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Activation of fly ash cementitious systems in the presence of quicklime
Part I. Compressive strength and pozzolanic reaction rate

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Abstract

In the first part of this study, the effect of industrially produced quicklime on the strength development and pozzolanic reaction rates of different fly ash/cement (FC) systems was investigated. Two high calcium fly ashes, diversified on their active silica and calcium oxide contents, and one with moderate calcium content were used. Strength development, hydration evolution, and pozzolanic reaction rates of the quicklime–fly ash–cement (QFC) systems were monitored and presented. Moreover, new efficiency factors were calculated for the activated systems in an attempt to optimize the quicklime addition in each case, whilst correlations were attempted between the nonevaporable water contents (W_n) and the cementitious efficiency factor (k values) of the activated systems. The addition of quicklime increased both the early and later strengths of the high-calcium fly ash specimens. For the two high-lime ashes tested, a 3% addition of quicklime was found to be the optimum dosage both for short and longer curing periods. It is possible that such an offer of lime fully employed the available silica from the ashes to form additional cementitious compounds, principally pozzolanic C–S–H. In the case of lower-lime fly ash, a small quantity of added lime (5%) was found to be effective only during the initial stages of the hardening process. When quicklime additions increased, no accelerating effect was detected, as a result of the diminished proportion of soluble silica in the pore solution. Identification of the generated hydration products, porosity of the activated mixtures and examination of their microstructure will be presented in Part II of the study.

Keywords: Acceleration; Quicklime; Mechanical properties; Blended cement; Modeling

1. Introduction

Incorporating fly ashes of both types (low and high calcium) in cementitious systems is nowadays considered a common practice in the construction sector. However, the fly ash quantities that are produced globally are steadily increasing, exceeding the utilization rates that in most countries remain low. In Greece for example, a recent report [1] revealed that although about 10 million tons of fly ash are generated annually, their adsorption in several applications (mainly the cement industry) is stuck at 10%. The amounts that remain unused obviously create acute environmental problems and moreover inhibit the path towards sustainability [2]. For increasing the utilization rate of this by-product, it is necessary to fully explore its dynamic and pozzolanic potential, but also to come up with methods of enhancing its slow reaction. This task however becomes difficult when dealing with a very heterogeneous product, where not all streams are the same, chemically or physically, and furthermore, when the effect of each of those parameters on the hydration of fly ash/cement (FC) systems has not yet been completely understood.

In the past, several activation techniques have been adopted by numerous researchers to deal with fly ash shortcomings. The principal aim of these attempts was to enhance the reactivity of the pozzolan, so as to improve the mechanical and durability properties of the final product. Prolonged grinding [3], curing at elevated temperatures [4], alkali activation [5,6] and chemical activation [7,8] are some of the methods that have been used to achieve that target. The efficiency, however, of some of these methods is debatable since some are too energy demanding, while others fail a simple cost-benefit analysis.

In the literature, there is an extensive body of information concerning fly ash activation by chemical means, and more particularly with the use of lime either hydrated or in

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powder form. Huang and Cheng [9], for example, investigated the fly ash–$Ca(OH)_2$–H_2O system to find out that the addition of hydrated lime accelerated the reaction degree of fly ash both in the early and later ages. He emphasized the fact that this acceleration effect would be minimal unless curing takes place at higher than room temperatures. This confirmed an earlier remark stressed by Gray and Lin [10] who reported that both the rate of strength gain and the ultimate strength of lime-treated fly ash are highly dependent on the curing temperature.

The interaction between fly ash and CH[2] has attracted the attention of several researchers. They all seem to agree that the quality and quantity of calcium hydroxide that is present in the matrix of a fly ash–cement system is crucial for the future performance of these systems. From the early 1980s, Takemoto and Uchikawa [11] have suggested that the rate of CH consumption in mixtures of CH and fly ash increases notably with increasing CH content in the initial mixture. They attributed that phenomenon to an increase in available calcium ions due to the increases in CH surface relative to the fly ash surface. Biernacki et al. [12] have recently confirmed the results of the aforementioned authors, but they questioned the explanation provided. Furthermore, they demonstrated that since ash hydration is the only reaction that consumes CH and since the C/S ratio does not change appreciably, it seems that the rate of ash hydration increases too with CH/fly ash ratio. Ma and Brown [13] hydrothermally treated both types of fly ash with $Ca(OH)_2$. They observed that C–S–H formation was more extensive when CH was added in high-lime fly ashes. In contrast, mild hydrothermal treatment of low-lime ash in the presence of $Ca(OH)_2$ did not appear to accelerate the formation of any of the cementing phases.

According to Fraay et al. [14], for dissolving the alumina and silica from the firm chain existing in the ash surface, a pH value of 13.3 or higher is required. The fact that the pH of the system fly ash–CH rarely exceeds 13 and the anticipation that lime and fly ash interaction is quite complex and not very fast led several workers in the introduction of a third component in the mix. Aimin and Sarkar [15] introduced 3–6% gypsum into a cement system with a Class F ash and observed a distinct increase in the strength of the new blend. They attributed that fact to the reaction between the sulfate ions and the alumina of the ash, which eventually led to the dissociation of the glass structure and finally to a denser microstructure. Similar results were reported by Huang [16] and Ma et al. [17], who provided an additional explanation for the beneficial role of the adding components, emphasizing on the formation of hydration products with filling properties, such as ettringite (AF_t) and monosulfoaluminate hydrate (AF_m). Poon et al. [18] used anhydrite to achieve a greater reaction degree in cement mortars with high fly ash replacement (i.e. 55%), while lately, Fan et al. [19] added a small quantity of Na_2SiO_3 into the fly ash–CH blend. They stressed the effect of Na_2SiO_3, which formed NaOH in the pore solution. As a result, the pH of the system was substantially higher, thereby facilitating silica–alumina glassy chain corrosion.

