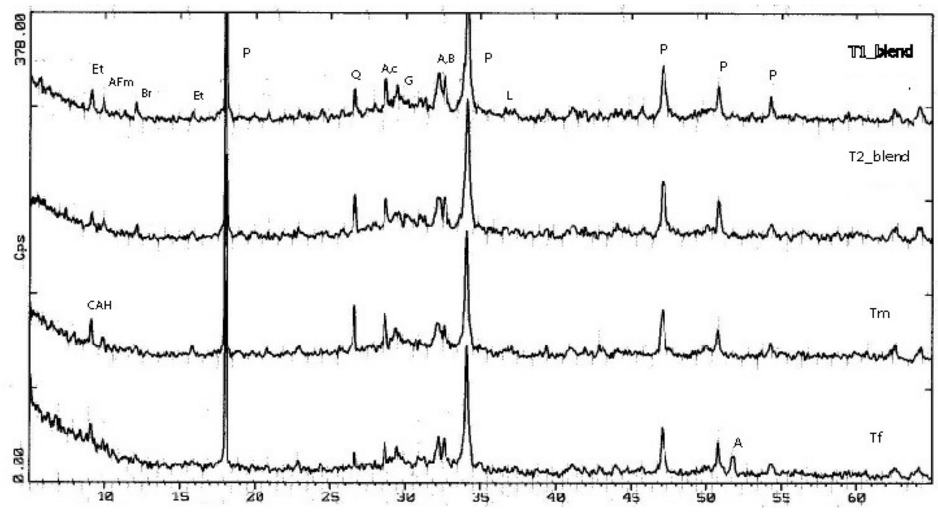


Figure 3 XRD patterns of hydrated pastes after 7 days of hydration.

The following notations were used for the various minerals identified: Et: ettringite, AF_m: monosulphate, P: portlandite, Q: quartz, CAH: C_4AH_{13}, L: lime, c: calcite, G: gypsum, A: alite, B: belite.

Figure 3 shows the XRD patterns of the hardened fly ash-cement pastes at 7 days. Main hydration products observed for all specimens at this age were portlandite, AF_t, and AF_m. Especially for low-lime T_m ash and given that its SO_3 content is relatively low (1.49 percent), the unexpected intensification of the AF_m peaks can be attributed to the formation of C_4AH_{13} instead of AF_m, because AF_m and C_4AH_{13} have very similar diffraction peaks. Accessory differences between the initial fly ashes (such as variable intensity in the quartz and gypsum peaks) are mainly due to differences in their mineralogy. However, no other significant differences could be detected in the nature of the hydration products. The contribution of blended ashes seems to have no beneficial effect on the reaction rate of the minerals contained in the clinker. Moreover, portlandite is continuously produced in all samples, indicating the absence of pozzolanic reaction at such an early age. An important observation, that possibly denotes that synergetic action between the utilized ashes is not in full progress 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 50% in T_2 to 75% in T_1 blend) an intensification of the AF_t and portlandite peaks was observed as a result of the excess of free lime and sulfur contained in this ash. On the contrary, intensity of crystalline silica (Quartz) diminished due to the limited T_m content in those blends.