Despite the fact that lime has been added in various forms into the fly ash–cement blend, such as hydrated [13,17,21] or in slurry [20], providing very promising results, a thorough investigation in the literature has revealed that only Shi [21] has used it in the form of quicklime. He actually compared the effect of additional hydrated lime and quicklime in natural pozzolan/cement systems. He concluded that the cement made with quicklime shows significantly higher strength than the cement made with hydrated lime at all ages of hydration. The difference was much more pronounced during the early stage of hydration and remained constant after the first month of the hardening process.

The work presented herein is the first part of an exploratory study on the activation potential of FC systems by industrially produced quicklime. An innovative part of the study was that added quicklime actually replaced equal amount of fly ash in the mix. The gained compressive strength and alterations in the hydration of fly ash mortars and pastes have been examined. Comparisons are made regarding the efficiency of the added activator in each fly ash used, emphasizing on the role of active silica contained in them.

2. Experimental procedures

2.1. Materials

Two high-calcium (Class C according to ASTM classification) fly ashes designated as T_f and T_d, respectively, and one with lower calcium content (T_m), all received in a dry state, were used in the present study representing the diversity of the fly ashes derived in Greece. The high-lime ashes were selected so as to differentiate on their active silica and calcium oxide contents, since the influence of these factors (especially of the former) on the performance of the activated blends was one of the major objectives of the study. A normal hardening Portland cement (CEM I 42.5 according to European Standard EN 197-1) was used during the construction of the mortar and paste specimens. Commercial quicklime of high purity was used as the activator. The chemical composition and some physical characteristics of the cement and fly ashes are given in Table 1.

2.2. Addition of quicklime and construction of new blends

In order to incapacitate the effect of fineness on the performance of each fly ash used, the raw ashes were ground before use in a lab mill, so as to obtain ashes of similar fineness. The particle size distribution of the ground

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

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

	Materials			
	Cement	T_f	T_d	T_m
CaO	65.01	29.79	34.13	13.80
CaO_f	0.63	7.96	8.93	0.95
CaO_{re} *	–	21.52	26.33	9.42
SiO_2	20.28	36.92	29.73	51.36
SiO_{2re} *	–	29.13	24.07	31.36
Al_2O_3	4.75	13.50	13.90	16.73
Fe_2O_3	3.76	7.06	6.49	8.75
MgO	1.61	2.69	3.56	2.26
SO_3	2.55	5.10	5.13	1.49
Na_2O	0.17	0.92	1.12	0.77
K_2O	0.35	0.50	0.68	1.52
LOI	2.31	4.36	4.03	4.86
IR (%) *	0.18	14.52	9.51	25.16
Glass content, S** (%)	–	85.48	90.49	74.84
Blaine Fineness (cm^2/g)	3.760	5.450	5600	5.550
Specific gravity	3.13	2.83	2.72	2.59

* 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.

** 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 ($S = 100 - \mathrm{IR}$).

fly ashes, presented in Fig. 1, indicates the absence of any significant differences in their final granulometry. When quicklime was added, an equal mass of fly ash was replaced in the mix. The amount of quicklime added in each new blend depended on the initial lime content of the fly ash included in the mix. For instance, in the case of high-calcium ashes T_f and T_d, 3% and 6% fly ash replacement (by equal weight of quicklime) was adopted, whilst in the case of T_m ash, higher replacements (i.e. 5%, 10% and 15% by weight of fly ash) were applied to compensate for its lower lime content. The activated blends were named after the ash contained in them and the proportion of quicklime added. For example, T_f_6c corresponds for the specimen prepared when 6% of quicklime replaced equal weight of T_f fly ash. The detailed proportioning summary of all the specimens tested is given in Table 2.

2.3. Preparation of mortars and pastes

For studying the effect of quicklime on the compressive strength of the new blends, mortar mixes were prepared by adopting a cementitious materials-to-sand ratio of 1:3 and water/binder ratio (w/b) of 0.5. The constructed blends were used to substitute 20% by weight cement in all mortars. Keeping the w/b ratio constant, a cement mortar without any fly ash or quicklime was prepared as the control. Additionally, three mortars incorporating the initial fly ashes, without any activator added, were constructed for comparison purposes.

The dry materials were sufficiently mixed before they were cast into 40 × 40 × 160 mm prisms. One day after casting, the samples were stripped from their molds and the specimens were placed in lime-saturated water at 20 °C until testing. A Toni Tecknik compression machine with a load cell of 0–300 kN and a loading rate of 2.4 kN/s was used during the compression test. At 2, 7, 28 and 90 days

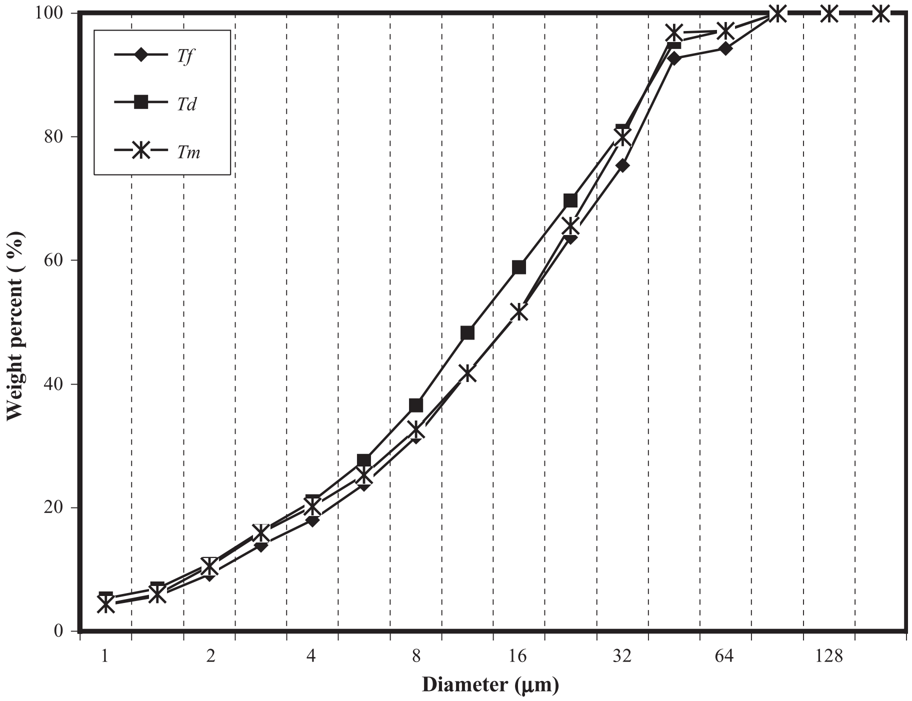

Fig. 1. Particle size distribution of ground fly ashes.

Table 2
Mix proportions of series of specimens tested (given as percentage by weight of total cementitious materials content)

	Control	T_f	T_f–*3c*	T_f–*6c*	T_d	T_d–*3c*	T_d–*6c*	T_m	T_m–*5c*	T_m–*10c*	T_m–*15c*
Cement (%)	100	80	80	80	80	80	80	80	80	80	80
Fly ash type	–	T_f	T_f	T_f	T_d	T_d	T_d	T_m	T_m	T_m	T_m
FA content (%)	0	20	19.4	18.8	20	19.4	18.8	20	19	18	17
Quicklime (%)	0	0	0.6	1.2	0	0.6	1.2	0	1	2	3

after mixing, the specimens were removed from water and tested according to European Standard EN 196-1. For each age, three specimens of every mixture were tested, and the mean value of these measurements is reported. The corresponding pastes were prepared using a similar procedure, adopting the same w/b ratio and curing under water at 22 °C, in order to monitor the hydration process of the fly ash–cement–quicklime systems.

2.4. 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 (and in other cases on durability properties) 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) [1]. In this work, the efficiency factors were determined in order to draw conclusions regarding the effectiveness of each activation dosage applied.

2.5. Stopping hydration and evaluation of the hydration process

At the dates of testing, the paste samples were fractured into pieces. The hydration was stopped with the addition of acetone and diethylether, followed by drying in a vacuum pump to remove the evaporable water. The dried fragments were further pulverized in order to obtain samples in a powder form. They were then sieved to assure that they all run through the 125-μm sieve. Representative dried paste fragments were also selected for microstructural and porosimetry tests. The results from this experimental section will be discussed in the second part of the study. Both types of samples (in powder form and small fragments) were finally placed into polypropylene bags and stored in a dryer until they were tested.

2.5.1. Thermal analysis and determination of free calcium hydroxide in the hardened pastes

Thermogravimetry and differential thermal analysis (DTA) were carried out to monitor the progress of the pozzolanic reaction in each blend. This can be accomplished by determining the amount of unbound CH in the hardened paste at the testing ages. The measurements were performed in a Mettler STARe 851/LF/1600 TG/SDTA. A platinum crucible with 70-μl capacity was used, and mass of the examined samples ranged from 45 to 55 mg. The samples were tested in a surrounding nitrogen atmosphere (50 ml/min) at a heating rate of 10 °C/min 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 atmospheric carbonation) were estimated and afterwards added to determine the total CH percentage in all specimens. The contribution of the resulting calcium carbonate in the estimation of free lime contents could not be neglected, since all samples presented peaks corresponding to the decomposition of $CaCO_3$. Despite the careful handling of the samples, carbonation could not be avoided in such alkaline systems.

2.5.2. Nonevaporable water contents

To determine the nonevaporable water content (W_n) of the hydrated samples, 1 g from the hydrated sample was first dried at 70 °C overnight (dried weight of paste) and was afterwards ignited at 950 °C in an electric furnace for 1 h (ignited weight of paste). Then the W_n content of the samples was calculated by using the following equation proposed by Zhang et al. [22] after subtracting the amount of calcium carbonate present in all blended cements (as this was estimated from the data derived from the thermogravimetric analysis and the weight loss observed in the temperature area between 750 and 800 °C):

$$W_\mathrm{n} = \frac{W_1 - W_2}{W_2} - \frac{r_\mathrm{fc}}{1 - r_\mathrm{fc}}, \tag{1}$$

where W_n is the nonevaporable water content, W_1 and W_2 are the weight of specimens before and after ignition, respectively, and r_fc is a coefficient taking into account the loss on ignition and weights of the cement and fly ash used in each blend. The latter is calculated as follows:

$$r_\mathrm{fc} = p_\mathrm{f} r_\mathrm{f} + p_\mathrm{c} r_\mathrm{c} \tag{2}$$

where p_f and p_c are the weight percentages of fly ash and cement, respectively, and r_f and r_c are the loss on ignition of fly ash and cement, respectively. Obviously in the present study, where the fly ash–quicklime blends substituted 20% by weight cement in all constructed pastes, $p_\mathrm{f} = 0.2$ and $p_\mathrm{c} = 0.8$.