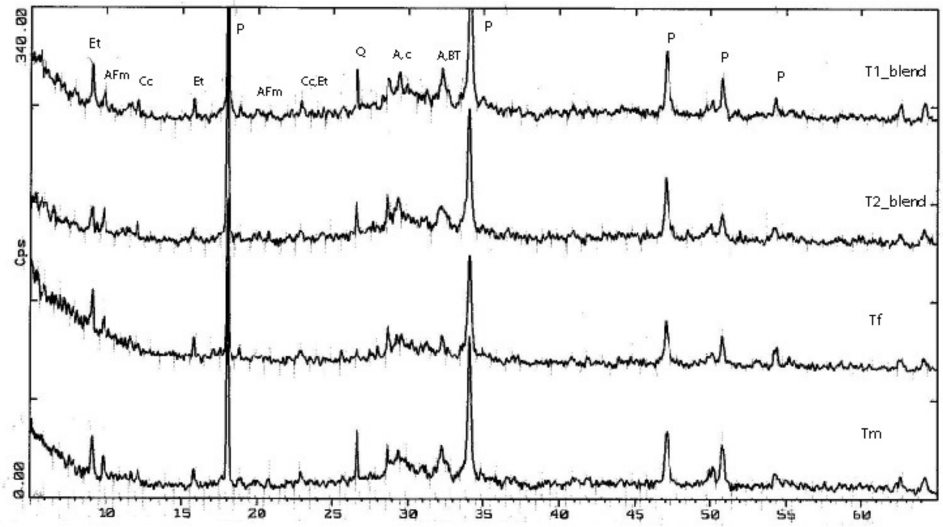


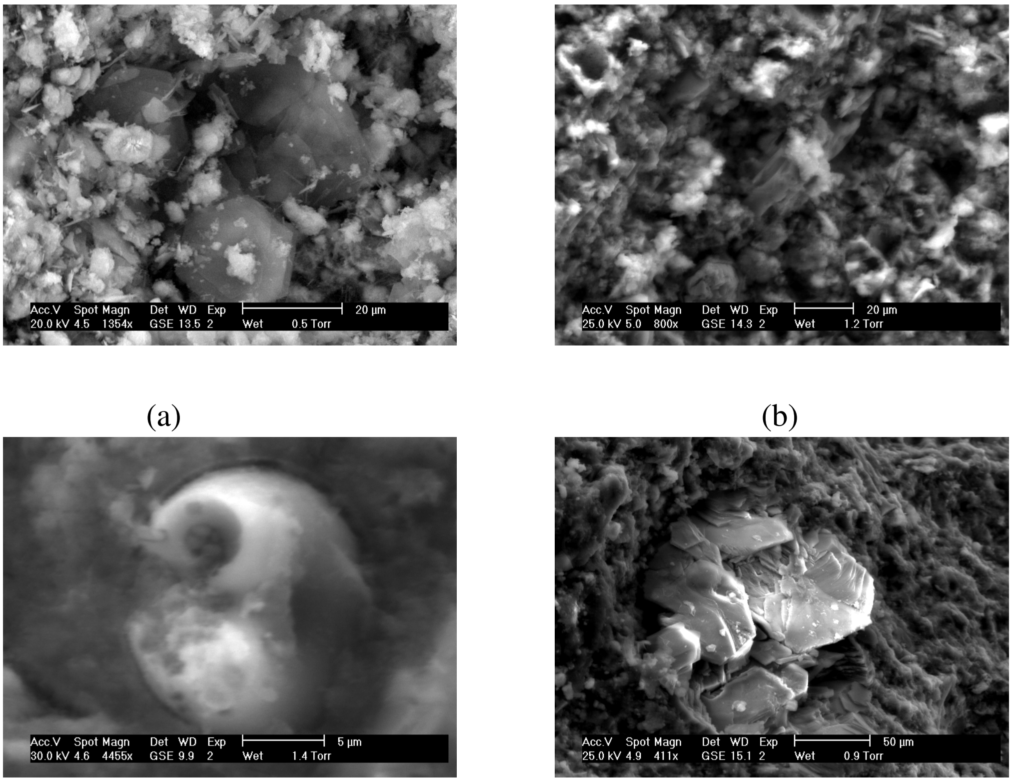
Figure 4 XRD patterns of hydrated pastes after 90 days of hydration.
The following notations were used for the various minerals identified: Et: ettringite, AF_m: monosulphate, P: portlandite, Q: quartz, Cc: $C_4A\underline{C}H_{11}$, c: calcite, A: alite, B: belite.

Three months after the start of the curing process, some changes in the XRD patterns of the specimens (Fig. 4) are easily detectable. The decrease of the portlandite peaks for instance, indicates the significant progress of the pozzolanic reaction mainly expressed as the consumption of crystalline CH by active silica of fly ashes. Carbonate hydrates are also appearing in both blended samples after 90 days. It is possible that a nontrivial part of CH was carbonated. Calcium silicate peaks are getting relatively smaller with hydration age, especially in the case of T_2 blend. However, the presence of alite and belite after 90 days indicates that the hydration of the two phases is not yet complete. Impressively, AF_t and AF_m peaks are not only increasingly generated, but contrary to what is stated in the literature [19] the AF_m peaks seem to grow independently of the AF_t ones. The fact that this phenomenon 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 late stages, obviously contributes to the final strength of the blended systems and provides an additional explanation for their superiority at later ages.

ESEM and EDAX Examination

ESEM examination testified the results presented in the previous sections. Figures 5(a) and (b) depict the SEM images of the T_f and T_2 (the most effective) fly ash-cement systems respectively after 7 days curing. Despite the fact that some of the fly ash particles appear to be etched, or covered with hydration products, in both cases the majority retains its smooth shape indicating the absence of reaction. Voids visible in the images suggest that the systems are fairly porous.

When hydration progressed (28 days), the erosion of fly ash particles (fig. 5(c)) in T_2 blend has progressed dramatically, bringing about a breaking down of their glassy surface and release of additional active constituents inside the matrix. It is postulated that a sunbstantial participation of a high-lime ash in the blend activated the ash particles in thematrix. A possible reason for that could be the high free lime contents of T_f ash that is easily dissolved from the outer shell of the glass, creating an excess of portlandite in the system.



(a) (b) (c) (d)

Figure 5: ESEM images of initial and blended fly ash systems

The increase in the alkalinity of the system initiates the corrosion of the so far inert particles contained in the T_m ash [20]. Accordingly the period before the initiation of the pozzolanic reaction is notably diminished, leading with sufficient curing (at 90 days) at a more compact structure (fig. 5(d)). The evident decrease in the porosity of the system accounts for the strength superiority of the T_2 blend, especially after the first month of the hardening process.

CONCLUDING REMARKS

The use of blends of high-calcium and low-calcium fly ash is an effective means for dealing with mutual shortcomings related with each type of fly ash. It was demonstrated that blends with equal contributions from each fly ash was found to be the most effective in terms of mechanical properties for moderate cement substitution, whilst at advanced replacements the intermixture possessing the highest active silica content shows supremacy especially at all hydration ages. The encouraging performance of the constructed supplementary cementing materials was mainly attributed to synergistic effects detected between the utilized ashes. While such composite cements are not a panacea for all concrete problems, they constitute a unique opportunity to produce concrete avoiding non environmental-friendly tactics with excessive cost.

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