3. Results and discussion

3.1. Compressive strength

The compressive strength results of all constructed systems are plotted against hydration time in Fig. 2. In Fig. 2a, the effect of added quicklime on the strength of mortars incorporating T_f ash is shown. Both a 3% and 6% fly ash replacement by quicklime slightly enhanced the compressive strength of the initial fly ash mortar from the early period of hardening. However, the specimen with no cement replacement (control) outperformed all fly ash mortars (with or without activator) during the first week of hydration. It seems that the addition of lime in the matrix cannot compensate for the cement loss during that stage. From the first week onwards, the fly ash specimens are approaching the value of the control and even exceed it (at 90 days), as a result of the evolution of their pozzolanic action.

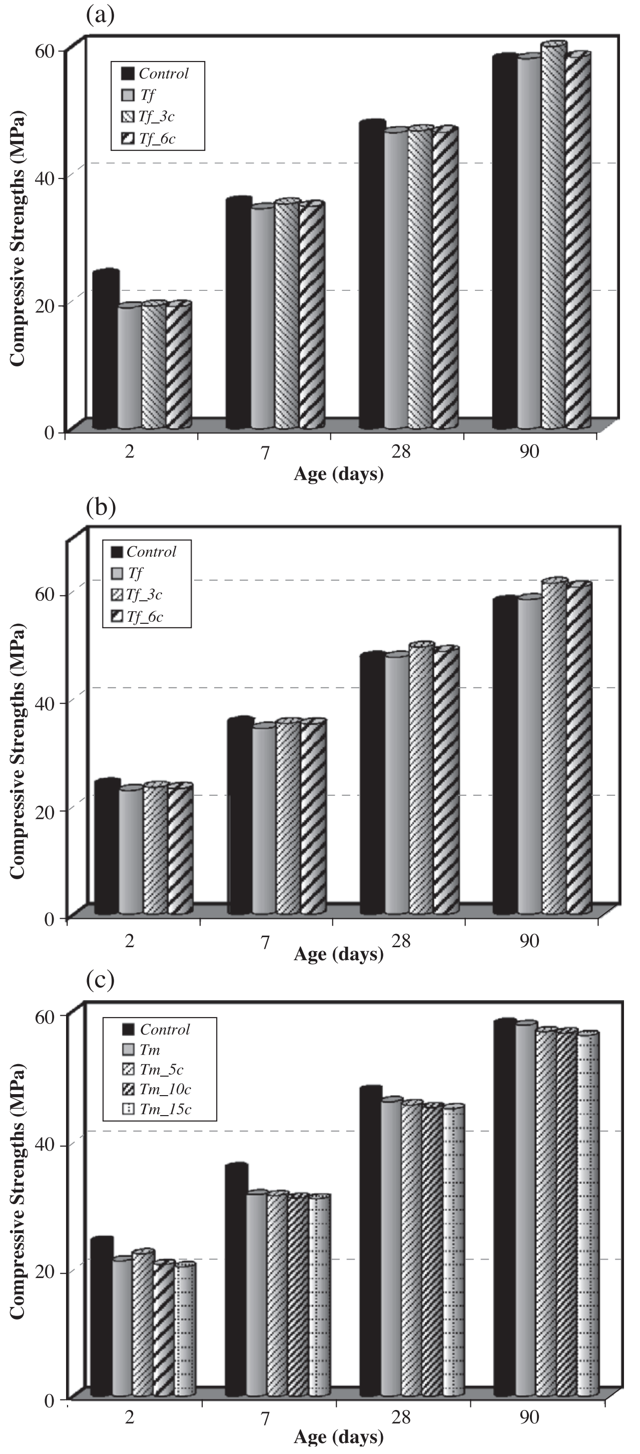

Fig. 2. (a) Compressive strength of the quicklime-activated T_f ash mortars. (b) Compressive strength of the quicklime-activated T_d ash mortars. (c) Compressive strength of the quicklime-activated T_m ash mortars.

A similar trend is observed in the mixes containing T_d ash (Fig. 2b). In that case, small replacement (3%) of T_d ash with lime resulted in an increase of the strength of the activated ash at all ages and most importantly in a significant acceleration of the early strengths of the new blend that exceeded the corresponding values of the control specimen. It is apparent that the good performance of T_d ash at early ages, due to its high specific surface and active CaO, was further improved because of the presence of extra lime in the matrix. When the fly ash replacement by quicklime increased to 6%, the strength of the activated mortar was higher than that of the control specimen at all ages, but slightly diminished compared to the values attained with less lime addition. This is an indication that in the case of ashes bearing high calcium contents, addition of lime must be limited to small percentages (i.e. 3%). From the above results, it can be deduced that 3% lime is the optimum content both for short and longer curing periods. It is possible that a small offer of lime fully employed the available from the fly ashes amorphous silica to form additional cementitious compounds, prevailing pozzolanic C–S–H. Observations formulated by Lokken et al. [23] and Brown [24]—that in the presence of $Ca(OH)_2$, the solubility of SiO_2 increases notably—indicate that as the hydration progresses, greater quantities of soluble silica are released from the reacted fly ash particles into the matrix [20]. This accounts for the improved strengths of activated high-calcium ash observed at later ages. During the early stages of hydration, added lime works alternatively to enhance the strength of the system. Lime addition and its subsequent formation to $Ca(OH)_2$ result in a higher basicity inside the matrix. The pH increase leads to the corrosion of the densified outer layer of fly ash particles [21] leaving more active cores exposed for reacting forming additional hydration products. An additional explanation for the improved early age strengths observed in lime-activated fly ash systems is the formation of flocs inside the matrix due to lime hydration. Pandian and Balasubramonian [25] noted that these flocs reduce the effective voids, and hence the interconnectivity of the pores, leading to a denser microstructure.

When comparing the effect that added quicklime had on the two different high-lime ashes (T_f and T_d) that were used in the study, it can be noted that their inherent characteristics (principally their main active constituents) determined to a large extent their strength development during hydration. In particular, it is the high active calcium oxide of T_d ash that accounts for its impressive superiority at the initial stages after mixing (since the ashes are of the same fineness), while at later ages, rich in active silica T_f ash exhibits a higher strength development than the corresponding systems (activated or not) that utilize T_d ash. This is in accordance with the findings of Antiohos and Tsimas [26] and Sharma et al. [27] who emphasized the effect of soluble silica of fly ashes during the later stages of hydration.

The effect of added lime on the strength development of low-lime ash (T_m) mortars is shown in Fig. 2c. It can be seen that quicklime addition, even at small dosages, did not improve the strength of the constructed systems. On the contrary, every addition tested produced a negative effect on the compressive strength of all examined blends at almost all ages. Only when T_m was replaced by 5% quicklime, a noticeable increase in the early age strengths was observed, but after 7 days of hydration, the blend with no lime addition outperformed the activated one. With increasing quicklime content, the strength of the new blends not only remained lower than the control, but they also diminished notably when compared to the initial fly ash blend with no lime addition. The gradual decrease observed in strength with lime content is probably due to the fact that the reactive silica present in the pore solution decreased (due to fly ash replacement) and was therefore insufficient to react completely with the surplus of hydrated lime. This accounts for all fly ashes tested, but it is definitely more pronounced in the case of high-siliceous active T_m.

3.2. Efficiency factors

For estimating the k values, the procedure described by Papadakis and Tsimas [1] was followed. 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:

$$f_c = K\left(\frac{1}{W/(C+kP)}\right) \tag{3}$$

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 á is a parameter depending mainly on time and curing. In the frame of this study, where a small replacement of fly ash by quicklime took place, P was considered as the sum of fly ash and quicklime in each blend. Applying in the above equation, the measured values of the compressive strength, the k values, for the activated systems were calculated and presented in Table 3.

Table 3
Efficiency factors (k values) for cement–fly ash and cement-activated fly ash mortars

	k Values			
	Age (days)			
	2	7	28	90
T_f	0.67	0.92	0.92	1.00
T_f–*3c*	0.69	0.97	0.94	1.12
T_f–*6c*	0.69	0.95	0.93	1.01
T_d	0.93	0.92	1.00	1.01
T_d–*3c*	1.04	1.01	1.12	1.21
T_d–*6c*	1.03	1.01	1.07	1.17
T_m	0.81	0.72	0.88	0.97
T_m–*5c*	0.88	0.72	0.85	0.91
T_m–*10c*	0.77	0.69	0.82	0.90
T_m–*15c*	0.75	0.68	0.81	0.87

In previous attempts [1,28] dealing with Greek fly ashes, the reported k values were below 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 substitute, equivalently, for Portland cement. For a similar pozzolan addition (20% by weight of cement) applied here, the results given in Table 2 verify the remarks made in the previous section. All samples with raw ashes (T_f, T_d 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. In the case of high-lime ashes, none of the activated fly ash systems present the smallest value at any stage of hydration. On the contrary, the estimated k values of the new constructed specimens exceed the corresponding k values of the nonactivated high-calcium fly ash systems during the early and later ages of hydration. Especially for the blends including T_d ash, the addition of quicklime provided for the excellent values (even higher than that of the control specimen) attained from the beginning of the hardening process. As the hydration progresses, the efficiency of all high-lime activated systems increases, reaching k values significantly higher than unity.

The negligible or even negative effect of quicklime in the case of low-lime ash T_m is also highlighted through the concept of the efficiency factor. Only when a small replacement of T_m ash by quicklime (5%) was applied, and for the very early period of hydration (2 days), the k value of the new blend was higher compared to the nonactivated one. In all other cases, the addition of quicklime brought about negative consequences in the performance of the mortars with T_m ash. This is clearly manifested from the dramatic decrease of the k values of the quicklime–T_m blends during the hydration procedure, which is even greater when quicklime content in the mix increases.

3.3. CH content and pozzolanic reaction ratio

The fraction of unreacted CH in the pastes was determined at various ages. To interpret the effect of each type of ash used, the authors mainly dealt with the most efficient of the activated blends that contained high-calcium ashes (i.e. T_d) and the ones with low-lime ash (T_m). The CH contents of the T_d fly ash–cement and T_d ash–quicklime–cement pastes with hydration age are shown in Fig. 3a. It can be seen that the cement paste without any fly ash substitution (control mixture) is constantly producing CH throughout the hydration period. On the contrary, the peculiar behaviour of the specimens with fly ash present can be explained by the simultaneous production and consumption of calcium hydroxide. In the frame of this work, the erratic behaviour of the examined samples can be attributed to the fact that there are three sources of calcium hydroxide production inside the matrix. Apart from that fraction of cement grains that react 'instantly', free lime contained in the high-calcium fly ash and added quicklime are hydrated to provide an excess of CH in the matrix of the activated systems.

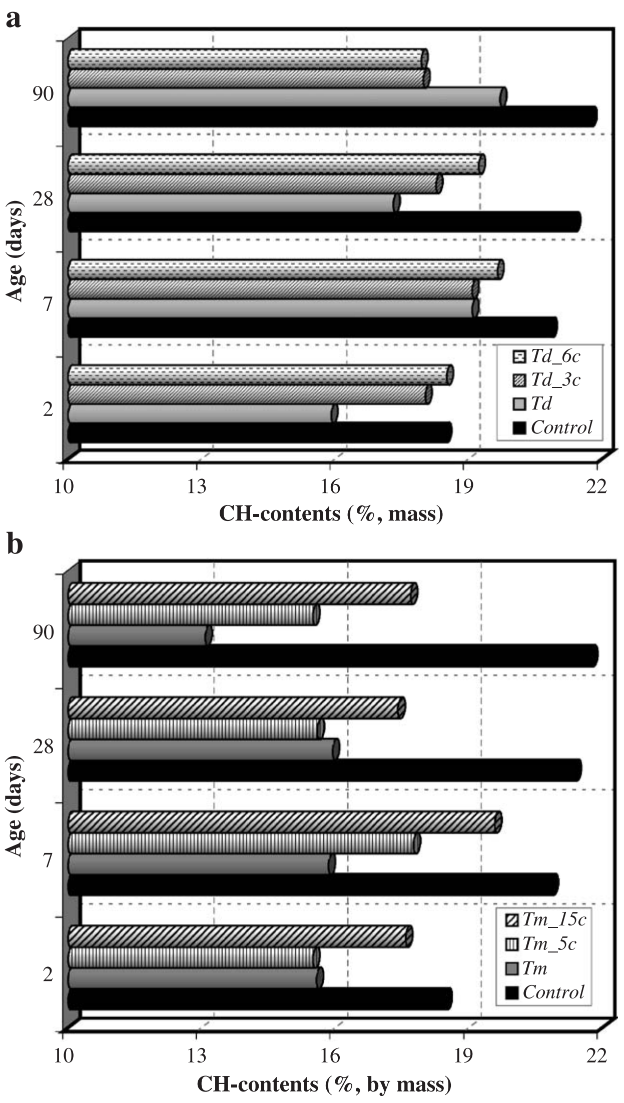

Fig. 3. (a) CH contents of the cement, cement–T_d fly ash, and quicklime-activated T_d pastes with hydration age. (b) CH contents of the cement, cement–T_m fly ash, and quicklime-activated T_m pastes with hydration age.

From the same figure, it becomes clear that a small fly ash replacement by lime (3%) accelerated the CH depletion from the early period of hardening. This is especially pronounced after the first 2 days, when despite the fact that the activated blend contains initially more lime than the corresponding fly ash–cement system, less CH is present in the paste after the first week of hydration. As the hydration progresses, it becomes obvious that the addition of 3% quicklime accelerates the consumption of $Ca(OH)_2$. High values of $Ca(OH)_2$ measured for T_d paste after 28 days (and even more at 90 days) indicate the inability of its low active silica content to combine significant quantities of lime. On the other hand, although the blend with 3% of lime lacks pozzolan, more $Ca(OH)_2$ is combined. This is obviously the outcome of the activation of the glass constituents of the ash, due to the formation of a higher alkalinity environment. The addition of lime led to the corrosion of the chemically stable surface layer of the ash allowing more active centres to run freely in the pore solution and participate in the pozzolanic reactions. This obviously accounts for the improved strength observed in lime-activated specimens. Increased quicklime addition (6%) slightly increased uncombined CH inside the matrix. Especially noticeable is the fact that from the first month onwards, the blend with 6% quicklime seems to bind greater quantities of calcium hydroxide, completely consuming the extra 3% of quicklime provided. However, according to the strength results plotted in Fig. 2b, when lime addition increased, the fly ash mortars exhibited a strength decrease. This means that strength loss could be due to differences in the nature of the formed hydration products.

The effect of added quicklime on the CH consumption of low-lime fly ash–cement systems is presented in Fig. 3b. The presence of 5% lime significantly accelerated the depletion of $Ca(OH)_2$ at 2 days, but thereafter, the reaction rate diminished notably. From 7 to 28 days of curing, the degree of reaction increased again and more hydrated lime was consumed by the 5% lime-activated fly ash. The $Ca(OH)_2$ consumption however is not accompanied by a strength increase (Fig. 2c). This can be possibly ascribed to the quality of the high-lime hydration products that resulted from the conversion of low lime ones, a factor that will be discussed further in the second part of the study. After 3 months curing, the activated system is incapable of incorporating additional portlandite into hydration products, thereby leaving uncombined $Ca(OH)_2$ in the matrix. This becomes more evident when fly ash is substituted by more quicklime (15%). In that case, CH is similarly depleted from the active constituents of low-lime fly ash, but even more hydrated lime remains contingent in the pore solution due to lower active silica present. It is well known that $Ca(OH)_2$ does not have any cementitious properties. Therefore, the significant presence of unreacted CH in the system will most certainly reduce the strength of the hardened paste. According to Shi [21], the residual CH in such systems brings about an increase in the fraction of larger pores of the

Table 4
Nonevaporable water contents of the initial and activated fly–cement pastes

	W_n contents (%)			
	Age (days)			
	2	7	28	90
Control	10.63	11.09	15.31	16.75
T_f	9.21	12.52	14.87	18.92
T_f_3c	10.69	12.57	16.57	19.85
T_f_6c	10.87	12.34	15.19	20.03
T_d	9.91	12.59	14.17	17.98
T_d_3c	11.15	12.45	15.97	20.27
T_d_6c	11.26	12.11	16.75	20.52
T_m	9.84	14.28	16.93	18.07
T_m_5c	9.45	13.72	17.20	17.92
T_m_15c	9.21	13.68	16.85	20.27

paste leading to their severe weakening. This provides an explanation for the decline of the later age strengths of all the T_m–quicklime systems.

3.4. Non evaporable water contents (W_n)

Since the processes of pozzolanic reactions are far more complex than cement hydration and the amount of water bound in the reaction products of fly ashes is uncertain, direct determination of the degree of hydration from the nonevaporable water data cannot be accomplished [22,29]. However, in this work, the amount of W_n of the constructed pastes was determined so as to obtain a view regarding the quantity of the formed hydration products in each case, providing thereby an additional indication for the effectiveness of quicklime in activating the examined systems and furthermore the role of each dosage applied.

The data of the combined water contents of all specimens as a function of curing time are presented in Table 4. It becomes clear that for all hardened pastes, the chemically combined water content increases gradually with hydration age. This is obviously the outcome of the progress of the hydration and the continuing accumulation of hydration products. In the case of quicklime-activated high-calcium fly ash–cement pastes, a notable increase in the amount of combined water can be observed at all ages. In fact, the nonevaporable water contents of all the activated pastes incorporating high calcium fly ashes are higher than that in the paste made either with neat cement or with the raw fly ashes solely throughout the examined period of hydration. Even though added quicklime will hydrate to calcium hydroxide, contributing in this way to the overall W_n values, the fact that a negligible amount of water (0.32 g H_2O per g of CaO) is needed indicates that the hydration of quicklime makes only a minor contribution to the final W_n values of the activated systems. Since the presence of quicklime cannot be held responsible for the significant increases seen in those systems, it is believed that this is due to the acceleration of fly ash reaction (due to quicklime presence). Active silica and alumina are increasingly dissolved from the glassy phase of the ash into the pore solution and are subsequently binding available lime (and water) towards the generation of additional (secondary) hydration products. The beneficial effect of quicklime on the amount of water bound in the hydration products becomes even more pronounced in Fig. 4, where the W_n contents of the activated pastes relative to the cement content are plotted against curing time. In any case of addition and for all hydration stages, the W_n contents are significantly higher than in the PC pastes. It seems that apart from the contribution of the

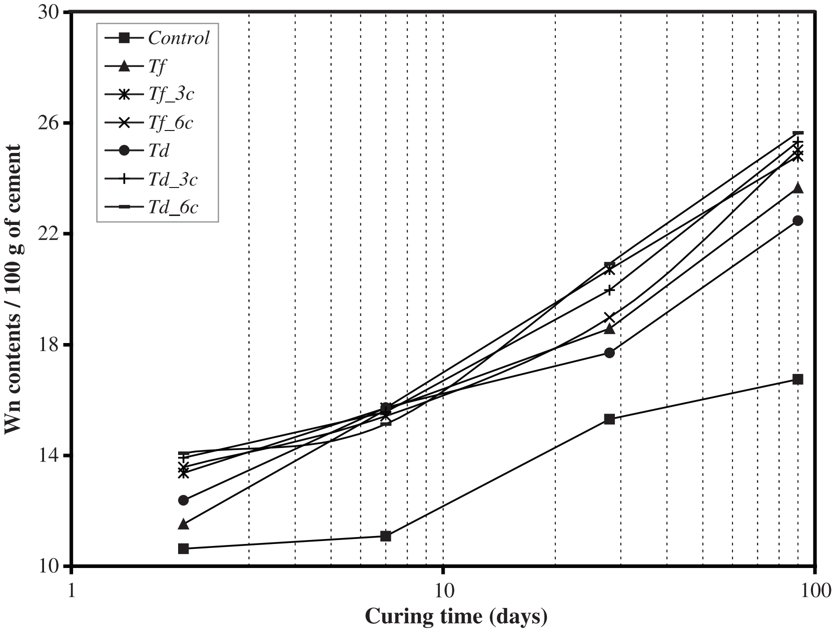

Fig. 4. W_n contents relative to the cement content in the T_d ash–cement and quicklime-activated T_d ash–cement pastes.

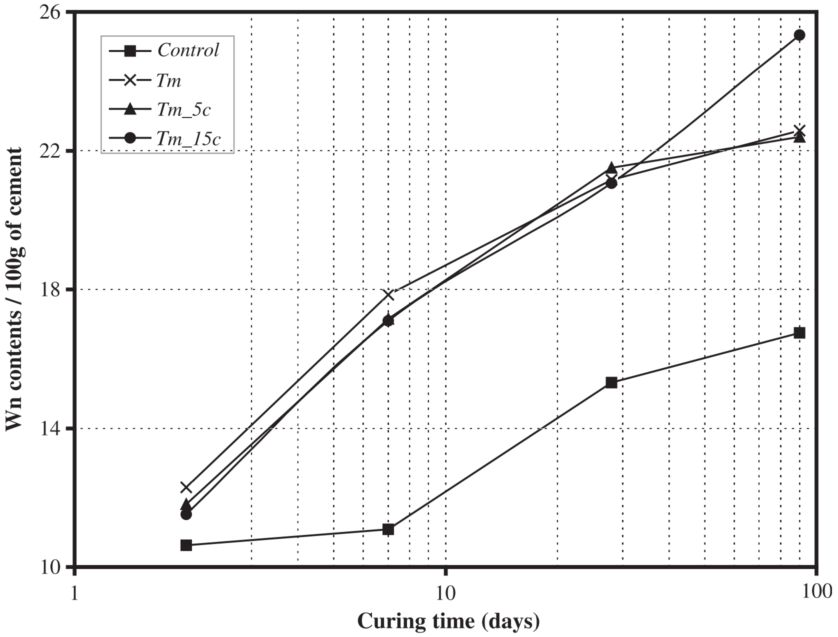

Fig. 5. W_n contents relative to the cement content in the T_m fly ash–cement and quicklime-activated T_m ash–cement pastes.

fly ash pozzolanic reaction and the enhanced hydration due to the higher effective w/c ratio, the presence of quicklime accelerated the rate that hydration products are generated. According to Shi [21], when quicklime contacts water, it hydrates rapidly liberating much heat. The liberated heat can also accelerate the pozzolanic reaction between the fly ashes and CH contained in the matrix, leading to a higher pozzolanic reaction rate. This rapid acceleration could be also responsible for the higher W_n contents observed in all high-lime fly ash–quicklime–cement pastes from the very early stages of hydration.

When quicklime replaced the fly ash with moderate calcium content (T_m), the nonevaporable water of the pastes presented a different image (Fig. 5). Despite the fact that the relative amount of combined water in all T_m–pastes remains higher than in the control pastes, the addition of quicklime brings about a decrease in the W_n contents of the activated pastes at almost all ages. In particular, the amount of combined water in the quicklime–fly ash–cement specimens decreased with increasing quicklime replacement. This is consistent with the compressive strength development of the same samples, where the presence of quicklime

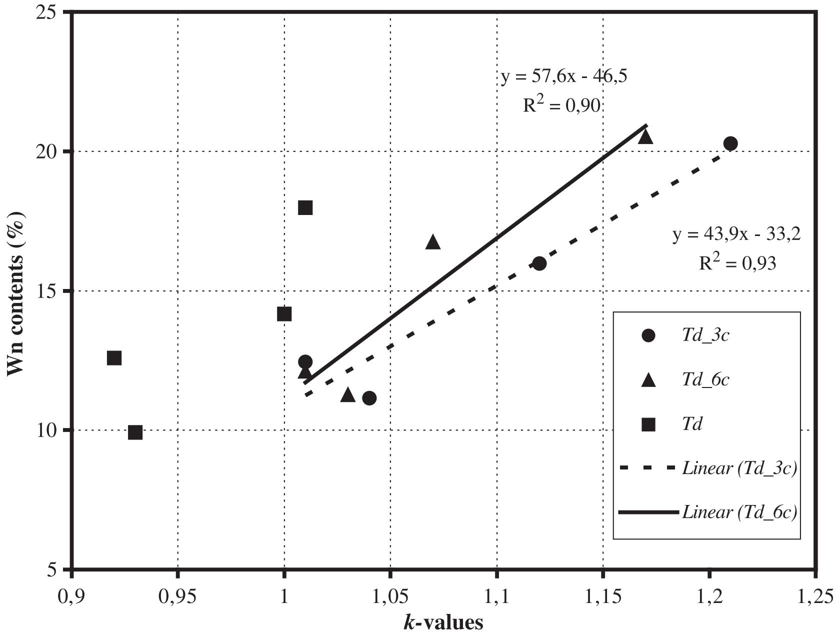

Fig. 6. Correlation between W_n contents and the efficiency factors in the case of T_d ash–cement and quicklime-activated T_d–cement pastes.

was ineffective in activating the examined systems. The fact that the surprisingly high value of the T_m*_15c* at 90 days of hydration is not associated with a respective strength increase can be attributed to the nature of the hydration products formed.

3.5. Correlating efficiency factors with W_n contents

The mixtures in which added quicklime had the more pronounced effect (i.e. T_d mixtures) were used to develop correlations between the measured W_n contents and the calculated efficiency factors (k values). In Fig. 6, the nonevaporable water contents of the initial and quicklime-activated T_d specimens are plotted against the corresponding k values at each curing time examined. It is seen that in the case of the nonactivated blend (T_d–cement), the W_n contents and their efficiency factors are not correlated. However, when quicklime was added in the mixtures, it becomes evident that the two examined factors (W_n contents and k values) are almost linearly correlated. It is interesting to note that the T_d blend with the optimum quicklime addition (i.e. 3%) exhibits the best correlating linear capability. It could be argued that since in the presence of quicklime, activation of fly ash takes place, it is somehow expected that the W_n contents (a factor that expresses the amount of hydration products generated) and the corresponding k values (a factor fairly well associated with strength development) of the activated samples would be linearly correlated. The absence of such a correlation in the cases of the other mixtures tested (activated or not) could be attributed either in the formation of different hydration products (T_f series) or in the negligible activating effect of added quicklime (T_m series).

4. Concluding remarks

Adding quicklime in FC systems is an effective, relatively inexpensive and environmental sound way to accelerate the degree of fly ash reaction. It proves to be more effective in the case of high-lime fly ashes, where both early and later strengths were improved. On the contrary, when quicklime replaced equal volumes of a low-lime fly ash, acceleration was limited to the initial stages of the hardening process. Since in this work, quicklime actually replaced fly ash and was not additionally added in the mix, the loss of active silica (due to fly ash replacement) was critical in the final performance of the newly constructed activated blends. Obviously, when quicklime will be added separately in the mix, a more drastic effect is expected. For ultimately confirming the remarks stated here, the examination of the morphology and nature of the generated hydration products as well as the formed microstructure is considered of paramount importance. The authors have worked in this direction and findings will be presented in the second part of this study.

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